LATTICE RELAXATION IN MOLECULAR CRYSTAL PACKING CALCULATIONS

by

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ABSTRACT

A detailed computational study of the rôle of lattice constraints in the reactivity of certain hydrocarbon molecular crystals is reported. The method of computation, which is based on the technique of atom-atom potentials, enables the investigation of the optimum packing at, and in the neighbourhood of, the reactive site. In particular cases energy minimizations in 200-300 variables are performed. Hitherto, such detailed calculations have not been reported.

It is shown that the parametrization of the rigid body rotation matrix is of paramount importance for the efficiency and reliability of static lattice energy minimizations. Minimizations using Euler angles can be very inefficient and under certain conditions may result in convergence to incorrect solutions. These problems are overcome by parametrizing the rotation matrix in terms of quaternion parameters.

As a test of the method of computation a detailed study is made of some simple point defects such as mono- and divacancies, and mixed crystals in which the guest molecule is either larger or smaller than the replaced host molecule. A brief study of self-diffusion in aromatic hydrocarbon molecular crystals is reported.

The method of computation is applied in a detailed study of the conformations adopted by isolated anthracene dimers in a dianthracene lattice [60], and 1,2-di-(9-anthryl)ethane in a lattice of its photodimer [2].
PREFACE

The work recorded in pp 41-53 of Chapter 3 was undertaken in collaboration with Andreas Griewank and Denis Evans, Computing Research Group, A.N.U. It was Andreas Griewank's idea to perform the static lattice energy minimizations using quaternions. He was directly involved in the implementation of the method.

Unless otherwise stated in the text, the work described is my own.

Bruce R. Markey
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CHAPTER 1

INTRODUCTION

The principal aim of this work is to further the understanding of the rôle of lattice constraints in the reactivity of organic molecular crystals, in particular those of the aromatic hydrocarbons. This aim is pursued through detailed calculations of the packing at, and in the neighbourhood of, reactive sites. The problems with which we shall be primarily concerned are the ground state conformations adopted by two anthracenes formed by the photocleavage of a parent dianthracene molecule in a dianthracene lattice [60], and the related, but more complicated, conformational problem involving a molecule of 1,2-di-(9-anthryl)ethane photodimer (CAEA) [2] in a lattice of the photodimer. The molecular structures are illustrated in Chapter 5.

The specific reason for preparing the anthracene dimer and AEA in this way was to enable the close study of the reverse dimerization reactions in which the anthracenes react to give dianthracene and the molecule of AEA reacts internally to give the photocycloadduct CAEA. The surrounding lattice constrains the molecules in such a way that the reaction mechanism can be elucidated more readily than can be achieved in solution. In the course of the experimental investigations a number of conformational problems emerged.

In the case of the anthracenes in dianthracene the molecules were found to adopt a conformation in the ground state that is partially eclipsed. The rate of photodimerization was found to be temperature dependent, proceeding with unit quantum yield at room temperature and with zero quantum yield below 10K. Analysis of the experimental results showed that there was a large thermal activation energy. This was interpreted as being due to the energy required to bring the anthracenes into a perfectly eclipsed conformation.
whence photodimerization can occur. We perform packing calculations to determine the dimer configuration in the dianthracene cage allowing for lattice relaxations.

In the case of AEA in CAEA it was found that AEA adopted four different conformations upon the photocleavage of CAEA. Interestingly, the conformations were found to arise from different sets of parent molecules. In the reverse process it was found that two conformations fluoresce upon irradiation while the remaining two conformations do not fluoresce, i.e. they undergo the intramolecular photocyclization reaction to reform CAEA. The fluorescent conformations were found to arise from the same set of CAEA molecules while the two non-fluorescent conformations were each found to belong to different sets. There were no conclusions drawn on the nature of the three sets of parent molecules. However, analyses indicated that the anthracene moieties of AEA in the fluorescent conformations were displaced in particular ways while those in the non-fluorescent conformations are thought to be perfectly eclipsed. We give more details of the experimental work in Chapter 5. Our aim is to clarify this situation by performing packing calculations. The results are reported in Chapter 5.

We have developed a computational scheme to investigate these conformational problems. Our scheme is based on the well known method of atom-atom potentials [98]. There are two main reasons for the choice of this method of calculating the intermolecular potential. Firstly, it has proved to be very successful in the study of packing in pure crystals [98, 165,170,171], particularly those of the aromatic hydrocarbons. Secondly, for systems as complicated as AEA in CAEA we require the simplest but most realistic method for computational efficiency and reliability in interpretation. We believe that the method of atom-atom potentials is the most suitable for
our purposes. In this method the potential energy of interaction of two molecules \( i \) and \( j \) is assumed to be given by the pairwise sum of atom-atom interactions of the form

\[
V_{ij} = \sum_{\lambda,k} v_{\lambda,k}(R_{\lambda,k}) = -\frac{A_{\lambda,k}}{R_{\lambda,k}^6} + B_{\lambda,k} \exp\left(-C_{\lambda,k} R_{\lambda,k}\right)
\]

where \( \lambda \) labels the atoms of molecule \( i \) and \( k \) labels the atoms of molecule \( j \). \( R_{\lambda,k} \) is the distance of separation of atoms \( \lambda \) and \( k \), and the empirically determined constants \( A_{\lambda,k}, B_{\lambda,k} \) and \( C_{\lambda,k} \) depend on the particular atomic interaction. These parameters have been accurately determined for the aromatic and aliphatic hydrocarbons [170,171].

The importance of structural imperfections such as dislocations, domains and stacking faults in determining the reactivity of organic molecular crystals has been well established [174,155] following the early work of Craig and Sarti-Fantoni [42], and Thomas and Williams [154]. In such regions reaction may be facilitated by the local packing: the requirements of the topochemical principle [73] being satisfied. However, despite the large number of experimental investigations of the role of defects in determining reactivity in the organic solid state [174] very few sophisticated calculations have been performed. There have been a few calculations on extended defects [111], disordered lattices [9], and excimers [163,166], in all of which complete relaxation of the surrounding lattice has been ignored, although it is thought to be important. Reynolds [137(a)] has calculated rotational barriers for diazo-bicyclo [2,2,2] octane in which the effect of lattice relaxation has been included. While this study is not of photochemical interest, it is of interest for its inclusion of relaxation effects. Reynolds has also studied stacking disorder in hexachlorobenzene crystals [137(b)]. Lattice relaxation effects were included. Ramdas et al [134] have studied symmetry-constrained relaxations at an extended defect.
It is a logical conclusion that the molecules in a defective region of crystal will differ in position and orientation from those of the pure, perfect lattice. It is clear from an examination of the literature that very few attempts have been made to study theoretically these departures from perfect crystallinity. In this thesis we present an efficient and reliable computational method for undertaking such studies. The method has been applied routinely to minimizations in 200-300 variables; however, larger systems can easily be treated. Total environments of molecules have, on occasions, numbered 600. The method has not been applied to stacking faults but these can easily be treated with the present computer program, as can most other forms of structural imperfection in hydrocarbon molecular crystals.

The conformational problem is approached in the following way. In Chapter 2 we discuss the thermodynamics and theory of intermolecular potentials which form the basis of the method of computation detailed in Chapter 3. In Chapter 4 the method is tested on simple point defects. In Chapter 5 we undertake the investigation into the conformational problems stated earlier. In Chapter 6 flow diagrams are given for the relevant parts of the computer program written to perform the calculations. A copy of the program accompanies the thesis. The Appendices, in part, detail other methods used in the computer program.
CHAPTER 2

THEORETICAL BACKGROUND TO THE METHOD OF COMPUTATION

INTRODUCTION

In this chapter we consider the aspects of equilibrium thermodynamics and the theory of intermolecular potentials that form the basis for the method of computation detailed in Chapter 3. We begin by introducing the principle of close packing and show how the method of atom-atom potentials, which originated from this principle, is connected with the theory of intermolecular potentials. This is followed by the discussion of the thermodynamics, and the theory of medium- to long-range intermolecular potentials and short-range overlap dependent repulsions. We conclude with a closer examination of certain aspects of the method of atom-atom potentials and present a résumé of alternative computational methods.

THE PRINCIPLE OF CLOSE PACKING

Many years ago Kitaigorodsky [95, 96] observed that crystal packing arrangements could be well reproduced by simple space-filling molecular models. The closest packings found by putting the models together in different ways often were found to correspond to the observed crystal packing. This led to the formulation of the "principle of close packing". This has been stated [97] in the following way:

"it is possible to select sufficiently universal intermolecular radii with the help of which a certain shape may be given to a molecule. This done, a crystal will turn out to be a close packing of solids: adjacent molecules dovetail. When comparing an actual structure with imaginary ones having different cells and symmetry, we (shall) see that
it is impossible to select structures that would be appreciably more closely packed than the actual one."

Thus for a crystal of known space group symmetry the unit cell volume is close to, or at, a minimum with respect to displacements in the unit cell lengths, interaxial angles, and orientation and translation variables of the molecules in the unit cell. Minima on the analogous free energy surface must be close to, or coincide with, the minima on the volume surface.

This principle led Kitaigorodsky to postulate that the interactions of molecules in a crystal could be regarded as a pairwise sum of interacting atoms [96]. He regarded as a justification the observation that the electron density of a molecule is mostly confined to a spherical distribution about the constituent atoms. To represent these interactions he introduced isotropic atom-centred potential functions which depended only on one parameter; this was an intermolecular Van der Waals radius [96]. For convenience he chose the Buckingham (exp-6) potential for the functional form of the atomic interactions. In this way he could theoretically simulate the volume of a molecule and secondly obtain an estimate of the binding energy of the lattice. Thus the ideas underlying the method of atom-atom potentials are geometric in nature. This origin is somewhat obscured by the form of the Buckingham potential.

**THERMODYNAMICS OF PURE AND IMPURE CRYSTALS**

In the later chapters we shall be concerned with the calculation of the structure and energetics at guest sites in mixed aromatic hydrocarbon molecular crystals in which the guest is assumed to be in high dilution. It is well known that the only tractable way in which such calculations can be undertaken at present is to assume that the molecules are rigid bodies
and to approximate the free energy of the lattice by the total intermolecular potential energy. In the following discussion we will consider the magnitude of the errors introduced by these approximations. For the purposes of the discussion we may neglect changes in pressure and volume and therefore we need only consider the Helmholtz free-energy function $A$.

**The Rigid Body Approximation**

The assumption of rigid bodies is justified only if upon the transition from the gas phase to the solid state the changes in molecular geometry and vibrational frequencies are small. Pawley and Cyvin [128] have shown in naphthalene that significant changes in internal and external mode vibrational frequencies do occur. For reasons which will be given presently this effect is unlikely to be a significant error in our calculations but probably would be, if neglected, in calculations dependent on a sum over normal mode frequencies. The largest error that this approximation is likely to produce in our calculations is in the computation of the total intermolecular potential energy, since, as will be shown, small changes in molecular geometry produce large energy changes but minor changes in structure. It is difficult to estimate by how much a molecule will be deformed upon entry into a solid. The effect has been considered by Kitaigorodsky [97], Bernstein and Hagler [8], and Banerjee [4].

**On the Neglect of Rigid Body Motion**

The Helmholtz free-energy function $A$ is given by [156]

$$A = -kT \ln Z$$  \hspace{1cm} (2.1)

where $k$ is the Boltzmann constant

$T$ the absolute temperature
\[ Z = \sum_{n} e^{-E_n/kT} \] is the sum-over-states. The summation is carried out over all the steady-state energy eigensolutions \( n \) of which the system is capable.

For an \( N \) molecule lattice, either pure or impure, in its electronic ground state

\[ A = E_0 + kT \sum_{i=1}^{6N} \ln \left( 1 - e^{-\hbar \nu_i/kT} \right) + \sum_{i=1}^{6N} \frac{\hbar \nu_i}{2} - kT \ln G_0 \]  

(2.2)

where

- \( E_0 \) is taken to be the total intermolecular potential energy.
- \( \hbar \) is Planck's constant.
- \( \nu_i \) is the frequency of the \( i \)-th normal mode.
- \( G_0 \) is the degeneracy of the system in its electronic ground state.

For a pure, perfect crystal this is usually taken to be unity.

Obviously, for all arrangements of molecules on a pure, perfect lattice \( E_0 \) and \( \{\nu_i\} \), the set of all normal mode frequencies, will remain unchanged. This is true even without invoking infinite translational periodicity. However, we need to make the following assumptions for a lattice containing point defects. We assume that in the infinite dilution limit all arrangements of the guests and/or vacancies on the lattice have the same \( E_0 \) value and \( \{\nu_i\} \). For this to be strictly true the infinite lattice assumption needs to be made. Having accepted these approximations we can be content that \( G_0 \) will take care of all configurational problems.

Estimates of the vibrational contribution to \( A \) for pure crystals can be made by introducing the Debye approximation [156]. The Helmholtz free-
energy function can be rewritten [156] (in molar quantities) for (i) the low
temperature case, and (ii), the high temperature case, as

(i) \[ A = E_0 - \frac{\pi}{5} RT \left( \frac{T}{\Theta} \right)^3 + \frac{g}{8} R \Theta - RT \ln G_0 \]  

(ii) \[ A = E_0 - 3RT \ln \left( \frac{T}{\Theta} \right) - RT + \frac{g}{8} R \Theta - RT \ln G_0 \]

where

\( \Theta \) is the Debye characteristic temperature which is given by

\[ \Theta = \frac{\hbar \nu_m}{k} \]

with \( \nu_m \) a limiting frequency characteristic of a particular
molecular crystal.

For a typical molecular crystal \( \nu_m \) can be taken to be equal to 80 cm\(^{-1}\),
and thus \( \Theta \approx 100K \). At \( T = 0K \) only one vibrational term contributes to
Eqn. (2.3). The magnitude of this term is approximately 1 kJ mol\(^{-1}\).
At \( T = 300K \) the vibrational terms (Eqn. (2.4)) contribute approximately
-10 kJ mol\(^{-1}\) to \( A \).

For the high temperature case the vibrational contribution to \( A \) from
the internal energy \( E \) and the vibrational entropy \( S_{vib} \) can be estimated
from the following equations after making the appropriate substitutions
using Eqns. (2.1) and (2.4), and introducing molar quantities:

a) \[ E = kT^2 \frac{\partial \ln Z}{\partial T} \]

\[ = E_0 + 3RT + \frac{g}{8} R \Theta \]

\[ = E_0 + E' \]

\[ \therefore \text{ at } 300K \ E' \approx 7 \text{ kJ mol}^{-1} \]
b) \[ S = \frac{E}{T} + k \ln Z \]

\[ S_{\text{vib}} \approx 7R \]

\[ \approx 0.06 \text{ kJ mol}^{-1} \]

and thus \(-TS \approx -17 \text{ kJ mol}^{-1}\)

### The Configurational Entropy

For a crystal containing an impurity in high dilution the configurational entropy can be estimated using the following equation [156]

\[ \ln G_0 = n_L \ln C_L + n_G \ln C_G \] (2.5)

where

- \(n_L\) is the number of moles of solvent
- \(n_G\) is the number of moles of solute molecules or vacancies
- \(C_L\) is the mole fraction of solvent
- \(C_G\) is the mole fraction of solute

For the purpose of illustration reasonable estimates of these values can be taken to be \(n_L \approx 1, n_G \approx 10^{-4}, C_L \approx 1, \) and \(C_G \approx 10^{-4}.\) Upon substitution into Eqn. (2.5) and multiplying by \(-RT\) we find that the configurational entropy at 300K is approximately \(10^{-3}\) kJ mol\(^{-1}\).

### Summary of Thermodynamic Considerations

The thermal contribution to the Helmholtz free-energy function for crystals such as naphthalene and anthracene, expressed as a percentage of the total intermolecular potential energy \(E_0\), is \(<1\%\) at 0K, and 10-15\% at 300K. Therefore, the error introduced into the calculations by the neglect of thermal motion is negligible at 0K. Thus structures
can be expected to be close to those for which \( A \) is a minimum. At 300K the error is large. One could expect that calculated structures would differ significantly from those observed. However, it will be shown in Chapter 4 that this is apparently not so in practice. The reason for this is that the (exp-6) potential that we have chosen to use was parametrized from data collected over a 250K temperature range, and therefore, thermal effects are incorporated. The contribution to \( A \) from the configurational entropy is negligible.

**INTERMOLECULAR POTENTIALS**

**Medium- to Long-Range Potentials**

1. **Classical Treatment**

Classically, the potential energy of interaction of two discrete, non-overlapping, motionless charge distributions \( i \) and \( j \) is given by the integrated form of Coulomb's law, which in atomic units [55] is written as:

\[
V_{ij} = \sum_{\ell} \sum_{k} \frac{q_\ell q_k}{r_{\ell k}}
\]

where

\( q_\ell \) is the charge on the \( \ell \)-th particle in \( i \).

\( q_k \) is the charge on the \( k \)-th particle in \( j \).

\( r_{\ell k} \) is the distance of separation of the two charges.

If \( i \) and \( j \) have arbitrarily chosen centres separated by a vector \( R \), of norm \( R \), with the sense \( i \) to \( j \) Eqn. (2.6) can be rewritten as

\[
V_{ij} = \sum_{\ell} \sum_{k} \frac{q_\ell q_k}{||R - r_{\ell} + r_k||}
\]

where \( r_\ell \) is the position vector from the origin in \( i \) to the \( \ell \)-th charge in \( i \), and \( r_k \) is the position vector from the origin in \( j \) to the \( k \)-th
charge in \( j \), with the symbol \( \| \| \) indicating the norm of the enclosed vector. Since we assume \( \| R \| \gg \| r_k \| + \| r_j \| \) a Taylor series expansion of Eqn. (2.7) can be performed about the centres of the charge distributions [86,104]. The resultant expression is an inverse power series in \( R \).

Introducing the multipole moments of each charge distribution [104] one can readily identify terms expressing the interaction of the various moments. Each interaction is characterized by a dependence on an inverse power of \( R \). The most important contributions to the interaction potential for charge distributions of net charge zero, and their respective \( R \) dependences, are the dipole-dipole \( (R^{-3}) \), dipole-quadrupole \( (R^{-5}) \), dipole-octupole \( (R^{-7}) \), quadrupole-quadrupole \( (R^{-5}) \), quadrupole-octupole \( (R^{-6}) \), and octupole-octupole \( (R^{-7}) \) interactions. Using symmetry arguments it may be possible to eliminate certain of these interactions. The dispersive and inductive potentials of molecules which give rise to attractions between spherically symmetric charge distributions enter in the quantum mechanical treatment in the second order of perturbation theory. In a simplified picture the above interactions appear as transition moment interactions which lead to terms dependent on \( (R^{-n})^2 \).

2. **Quantum Mechanical Treatment**

In the quantum mechanical treatment of intermolecular potentials Eqn. (2.7) is assumed to be the operator for the molecular interaction. In order to derive tractable expressions for the interaction of aromatic hydrocarbon molecules, in their electronic ground states, zero overlap of molecular wavefunctions is usually assumed; although the theory for small overlap has been developed [1,115]. Since we are concerned only with a description of the dominant molecular interactions the zero-overlap formalism will suffice.
The electronic Hamiltonian $H$ for two interacting molecules $i$ and $j$, whose nuclei are considered to be fixed in their free molecule ground state equilibrium positions, is written as the sum of the unperturbed free molecule electronic Hamiltonians $H_i$ and $H_j$ plus the perturbation term Eqn. (2.7). If $|k_i\rangle$, $|n_j\rangle$ are eigenstates of the Hamiltonians $H_i$ and $H_j$ respectively, the eigenstate for the non-interacting system with molecule $i$ in the state $|k_i\rangle$, and molecule $j$ in the state $|n_j\rangle$ may be written as the simple product $|k_i\rangle|n_j\rangle$. $H$ is non-diagonal in a basis of such product vectors but provided that overlap is negligible such a product will give an upper bound to the expectation value of $H$ in the interacting state $|k_i,n_j\rangle$ [115]. Hence the complete set of product vectors $|k_i\rangle|n_j\rangle$ is adopted as a basis in which to expand the eigenstates of the interacting system. For convenience the non-interacting product is written as $|k_i,n_j\rangle$. The total ground state energy $E_{0i0j}$ of the interacting system is found by solving:

$$H|0_i,0_j\rangle = E_{0i0j} |0_i,0_j\rangle$$

The solution to this equation can be found by using time independent Rayleigh-Schrödinger perturbation theory. The energy is expressed as

$$E_{0_i0_j} \approx E_{0_i} + E_{0_j} + E^{(1)}_{ij} + E^{(2)}_{ij}$$

where

$$H_i|0_i\rangle = E_{0_i} |0_i\rangle$$

$E^{(1)}_{ij}$ and $E^{(2)}_{ij}$ are the first and second order corrections to the total energy. Higher order terms are regarded, in general, as unimportant [104]. We now consider the expressions for $E^{(1)}_{ij}$ and $E^{(2)}_{ij}$. 

\[ \varepsilon^{(1)} : \text{Permanent Moment Interactions} \]

\[ \varepsilon^{(1)} = \langle 0_i^0_j | V_{i j} | 0_i^0_j \rangle \]

This matrix element can be evaluated to any desired accuracy by introducing the multipole expansion for \( V_{ij} \) [104] and truncating the series at the appropriate term. \( \varepsilon^{(1)} \) can be written in the convenient tensor formalism of Jansen [92, 93] as

\[ \varepsilon^{(1)} = \sum_{m_i=0}^{\infty} \sum_{m_j=0}^{\infty} \frac{(-1)^{m_i+1}}{m_i! m_j!} \langle N^{(m_i)} \rangle [m_i] \mathbb{T}^{(m_i+m_j)}[m_j] \langle N^{(m_j)} \rangle \]

where

\[ \langle N^{(m_i)} \rangle \]

is the ground state expectation value of the \( m \)-th rank multipole moment tensor of molecule \( i \). This is defined by Jansen [92] as

\[ N^{(m_i)} = \sum_{\ell} q_{i\ell} r_{i\ell}^m \]

where the summation is over all particles \( \ell \) of charge \( q_{i\ell} \) in molecule \( i \). \( r_{i\ell}^m \) is the \( m \)-th outer product of the vector \( r_{i\ell} \) (the cartesian position vector of charge \( \ell \)).

\[ \mathbb{T}^{(m_i+m_j)} \]

is the \((m_i+m_j)\)-th rank tensor defined as

\[ \mathbb{T}^{(n)} = -\mathbb{U}^{(n)}(\mathbb{R}) \]

where the derivative is taken with respect to the components of the vector \( \mathbb{R} \), which was previously stated to have the sense \( i \rightarrow j \); thus

\[ \mathbb{T}^{n}_{i \rightarrow j} = -\mathbb{T}^{n}_{j \rightarrow i} \]

This tensor gives the orientational dependence of the particular multipolar interaction. We note that the
The first three terms of the multipolar interaction for uncharged, non-centrosymmetrical molecules are the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions. Obviously, for centrosymmetrical molecules the first two interactions vanish. The expressions for these terms are

\[
\begin{align*}
E^{(1)}_{\text{dip-dip}} &= \mathbf{u}^{(1)} \cdot T^{(2)} \cdot \mathbf{u}^{(1)} \\
E^{(1)}_{\text{dip-quad}} &= \frac{1}{2} \mathbf{u}^{(1)} \cdot T^{(3)} : \mathbf{Q}^{(2)} - \frac{1}{2} \mathbf{Q}^{(2)} : T^{(3)} \cdot \mathbf{u}^{(1)} \\
E^{(2)}_{\text{quad-quad}} &= -\frac{1}{4} \mathbf{Q}^{(2)} : T^{(4)} : \mathbf{Q}^{(2)}
\end{align*}
\]

where

\[\mathbf{u}\]

is the dipole moment vector

\[\mathbf{Q}\]

is the quadrupole moment tensor.

The tensor contractions have been denoted by \(\cdot\) and \(:\) \(\mathbf{u}\) and \(\mathbf{Q}\) can be specified initially in some convenient molecular frame but must obviously
be transformed into the same cartesian frame in which \( R \) is specified. This is usually taken to be the laboratory frame. Simplification of the tensor contractions can be achieved if the \( Z \) axis of the laboratory frame is made to be coincident with, and to have the same sense as, \( R \). It is more usual for \( \Omega \) to be defined as the traceless tensor [104]

\[
\Omega = \frac{1}{2} \sum_k q_k (3 \hat{r}_k \hat{r}_k - \hat{\mathbf{I}})
\]

where \( \mathbf{I} \) is the identity matrix. Use of this form for \( \Omega \) requires alteration to the coefficients in Jansen's expression. For higher multipole moment interactions it may be more profitable to work in the spherical harmonic representation [86,104].

\( \varepsilon^{(2)} \): Dispersion and Induction Potentials

The second order energy correction to the total energy of the system is given by [104]

\[
\varepsilon^{(2)} = \sum_{k_1, n_1} \frac{|\langle 0, 0 | V_{ij} | k_1, n_1 \rangle|^2}{E_{i} E_{j} - E_{k_1 n_1}}
\]

(2.8)

where \( E_{k_1 n_1} \) is the energy of the product state \( |k_1, n_1 \rangle \). This is \( \varepsilon_{k_1} + \varepsilon_{n_1} \). The assumption is made that the ground state is non-degenerate; however, if degeneracy is present it may be removed [141]. The multipolar expansion for \( V_{ij} \) is introduced into Eqn. (2.8). This leads to the following expression for \( \varepsilon^{(2)} \): [93]

* The prime indicates that the sum excludes \( |0, 0 \rangle \).
The sum over states \( k_i \) and \( n_j \) is conveniently divided into two terms. In the first we consider a sum over states in which \( k_i, n_j \neq 0_i, 0_j \), and in the second a sum over states in which either \( k_i = 0_i \) and \( n_j \neq 0_j \), or \( k_i \neq 0_i \) and \( n_j = 0_j \). The first term is the dispersion energy which arises from the interaction of multipolar transition moments, and the second term is the induction energy which arises from the interaction of the permanent moments of one molecule with the transition moments of the other molecule. For aromatic hydrocarbons the induction energy is considered to be of secondary importance to the dispersion energy \([39]\). Usually anisotropic multipolar interactions e.g. \( m_1 = l_1 = m_j \neq l_j \) are neglected.

The major problem associated with the numerical evaluation of the polarization energies lies with the calculation of the upper excited state contribution. This is simply due to the large number of terms that must be included. The individual contributions are usually small but their summed contribution may be large. A number of ways of solving this problem have been introduced. As an example consider the molecular polarizability tensor \( \alpha \) whose elements are given in the first order and dipolar approximations by \([115]\)

\[
\alpha_{\alpha \beta} = 2 \sum_k \frac{\langle 0|u_\alpha|k\rangle \langle k|u_\beta|0\rangle}{\epsilon_k - \epsilon_0} \tag{2.9}
\]

where \( \langle 0|u_\alpha|k\rangle \) is the dipolar transition moment with \( \alpha \) polarization.

Several convenient approximations can be made if a mean excitation energy...
is introduced into Eqns. (2.8) and (2.9). Application of the closure relationship for the complete set of expansion vectors to Eqn. (2.8) gives, essentially, Unsöld's approximation [104],

\[
\epsilon^{(2)} \approx - \frac{\langle 0, 0, 1 | v^2 | 0, 0, 1 \rangle}{\Delta E_{iav} + \Delta E_{jav}}
\]

and Eqn. (2.9) becomes

\[
\alpha^i_{\alpha\beta} \approx \frac{2}{\Delta E_{iav}} \langle 0, 1 | u_{\alpha\beta} | 0, 1 \rangle
\]

where the subscript \( 'iav' \) indicates a mean or average excitation energy for molecule \( i \).

The static polarizability \( \alpha \) is obtained by introducing a mean excitation energy into Eqn. (2.9) and spherically averaging the tensor [3]. This gives:

\[
\alpha^i \approx \frac{2}{3\Delta E_{iav}} \sum_k |\langle 0 | u | k \rangle|^2
\]

London's well known dipolar formula for the dispersion energy of interaction between two molecules is given in terms of mean excitation energies and experimentally determinable static polarizabilities:

\[
\epsilon^{(2)}_{\text{disp}} \approx - \frac{3}{2} \frac{\Delta E_{iav} \Delta E_{jav}}{(\Delta E_{iav} + \Delta E_{jav})^2} \frac{\alpha^i \alpha^j}{R^6}
\]

The mean excitation energy is usually taken to be between the first excitation energy and the first ionization energy. It is a good approximation if the excited states occupy a band of energies that is narrow compared with the magnitude of the first excitation energy.

The validity of the multipole expansion for \( ||R|| > ||r_k|| + ||r_k|| \) in crystals of the aromatic hydrocarbons has been investigated by Craig and Thirunamachandran [43]. They found that the multipole expansion is valid.
for benzene and to a good approximation is valid for naphthalene. However, significant errors may occur for anthracene.

**Short-Range Repulsive Potential**

In this section we shall be concerned with overlap dependent repulsions. For many years the short-range repulsion between rare gas atoms has been modelled by either an exponential term, as in the Buckingham (exp-6) potential, or an $R^{-12}$ term, as in the Lennard-Jones (12-6) potential. For aromatic hydrocarbon molecular crystals the repulsive potential has been modelled in the same or a similar way. The repulsive potential is usually assumed to arise from electron exchange between atom-centred filled orbitals. It is well known that the exchange integral $K$ can be approximated by the product of the corresponding coulomb integral with the square of the overlap integral for the two atomic centres. This result follows from Mulliken's approximation [104]. The interaction usually is reduced to one of two forms. In the first the repulsive interaction is given by

$$V_{\text{rep}}(R) = K = \frac{k S_{ab}^2}{R}$$

where $S_{ab}$ is the overlap integral for the orbital centred on atom $a$ of molecule $i$, and the orbital centred on atom $b$ of molecule $j$, and $k$ is a constant of proportionality which can be determined by either quantum mechanical calculations or by fitting the potential to experimental data. The coulomb integral is replaced by a $\frac{1}{R}$ term since it behaves in this manner for the distances over which short-range repulsions are important. In the second it is assumed that an exponential term alone will suffice since $S_{ab}$ behaves exponentially in the region of interest. Therefore

$$V_{\text{rep}}(R) = B \exp(-CR)$$
where the constants $B$ and $C$ can be estimated from quantum mechanical calculations and/or experimental data [71,170,173] for various atomic interactions.

**THE INTERMOLECULAR POTENTIAL AND CRYSTAL STRUCTURE**

In this section we are concerned with the importance of the permanent moment, polarization, and overlap repulsion interactions in determining the crystal structures of the aromatic hydrocarbons. Craig et al [38,39] have considered this in studies on naphthalene and benzene crystals. They reported the following findings:

i) The quadrupole-quadrupole energy is unimportant in determining the angular relations between translationally non-equivalent molecules in the unit cell.

ii) The dispersion energy, though large absolutely, is insufficiently sensitive to angle variations to affect the packing significantly.

iii) The molecular orientation is primarily fixed by the minimization of intermolecular hydrogen-hydrogen repulsions.

Several authors [98,170] have commented on the latter finding. They draw attention to the importance of the neglected C-H repulsive terms. In the calculations reported in this work it is immaterial which of these interactions determine the crystal structure since all interactions are included.

In all our calculations we assume that the total intermolecular potential energy is given by a pairwise sum of molecular interactions (see Eqn. (3.1)). The only study of non-pairwise additive terms in the total intermolecular potential energy of aromatic hydrocarbons was undertaken by Evans and Watts [54] for benzene. They found that triple-dipole dispersion,
and three-body quadrupole-induced dipole-quadrupole energies were significantly smaller than the pairwise additive contribution.

NOTES ON THE METHOD OF ATOM-ATOM POTENTIALS

The method of atom-atom potentials is well documented [98,99], as are the procedures for deriving the potential parameters [150,170,171,172]. In this section we note a number of features of the method of derivation of Williams' set IV [170] which are important in our computational applications. These are:

i) Since the potential accurately reproduces the crystal structures used in its derivation, (see Chapter 4) it must to a certain extent incorporate the effects of higher order terms and cross terms in the multipole expansion of the intermolecular potential. If for some reason the potential needs to be extended by the addition of extra terms then this feature should be taken into account.

ii) As stated previously thermal effects have been included in the potential in a peculiar way since the derivation was made from data which is representative of a 250K temperature range.

iii) The fitting procedure used to derive the potential parameters ensures that the difference between the attractive and repulsive contributions to the total potential energy is 'correct' while the magnitude of the terms depend on an externally determined approximate value for the pre-exponential constant for the hydrogen-hydrogen interaction. Thus we conclude that energy magnitudes should be considered cautiously. In part these features are manifest in the high degree of correlation between
the potential parameters [170].

iv) At short range, which we may consider to be the positive segment of the repulsive part of the potential, the $1/R^6$ term is still assumed to be valid. Thus for this region of interaction the potential curve has the incorrect functional form. In addition, since equilibrium data have been used to derive the potential parameters we can expect that the potential curves will not be well characterized away from the potential well. These considerations are important for self-diffusion calculations (Chapter 4).

We conclude this section by noting several useful articles by Mirskaya [109] and Taddei et al [152] which deal with the application of combining rules in the derivation of atom-atom potential parameters.

**ALTERNATIVE METHODS OF CALCULATING THE INTERMOLECULAR POTENTIAL**

Numerous attempts have been made to calculate the intermolecular potential energy of interaction of aromatic hydrocarbons. For solid state calculations there is no method that has proved to be as popular as the method of atom-atom potentials. The lack of popularity of the alternative computational schemes usually stems from the fact that a knowledge of permanent moments and complicated quantum mechanical sums is required. More often than not this information is either completely lacking or else is considered to be too difficult to compute; although in recent work the effort has been made to perform the necessary calculations. We conclude with a list of many of the alternative schemes that have been proposed [5, 7, 32, 75, 80, 94, 112, 114, 119, 124, 131, 140, 162].
CHAPTER 3

METHOD OF COMPUTATION

INTRODUCTION

The details are given of the method of static lattice energy minimization used in the following chapters to study the effect of lattice relaxation on the structure and energetics of point defects and the conformational preferences of bridged anthracenes in host lattices of their photodimers. Particular attention is paid to a discussion of several types of descent methods for minimization and the representation of molecular orientations since this is of paramount importance for the efficiency and reliability of the minimization procedure. Recommendations are made, based on the results of comparative calculations, on the most efficient and reliable method of computation to suit particular needs with an emphasis being placed on the ease of implementation.

NATURE OF THE MINIMIZATION PROBLEM

Consider a crystal lattice composed of rigid bodies in which there is an imperfect region (a defect) isolated in otherwise pure, perfect bulk crystal. This may be a dislocation, a vacancy, or a guest molecule in substitution. At low temperatures and pressures an equilibrium structure of the lattice closely corresponds to a minimum in the total intermolecular potential energy \( V \)

\[
V = \frac{1}{2} \sum_i V_i = \frac{1}{2} \sum_i \left( \sum_{j \neq i} V_{ij} \right)
\]  

(3.1)

where \( V_{ij} \) is the interaction energy of molecules \( i \) and \( j \), and the summations extend over all molecules of the lattice.
To compute the structure of such a defect a lattice of molecules is formed to simulate the isolated defect with the molecules being initially positioned to be as close to their final equilibrium positions as can be estimated. It will become apparent later that in most cases studied here this is a simple procedure. \( V \) is then minimized with respect to the position and orientation variables, which in some instances may number more than 200, of all the molecules constituting the defect. Therefore it is desirable to have a method of static lattice energy minimization that is efficient and reliable, and is as independent of computer storage as is possible, and is easily implemented. There are two principal ways in which this can be achieved using appropriate descent methods. The minimization of \( V \) can be undertaken simultaneously in all variables or, as has been done in this work, it can be resolved into one-molecule problems and solved iteratively, i.e. the relevant \( V_i \) in Eqn. (3.1) are consecutively minimized in a cyclic procedure.

An alternative procedure is to resolve the minimization into \( n \)-molecule problems in which \( n \) molecules, the choice of which would be problem-dependent, are simultaneously considered. However, while this method in theory exhibits the desirable properties of the other two methods, i.e. it accounts for coupling between molecules and only requires a small amount of computer storage, it is unlikely in practice to lead to markedly improved performance over the method which has been used in this work.

**Descent Methods for Minimization** [103]

In this section several types of descent methods are discussed in regard to their application to this minimization problem and in the elucidation of certain aspects of minimization that are perhaps, in general, not well known.
For the Buckingham (exp-6) potential which has been used in this work, the gradient $\nabla V$ (the N-column vector of first order partial derivatives, where $N$ is the total number of variables) and the blocks $\nabla^2 V_i$ in the diagonal of the Hessian $\nabla^2 V$ (the $N \times N$ symmetric matrix of second order partial derivatives) are calculable with little extra effort than is required for the computation of the $V_i$, and thus $V$ itself. The remaining cross-terms of the Hessian $\nabla^2 V$ which couple the displacement variables of different molecules are in principle calculable with again only a small amount of extra effort than is required to obtain the $\nabla^2 V_i$, however, for large calculations these terms would require very large amounts of computer storage and since it is thought that the n-molecule approach would lead to few benefits over the one-molecule approach then these cross-terms are not further considered. Clearly there is no need to use non-gradient methods which would be very inefficient; survey calculations with an implementation of Brent's algorithm [13] confirmed this. Therefore higher order methods are considered.

Steepest Descent

In this well known method the objective function $f(x)$, where $x$ is an $N$-dimensional column vector in a so-called generalized Euclidean N-space, is minimized by taking descent steps of the form

$$\delta x = -\alpha \nabla f(x)$$

with $\nabla f(x)$ the gradient vector. The multiplier $\alpha$ is chosen either to minimize $\phi(\alpha) = f(x - \alpha \nabla f(x))$ in a procedure called an exact line search or simply to produce a lowering of the function value in the direction $-\nabla f(x)$. This need not be minimal in this direction. We denote the solution vector of the non-linear system $\nabla f(x^*) = 0$, as $x^*$. 
Although this method rapidly reduces the value of the objective function initially it has a notoriously slow rate of convergence which has resulted in the method falling into disfavour as a sole scheme for performing minimizations. However, in combination with a Newton scheme, vide infra, it has proven to be very popular since the initial rapid descent can be combined with the second order rate of convergence of the Newton scheme close to the minimum, where the order of convergence is given in the following relation by \( n \), with \( c_k \) small, bounded constants:

\[
|x_{k+1} - x^*| \leq c_k |x_k - x^*|^n. \tag{3.2}
\]

The method of steepest descent can be used to illustrate some important aspects of minimization in general. The importance of proper scaling can be appreciated by considering a general quadratic function for which it can be shown that the reduction in the error \( E(x) = f(x) - f(x^*) \) obeys

\[
E(x_{k+1}) \leq \left( \frac{r-1}{r+1} \right)^2 E(x_k)
\]

where the condition number \( r \) is the modulus of the ratio of the largest to the smallest eigenvalue of the Hessian. The closer \( r \) is to 1, and thus the closer are the function contours to circularity, the larger will be the reduction in the function value at each step. Consequently it is important to have an eigenvalue structure of the Hessian that has a condition number close to 1. This can be achieved by introducing scale factors on each of the variables in such a way as to make the second derivatives with respect to each variable approximately the same. This of course does not correspond to a rotation of the coordinates which leaves the eigenvalue structure of the Hessian unchanged. The effects of a poorly conditioned Hessian on minimization procedures will be illustrated later in conjunction with Euler angles.
Conjugate Gradients

A conjugate gradient scheme could be applied to all variables simultaneously as only scalars and N-vectors are used. Therefore computer storage requirements are relatively small. This method is preferable to that of steepest descent since it has an improved rate of convergence close to the minimum. To illustrate its basic simplicity the following equations give the sequence of steps in the minimization procedure:

i) the initial step is steepest descent, so

\[ d_0 = -g_0 = -\nabla f(x_0) \]

and

\[ x_{k+1} = x_k + \alpha_k d_k \]

where a suitable \( \alpha_k \) is chosen in a line search.

ii) \[ d_{k+1} = -g_{k+1} + \beta_k d_k \]

where

\[ \beta_k = \frac{g_{k+1}^T g_{k+1}}{g_k^T g_k} \]

For an \( N \) variable problem the general algorithm should be reinitialized every \( N \) steps by taking a pure gradient step. This assures global convergence i.e. convergence to the solution point \( x^* \).

The term 'conjugate' arises from a formulation of the theory where the \( d \) vectors, i.e. the search directions, satisfy \( d_n^T \Theta d_m = 0 \), with \( \Theta \) the Hessian. These vectors are said to be \( \Theta \)-orthogonal or conjugate.

Since the number of steps necessary for the approximate location of the minimum of a quadratic function equals at least the number of distinct eigenvalues of the Hessian it is unlikely that the conjugate gradient method
applied to the minimization of $V$ simultaneously in all variables could converge in less than 6 steps. This would be necessary to be competitive with the methods described later. The $\nabla^2 V_i$ are obtained readily, therefore, there is no point in applying the method of conjugate gradients to the one-molecule problems since a Newton scheme would be superior.

Quasi-Newton Schemes

The quasi-Newton schemes are also known as variable metric or deflected gradient methods. They are essentially an extension of the method of conjugate gradients except that an approximating inverse Hessian is incorporated in the method in an endeavour to simulate a Newton step. The Hessian usually is initialized as a multiple of the identity matrix and is updated as the minimization progresses by taking gradient differences. Descent steps of the following form are taken

$$x_{k+1} = x_k - \alpha_k S^{-1}_k \nabla f(x_k)$$

where the multiplier $\alpha_k$ is chosen to guarantee a sufficient reduction in $f$ and $S^{-1}_k$ is the approximating inverse Hessian. This is usually stored in triangular form thus reducing storage requirements. The method has the advantages of not requiring matrix diagonalizations and of allowing the approximating Hessian $S^{-1}$ to be obtained at the solution point. Subsequently the eigenvalues and eigenvectors of $S^{-1}$, which are of qualitative value, can be obtained. The search direction is always 'downhill' as $S^{-1}_k$ is forced to stay positive definite by appropriate procedures. The method converges superlinearly (i.e. in Eqn. (3.2) $n = 1$ and $c_k \to 0$) to a minimum or possibly a saddle point.

In this work we have employed the quasi-Newton routine FUNMIN which is an implementation of Fletcher's algorithm [68] by Osborne and Saunders [121].
It has been applied to the minimization of the intramolecular potential energy of 1,2-di-(9-anthryl)ethane in Chapter 5 and, in some instances, to the solution of the one-molecule problems. The application of this routine to the minimization of $V$ simultaneously in 200 variables would require approximately 45 kwords of computer memory for the minimization routines alone, and for our computer program this would need to be added to approximately 40 kwords (depending on the system) for the remainder of the program. While these storage requirements are not too large the program becomes restrictive to work with.

FUNMIN exhibited two minor problems in the free molecule calculations (see Chapter 5). It would not leave the neighbourhood of a saddle point, and its efficiency was sensitive to the initialization of the approximating Hessian. The initialization can be used to advantage in performing grid point searches since the minimization can be forced to take small steps initially and thus avoid 'jumping' over local minima.

Newton Schemes

The classical Newton method takes steps of the form

$$x_{k+1} = x_k - \frac{V^2 f(x_k)}{V f(x_k)}$$

where $V^2 f(x_k)$ is the Hessian of $f(x_k)$ evaluated at $x_k$ and all other terms have their previously defined meanings. Newton's method approximates the objective function $f(x_k)$ locally by a quadratic function and minimizes this approximate function exactly, however, since $V^2 f(x)$ may have negative eigenvalues then the minimization may converge to a saddle point or a maximum. This can be averted by introducing modifications such as

$$x_{k+1} = x_k - \alpha_k \left[ I + (1 - \alpha_k) \frac{V^2 f(x_k)}{V f(x_k)} \right]^{-1} V f(x_k)$$
where $I$ is the identity matrix, and $\varepsilon_k$ is a positive constant which is chosen to ensure that the matrix enclosed in brackets is positive definite and thus the search direction 'downhill' (obviously when $\varepsilon_k = 0$ the method reduces to the pure Newton scheme and when $\varepsilon_k = 1$ it reduces to steepest descent). Modifications such as these usually ensure convergence to a minimum or possibly a saddle point where the Hessian is singular. The modified Newton routine HESMIN [77] has been implemented in our computer program in the solution of the one-molecule problems. However, it would be impractical to apply HESMIN to the minimization of $V$ simultaneously in 200 variables since this would require 204 kwords of computer memory for the minimization routines alone.

Recapitulation

The computation of the equilibrium structure of a defect proceeds in the following way. A large environment of molecules is formed in the centre of which the defect is created by choosing the molecular positions and orientations to be as close to the minimum-energy structure as can be estimated. The precise manner in which the environment of molecules is selected is given later. $V$ is then minimized with respect to the position and orientation variables of one molecule at a time, i.e. the relevant $V_i$ of Eqn. (3.1) are consecutively minimized, in a cyclic procedure using the quasi-Newton or Newton descent methods. During the minimization of each $V_i$ all molecules neighbouring the $i$-th are held fixed, for instance, in their experimentally determined or previously optimized positions. In order to reduce the likelihood of convergence to a system saddle point the accuracy of each molecular minimization is chosen to be fairly low initially and then is gradually increased after each cycle. The cycling procedure is terminated when $V$ differs between cycles by less than a chosen tolerance.
We may now write

\[ V_i = V_i(r,A) = \sum_{j \neq i} V_{ij}(r,A) \]  

(3.3)

where \( r \) is the centre of mass position vector of molecule 'i' and \( A \) is the rotation matrix which specifies the orientation of the molecule 'i' with respect to some initial set of coordinates. Where \( A \) is defined as transforming a laboratory vector \( x_{lab} \) to the body frame by

\[ x_{body} = A x_{lab} \]

THE REPRESENTATION OF ORIENTATIONS

The parametrization of the rigid body rotation matrix \( A \) has proved to be a troublesome problem for numerical work for a long time. Customarily \( A \) has been parametrized in terms of Euler angles, the definitions of which in this work are taken from Goldstein [74], see figure 1. The disadvantage of these variables is that they possess a plane of singularities at \( \theta = 0 \) (where \( \theta \) is the azimuthal angle between the laboratory and the body z axes); here the Euler angles are no longer suitable as generalized coordinates. Even though this problem is well-known it appears that sometimes in static lattice energy minimization procedures \( A \) is initialized as the identity matrix, i.e. the three Euler angles are set to zero, and thus the minimization commences at a singularity. It will be shown that from this starting point minimization procedures can at best be very inefficient, and at worst can even converge to incorrect solutions.

In an attempt to overcome the problem of the singularity \( A \) is sometimes parametrized in terms of the small rotations about the laboratory \( x, y \) and \( z \) axes. These rotations commute in the infinitesimal limit which in practice may be taken to be 5-10 degrees. This procedure is not
Figure 1. Goldstein Euler angles illustrated as a transformation of the laboratory frame.
necessary since in the majority of static lattice energy minimizations the problem can be overcome by pre-rotating the atomic position coordinates about the laboratory x axis by 90° and then setting θ to ±90° to return the molecule to its original orientation, where the sign of θ is simply related to the handedness of both rotations. It will be shown that this procedure leads to the most efficient minimization in terms of Euler angles while the problem of the singularity can be overcome completely by parametrizing the rotation matrix in terms of quaternion parameters.

The Three Dimensional Rotation Group: SO(3) [169]

We begin this section by recalling the theory of the three-dimensional rotation group SO(3). The elements of SO(3) are all the 3 x 3 real orthogonal matrices of determinant +1. A denotes a matrix of this group. According to Euler's theorem, A describes a right-handed rotation through an angle ω on the interval [0, π] about a normalized invariant axis

\[ \mathbf{u}_0 = (\xi_0, \eta_0, \zeta_0) \, . \]

SO(3) is a continuous group. By this we mean that each group element (matrix) "can be characterized by parameters varying continuously in a certain region. Every set of values of the parameters within the region defines a group element; conversely, to every group element corresponds a set of values of the parameters within the specified region. These regions are called group space; there is a one-one (1-1) correspondence between group elements and points in group space" (Wigner[169]).

It is because the parametrization of the rotation matrix in terms of Euler angles is not locally 1-1 that the problem of the singularity occurs. Realizing this and using Euler's theorem as a guide one may suspect that a
parametrization in terms of four parameters (with one constraint) would produce a locally 1-1 correspondence between a point in group space and an element of \( SO(3) \). This is so and has been well known for a long time. This parametrization is most familiar as the so-called Cayley-Klein parameters, and is known to a lesser extent as the quaternion parameters. Both sets of parameters lead to an entirely equivalent parametrization of \( A \). An appreciation of the local 1-1 correspondence can be obtained by considering the following geometrical representation.

**Geometrical Isomorphism** [169]

Each element of \( SO(3) \) can be associated with a point inside or on the surface of a sphere of radius \( \pi \). In this representation of the group \( SO(3) \) the length of a vector from the origin to a point inside or on the surface of the sphere represents the magnitude of the rotation angle \( \omega \), and its direction represents the direction of the invariant axis. Since antipodal points on the surface of the sphere correspond to the same rotation the representation is locally 1-1 with \( SO(3) \) but it is not globally 1-1. All paths within the sphere connecting two points are continuously deformable into each other, however, there is a second path linking the two points which goes to the surface of the sphere, then jumps to the antipode, and finally to the other end point. Since this path cannot be deformed into the path within the sphere it follows that \( SO(3) \) is a doubly continuously connected group.

In the following sections the review of the parametrization of the rotation matrix is completed by examining four sets of parameters.

**Small Rotations about the Laboratory \( x, y \) and \( z \) axes.**

In a right-handed axes system, to which all discussion is referred, a left-handed screw rotation about each of the laboratory \( x, y \) and \( z \) axes through the angular displacements \( \Omega_x, \Omega_y \) and \( \Omega_z \) is produced by:
\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & \cos\Omega & \sin\Omega \\
0 & -\sin\Omega & \cos\Omega \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
\cos\Omega & 0 & -\sin\Omega \\
0 & 1 & 0 \\
\sin\Omega & 0 & \cos\Omega \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
\cos\Omega & \sin\Omega & 0 \\
-\sin\Omega & \cos\Omega & 0 \\
0 & 0 & 1 \\
\end{pmatrix}
\]

Combining these we obtain for a general rotation:

\[
E = BCD.
\]

In the infinitesimal limit \( E \) is replaced by:

\[
\begin{pmatrix}
1 & d\Omega_z & -d\Omega_y \\
d\Omega_x & 1 & d\Omega_y \\
d\Omega_y & -d\Omega_x & 1 \\
\end{pmatrix}
\]

The matrix \( E \) produces a non-orthogonal transformation and is therefore of no practical value; however, Oliver and Walmsley [120] have shown how the matrix elements of \( E \) may be corrected so that the infinitesimal rotations become suitable generalized coordinates. The corrections they give are

\[
E_{\alpha\beta} = \delta_{\alpha\beta} - \delta_{\alpha\beta}\delta\Omega - \frac{1}{2}\delta_{\alpha\beta}\delta\Omega\delta - \frac{1}{2}\delta_{\alpha\beta}\delta\Omega\delta
\]

where \( \delta_{\alpha\beta} \) is the Kronecker delta.
\( \delta_{\alpha\beta\gamma} \) is the Levi-Cevita density

\( \Omega_0 \) is the infinitesimal rotation about the \( \delta \) cartesian axis.

A technique employed in our computer program is to use similarity transformations to perform rotations about principal molecular axes directly in the laboratory frame. However this technique is not required if quaternions are used, e.g. see the method of performing bond rotations in Chapter 5, but will briefly be discussed. Consider the \( 3 \times 3 \) matrix \( F \) whose row entries are the direction cosines specifying the orientation of a principal inertial axis with respect to the laboratory cartesian \( x, y \) and \( z \) axes. Since the rows of \( F \) downwards have been chosen to correspond to the axes of increasing inertial moment, which for the purposes of performing the rotations have been labelled \( x', y' \) and \( z' \), it follows that a rotation about one of the inertial axes e.g. \( x' \) in the laboratory frame is given by

\[
B_{\text{lab}} = F^{-1} B F.
\]

Another simple technique which is employed in our calculations is to put into a host crystal lattice a guest molecule of which the atomic position coordinates are given with respect to the principal inertial axes of the replaced host molecule. If the replaced host molecule has principal axes specified by \( F \) and the guest coordinates are denoted by \( x \) then the operation is achieved in the following way:

\[
x_{\text{lab}} = F^{-1} x.
\]

Euler Angles

In terms of Goldstein's Euler angles the rotation matrix \( A \) takes the form [74].
\[
A = \begin{pmatrix}
\cos \psi \cos \phi - \cos \theta \sin \phi \sin \psi, & \cos \psi \sin \phi + \cos \theta \cos \phi \sin \psi, & \sin \psi \sin \theta \\
-\sin \psi \cos \phi - \cos \theta \sin \phi \cos \psi, & -\sin \psi \sin \phi + \cos \theta \cos \phi \cos \psi, & \cos \psi \sin \theta \\
\sin \theta \sin \phi, & -\sin \theta \cos \phi, & \cos \theta
\end{pmatrix}
\]

(3.4)

For convenience we write the three Euler angles in vector form:
\[
\alpha^T = (\phi, \theta, \psi).
\]

We note that in the plane \( \theta = 0 \) the orientation of a body must remain constant along the lines \( \phi + \psi = \delta \), with \( \delta \) an angular constant. It follows that the eigenvectors of a potential energy function in this plane are \((1,-1)\) and \((1,1)\) with the corresponding eigenvalues \(0\) and \(\lambda\), with the value of \(\lambda\) depending on the system. Thus in this plane the Hessian is singular. In general this means that the minimization in the six molecular variables will be inefficient (when \( \theta \approx 0 \)) since the Hessian will be poorly conditioned - typically \( \nabla^2 V_1 \) was found to have a condition number of \( 10^6 \) whereas in the cases to be discussed the Hessian has a condition number of the order \( 10 \). This is very important for the efficiency and reliability of static lattice minimization procedures as will soon be shown.

**Cayley-Klein Parameters** [74]

There exists a two-fold homomorphism between the group \( SU(2) \), i.e. the group of which the elements are the \( 2 \times 2 \) unitary matrices of determinant \( +1 \), and \( SO(3) \). \( SU(2) \) is the covering group of \( SO(3) \). This means that there are as many elements in \( SU(2) \) for each element in \( SO(3) \) as there are paths from the identity to any element in \( SO(3) \) which cannot be deformed into one another. The elements of \( SU(2) \) are uniquely determined by a tuple of four complex parameters (more precisely the uniqueness is determined to within a sign change of these parameters).
We may denote a general element of $SU(2)$ by $\Omega$ and its matrix entries:

$$\Omega = \begin{pmatrix} \alpha & \beta \\ \nu & \delta \end{pmatrix}.$$ 

The four complex numbers $\alpha$, $\beta$, $\nu$, and $\delta$ can be shown to satisfy the following equations:

$$\nu = -\beta^* \quad \delta = \alpha^* \quad \alpha\alpha^* + \beta\beta^* = 1$$

where the $^*$ indicates that the complex conjugate is to be taken. In terms of these parameters the rotation matrix takes the form:

$$A = \begin{pmatrix} \frac{1}{2} (\alpha^2 - \nu^2 + \delta^2 - \beta^2) & \frac{1}{2} (\nu^2 - \alpha^2 + \delta^2 - \beta^2) & \nu\delta - \alpha\beta \\ \frac{1}{2} (\alpha^2 + \nu^2 - \beta^2 - \delta^2) & \frac{1}{2} (\alpha^2 + \nu^2 + \beta^2 + \delta^2) & -i(\alpha\beta + \nu\delta) \\ \beta\delta - \alpha\nu & i(\alpha\nu + \beta\delta) & \alpha\delta + \beta\nu \end{pmatrix}.$$

Defining the complex numbers $\alpha$ and $\beta$ in terms of the real numbers $\chi$, $\xi$, $\eta$, and $\zeta$ by

$$\alpha = \chi + i\zeta \quad \beta = \eta + i\xi$$

we find that Eqns. (3.5) and (3.6) lead to the following condition on the real numbers

$$\chi^2 + \xi^2 + \eta^2 + \zeta^2 = 1$$

Using Eqns. (3.6) the rotation matrix takes the form:
Thus we have arrived at a parametrization of the rotation matrix which has the desired property of being locally 1-1 with the elements of SO(3).

**Quaternion Parameters** [78,168]

The real numbers $\chi$, $\xi$, $\eta$ and $\zeta$ in terms of which the Cayley-Klein parameters are defined can equally as well be thought of as components of a quaternion of norm 1. The quaternions are an algebraic field endowed with a norm and a topology. As such they form an extension of the real numbers and the complex numbers. A general quaternion $q$ is defined as a linear form

$$q = \chi + \xi i + \eta j + \zeta k$$

in which the imaginary units $i$, $j$ and $k$ obey the following rules of multiplication:

$$i^2 = j^2 = k^2 = -1; \quad ij = -ji = k; \quad jk = -kj = i; \quad ki = -ik = j$$

The norm of quaternions is:

$$\|q\| = (\chi^2 + \xi^2 + \eta^2 + \zeta^2)^{\frac{1}{2}}$$

(3.9)

The addition and multiplication of two quaternions $q$ and $q' = \chi' + \xi' i + \eta' j + \zeta' k$ is defined:
\[ \mathbf{q} + \mathbf{q}' = (x + x') + (\xi + \xi') i + (\eta + \eta') j + (\zeta + \zeta') k \]

\[ \mathbf{qq}' = (x' - \xi') \eta' + \zeta' \]

\[ = (x' \xi + \xi' \xi + \eta' \zeta - \zeta' \eta) i + \]

\[ (\xi' \eta + \eta' \xi + \zeta' \zeta - \zeta' \zeta) j + \]

\[ (\xi' \zeta + \zeta' \xi + \eta' \eta - \eta' \eta) k \]

Quaternion multiplication is not commutative: \( \mathbf{qq}' \neq \mathbf{q}' \mathbf{q} \).

The correspondence of the quaternion parameters to those of the 2 \( \times \) 2 unitary matrices can be readily seen by employing the symplectic decomposition of the quaternion. This is a representation of the quaternion by a pair of complex numbers. The quaternion \( \mathbf{q} \) may be rewritten as

\[ \mathbf{q} = z_1 + z_2 j = (z_1, z_2) \]

where

\[ z_1 = x + k \xi \]
\[ z_2 = \eta + k \zeta \quad (3.10) \]

Thus if \( k \) in Eqns. (3.10) is identified with the imaginary unit \( i \) of the complex numbers in Eqns. (3.6) the correspondence follows immediately.

Whittaker [168] has shown that by defining the four parameters \( x, \xi, \eta, \) and \( \zeta \) in terms of the rotation angle \( \omega \) and the components of the normalized invariant axis \( \mathbf{u}_0 \), the rotation matrix takes the form of Eqn. (3.8). These definitions are

\[ \chi = \cos \frac{\omega}{2} = \cos \frac{\theta}{2} \cos \frac{(\phi + \psi)}{2} \]
\[ \xi = \sin \frac{\omega}{2} \eta_0 = \sin \frac{\theta}{2} \cos \frac{(\phi - \psi)}{2} \]
\[ \eta = \sin \frac{\omega}{2} \eta_0 = \sin \frac{\theta}{2} \sin \frac{(\phi - \psi)}{2} \]
\[ \zeta = \sin \frac{\omega}{2} \eta_0 = \cos \frac{\theta}{2} \sin \frac{(\phi + \psi)}{2} \quad (3.11) \]
where the second equality gives the relationship of the parameters to Goldstein's Euler angles. It can be shown using the definition of quaternion multiplication that the effect of the rotation operator $\mathbf{A}$ on a laboratory vector $\mathbf{x}$ is equivalent to the quaternion multiplication $\mathbf{q} \times \mathbf{q}^{-1}$, where $\mathbf{q}^{-1} = \frac{\mathbf{q}^*}{||\mathbf{q}||} = \mathbf{q}^*$ with $^*$ denoting conjugation, i.e. $\mathbf{q}^* = \chi - \xi i - \eta j - \zeta k$, and the vector $\mathbf{x}$ is expressed in quaternion notation.

In the developments which follow it is not necessary to refer to quaternion algebra as we shall only be concerned with the quaternion written as a tuple of four real parameters which satisfy the orthogonality constraint Eqn. (3.7). We may now write $\mathbf{q}$ in the form:

$$\mathbf{q}^T \equiv (\chi, \xi, \eta, \zeta) \equiv (\cos \frac{\omega}{2}, \sin \frac{\omega}{2} \mathbf{u}_0^T)$$ (3.12)

and the potential $V_i$

$$V_i \equiv V_i(\mathbf{r}, \mathbf{A}(\mathbf{q})) \equiv V_i(\mathbf{r}, \mathbf{q})$$ (3.13)

The Relationship between the Orientational Gradients and the Torque

In the previous sections it was shown that Euler angles in the plane $\theta = 0$ result in a singular Hessian and thus in practice leads to inefficient minimization. It was stated how this problem may be overcome by pre-rotating the atomic position coordinates, however, it is not at all obvious that the optimum value of $\theta$ should be $90^\circ$ nor is it obvious that the minimization can converge to incorrect solutions at $\theta = 0$. These aspects of the minimization are now considered.

Since Eqn. (3.13) cannot be differentiated independently with respect to the four quaternion parameters we define for any non-zero $\mathbf{q}$

$$\mathbf{A}(\mathbf{q}) = \mathbf{A}(\mathbf{q}/||\mathbf{q}||)$$ (3.14)
which ensures that the gradient $\nabla q \cdot V_i$ is always orthogonal to $q$, where $\nabla q$ denotes the first partial derivatives of $V_i$ with respect to the quaternion parameters. This may be written as

$$g^T(\nabla q \cdot V_i) = 0 = g^T(\nabla^2 q \cdot V_i)q$$

which is readily obtained by a Taylor's series expansion about the normalized point $q$.

For normalized $q$ we consider the infinitesimal rotation $d\tilde{\boldsymbol{q}} = \tilde{\omega}dt$, where the instantaneous angular velocity in body coordinates is given by [168]

$$\dot{\omega} = 2 \begin{pmatrix}
  -\zeta & \chi & \zeta & -\eta \\
  -\eta & -\zeta & \chi & \xi \\
  -\zeta & \eta & -\xi & \chi
\end{pmatrix} = 2 \mathcal{S} \cdot \dot{q}$$

with $\mathcal{S} = \mathcal{S}^T \mathcal{S} = I$.

Now

$$dV_i = (\nabla q \cdot V_i)^T dq = -T^T d\tilde{\boldsymbol{q}} = -2T^T \mathcal{S} dq$$

with $T$ the torque in the body frame.

Which implies that

$$\nabla q \cdot V_i = -2 \mathcal{S}^T T$$

because of Eqn. (3.15). Similarly for Euler angles we obtain

$$\dot{\omega} = \mathcal{S} \cdot \dot{\alpha}$$

and

$$\nabla \alpha \cdot V_i = -\mathcal{S}^T \mathcal{T} \cdot \dot{\alpha}$$

where [74]

$$\mathcal{S} \cdot \mathcal{S} = \begin{pmatrix}
  \sin \theta \sin \psi & \cos \psi & 0 \\
  \sin \theta \cos \psi & -\sin \psi & 0 \\
  \cos \theta & 0 & 1
\end{pmatrix}$$

and

$$\mathcal{T} = \begin{pmatrix}
  \cos \theta & 0 & 1 \\
  0 & 1 & 0 \\
  -\sin \theta & 0 & 0
\end{pmatrix}$$
A consideration of Eqns. (3.18) and (3.19) will lead to the conclusion that when \( \|\dot{\mathbf{v}}_i\| = 0 \) then \( \|\mathbf{I}\| \) must be zero, however, when \( \|\dot{\mathbf{v}}_i\| = 0 \) the torque may be arbitrarily large. The consequence of this is that the minimization can converge to an artificial stationary point. The possibility of this occurring will, in part, depend on the minimization routine used and the stopping criterion.

We now show that steepest descent in terms of quaternions produces a rotation of the rigid body about the axis of its current torque. This must produce the largest reduction in the potential energy as is implied in Eqn. (3.18). However, steepest descent in terms of Euler angles produces a rotation of a body about an axis which may form an angle up to \( \delta = |\pi/2 - \theta| \) with the axis of current torque. From Eqns. (3.16), (3.18) and (3.19) it can be seen that the displacements \( dq = -\lambda \frac{\mathbf{v}_i}{q_i} dt \) and \( d\alpha = -\lambda \frac{\mathbf{v}_i}{\alpha_i} dt \), with a multiplier \( \lambda > 0 \), in the directions of steepest descent produce rotations about axes which are related to the torque through the equations:

\[
\omega_q = 4\lambda \mathbf{S}^T \mathbf{T} = 4\lambda \mathbf{I}
\]
\[
\omega_\alpha = \lambda \mathbf{S}^T \mathbf{S}^T \mathbf{T} = \lambda \mathbf{M}^T
\]

where in the case of Euler angles the angle \( \delta \) between \( \omega_\alpha \) and \( \mathbf{T} \) is given by

\[
\cos(\delta) = \frac{\mathbf{T}^T \mathbf{M} \mathbf{T}}{(\|\mathbf{T}\| \|\mathbf{M} \|)}
\]

which can be shown [76] to produce the stated result. Thus the most efficient minimization in terms of Euler angles must be obtained when \( \theta = 90^\circ \). This is demonstrated later in comparative calculations.
MINIMIZATION OF THE POTENTIAL ENERGY

So far the general approach to the problem of calculating the structure of a defect has been considered. This has included a discussion of the currently available descent methods for minimization and their application to the minimization of the total intermolecular potential energy either simultaneously in all variables or in an iterative procedure in which one molecule at a time is considered. The three-dimensional rotation group and several parametrizations of the rotation matrix were discussed in association with the problems experienced in the use of Euler angles. The Euler angle problem was analysed and correcting procedures given. Quaternions were introduced as an alternative parametrization of the rotation matrix for which there is a correspondence between the elements of group space and those of SO(3) that is locally one to one. The use of these parameters as independent variables is complicated by the imposition of the orthogonality constraint Eqn. (3.7), however, in the following sections it is shown how to convert this constrained problem to an unconstrained minimization problem by modifying the potential function. The analytic first and second derivatives of this modified function are then given. The analogous expressions for the derivatives in terms of Euler angles are not given since they are obtainable in a similar way to that which is detailed for quaternions. This section concludes with the analysis of comparative calculations in which the minimization procedures have been based on either the Newton or quasi-Newton scheme with the rotation matrix being parametrized in terms of Euler angles or quaternion parameters. The comparative calculations demonstrate the superiority of quaternions over Euler angles for general use.
**Penalty Factor Method [103]**

It is possible to convert the constrained problem of minimizing $V_i$ as given in Eqn. (3.13) into an unconstrained minimization in seven variables by invoking Eqn. (3.14) (which allows for the independent differentiation with respect to the four quaternion parameters) and adding a penalty term to the potential energy function to direct $q$ on to the four-sphere of unit radius. Thus we may write

$$\overline{V}_i \equiv V_i + \frac{\sigma}{2} (\|q\|-1)^2$$  \hspace{1cm} (3.21)

Since the penalty function is exact the local minima of $\overline{V}_i$ are the solutions of the constrained problem. The penalty factor $\sigma$ was set to 20000 kJ mol$^{-1}$ in all calculations. This was chosen to lie between the smallest and largest eigenvalues of the Hessian so as not to increase the condition number. However it was found that the Newton and quasi-Newton schemes were not sensitive to the exact choice of $\sigma$.

**Derivatives of the Modified Potential Energy Function**

For the purpose of minimization the total intermolecular potential energy of the lattice can be reduced to the contribution of those molecules constituting the defect since the energy contributed by the remaining lattice molecules is constant. Therefore

$$V = \sum_{j \neq i_0} V_{i0,j} + \sum_{i \neq i_0} N_i V_{ij}$$

where $i$ labels the molecules of the defect

$i_0$ labels a particular molecule of the defect

$j$ labels all molecules of the lattice
\[ N_j = \begin{cases} \frac{1}{2} & \text{if } j \text{ is a molecule of the defect and} \\
1 & \text{otherwise.} \end{cases} \]

Thus

\[
\frac{dV}{dx_i} = \sum_{j \neq i} \frac{dV_{ij}}{dx_i} \tag{3.22}
\]

where \( x_i \) is a position or orientation variable of molecule \( i \).

Eqn. (3.22) simply says that to minimize \( V \) with respect to the position and orientation variables of molecule \( i \), we need only minimize the total interaction energy \( V_i \). Thus we now consider the minimization of the \( V_i \) as given in Eqn. (3.21) i.e.

\[ V_i = V_i(r, q) = \sum_{j \neq i} V_{ij}(r, q) \]

The following details are given for an atom-atom potential of the \((\text{exp-6})\) form, however, the method is completely general for any potential which can be expressed as a sum of pairwise contributions. Therefore we can write

\[ V_i = \sum_{\ell} \sum_{k} v_{\ell k}(r, q) \]

where \( \ell \) labels the atoms of molecule \( i \) and \( k \) the atoms of the environment. Each interaction \( v_{\ell k} \) depends on the norm of the difference vector \( s_{\ell k} = s_{\ell} - s_k \) between the atoms \( \ell \) and \( k \) with position vectors \( s_{\ell} \) and \( s_k \). We may then write for \( v_{\ell k} \)

\[
v_{\ell k} = - \frac{A}{\|s_{\ell k}\|^6} + B \exp(-C\|s_{\ell k}\|) \tag{3.23}
\]

where the subscripts \( \ell \) and \( k \) have been omitted from the constants \( A, B \) and \( C \) for convenience. Also for convenience we make the substitution

\[ \rho_{\ell k} = \frac{1}{2} \|s_{\ell k}\|^2 \]

and then derive the first and second derivatives.
First Derivatives

Let \( s'_{sk} = \|s_{sk}'\| \) then

\[
S_{sk}' = \frac{dv_{sk}'(s_{sk}')} {d\rho_{sk}'} = \frac{6A} {s'_{sk}} - \frac{BC} {s_{sk}'} \exp(-Cs_{sk}')(3.24)
\]

With \( x_{sk} \) the atomic position coordinates of atom \( k \) in the body frame of molecule \( i \) we obtain

\[
s_{sk} = r + A^T(q)x_{sk}
\]

and

\[
s_{sk}' = r + A^T(q)x_{sk}' - s_{sk}'
\]

(3.25)

Thus for the centre of mass derivatives

\[
\frac{\nabla}{\nabla x} s_{sk}' = \frac{\nabla}{\nabla x} \left( \frac{1}{2} s_{sk}' \right) = \left( \frac{\nabla}{\nabla x} A^T(q) \right) s_{sk}'
\]

\[
= I s_{sk}' \quad \text{(from Eqn. (3.25))}
\]

and

\[
\frac{\nabla}{\nabla} v_i = -\sum_{k} v_{sk}' s_{sk}'
\]

with

\[
f_{sk}' = -\sum_{k} v_{sk}' s_{sk}'
\]

the total intermolecular force operating on atom \( k \).

Now for the derivatives with respect to the quaternion parameters

\[
\frac{\nabla}{\nabla} q_{sk} = \left( \frac{\nabla}{\nabla} A^T(q) \right) s_{sk}'
\]

and thus by Eqn. (3.25)

\[
\frac{\nabla}{\nabla} q_i = -\sum_{k} q_{sk} f_{sk}'
\]

with

\[
q_{sk}' = \left[ A^T x_{sk} , A^T x_{sk} , A^T x_{sk} , A^T x_{sk} \right]^T
\]

and \( \frac{\partial}{\partial q_v} A(q) \) with \( q_v \) the \( v \)th component of the quaternion. To
calculate $A_{ij}$ for the general non-zero quaternion $q$ at the corresponding normalized point $\hat{q} = q/\|q\|$ the following procedure is adopted. We consider the matrix $R(q)$ at the unnormalized point where $R(q) = \|q\|^2A(q)$ and remember (Eqn. (3.8)) that $R(q)$ is quadratic in $q$ and therefore the first derivative $R_{ij}(q)$ must be linear. Therefore we obtain

$$A(q) = R(\hat{q}) \quad (i.e. \text{Eqn. (3.14)})$$

and

$$A_{ij}(q) = [R_{ij}(\hat{q}) - 2q_j A_i(\hat{q})] / \|q\| \quad (3.26)$$

To compute $V_i$ the total force on atom $i$ due to the atoms of the environment is calculated. The centre of mass derivatives are then obtained by summing the individual components of the force on each atom $l$ and multiplying by $-1$. The orientational gradients are obtained by evaluating $A(q)$ and the $A_{ij}(q)$, and thus the $4 \times 3$ matrix $\mathcal{O}_q$ for each atom $l$. Then $\nabla_q V_i$ is obtained by taking the inner product of the rows of $\mathcal{O}_q$ with $f_l$, multiplying by $-1$, and adding up the components of the $4 \times 1$ vector for each atom $l$. To each component of this 4-vector must be added the appropriate component of the derivative of the penalty term in Eqn. (3.21) i.e. $\sigma(\|q\|-1)\hat{q}_i$.

It is apparent that the first derivatives of $V_i$ (Eqn. (3.21)) are easily obtained as are those of $V_i$ (Eqn. (3.1)) in terms of Euler angles. Thus the implementation of a quasi-Newton scheme is in principal a straightforward procedure. It will also be shown that the application of a quasi-Newton scheme using quaternions or Euler angles with $\theta \approx 90^\circ$ is quite an efficient and reliable way of computing the structure of a defect.

Second Derivatives

We may re-write the first derivatives in the general form
\[
\n\nabla_{\mu} V_{i} = \sum_{k} \frac{1}{s_{\mu_k}} \bigg( \frac{\nabla_{\mu} s_{\mu_k}^{T}}{s_{\mu_k}} \bigg) \cdot s_{\mu_k}
\]

where \( \mu \) denotes together the variables \( \mathbf{r} \) and \( \mathbf{q} \), and \( \nabla_{\mu} s_{\mu_k}^{T} \) is a \( 7 \times 3 \) matrix. Thus the second derivatives take the general form

\[
\nabla_{\mu}^{2} V_{i} = \sum_{k} \left( \nabla_{\mu}^{2} s_{\mu_k}^{T} \cdot s_{\mu_k} \right) + \frac{1}{s_{\mu_k}} \left( \frac{\nabla_{\mu} s_{\mu_k}^{T}}{s_{\mu_k}} \right) \cdot \frac{\nabla_{\mu} s_{\mu_k}}{s_{\mu_k}}
\]

where it is noted that \( \nabla_{\mu}^{2} s_{\mu_k} \) is a three-dimensional array, with dimensions \( 7 \times 7 \times 3 \).

If we define the matrices

\[
F_{\ell} = \sum_{k} \left( \nabla_{\mu}^{2} s_{\mu_k}^{T} \cdot s_{\mu_k} \right)
\]

and

\[
F_{\ell} = -F_{\ell}^{T} A_{\mu \nu}(q) \cdot x_{\ell}
\]

with

\[
A_{\mu \nu}(q) = \frac{3}{3q_{\mu}} A_{\mu}(q)
\]

the Hessian may then be written in terms of the previously defined quantity

\[
\frac{\partial^{2}}{\partial \mu \nu} V_{i} = \sum_{k} \left( \frac{F_{\ell}}{s_{\mu_k}} , \frac{F_{\ell}^{T} \cdot s_{\mu_k}}{s_{\mu_k}} + \frac{F_{\ell}^{T} \cdot s_{\mu_k}}{s_{\mu_k}} \right)
\]

We obtain from Eqn. (3.26)

\[
A_{\mu \nu}(q) = \frac{\partial^{2}}{\partial \mu \nu} \left( \frac{\mu}{2} \right) - 2 \frac{\partial}{\partial \mu} \frac{\partial}{\partial \nu} \left( \frac{\mu}{2} \right) - 2 \frac{\partial}{\partial \mu} \frac{\partial}{\partial \nu} \left( \frac{\mu}{2} \right) + 8 \frac{\partial}{\partial \mu} \frac{\partial}{\partial \nu} \left( \frac{\mu}{2} \right) - 2 \delta_{\mu \nu} A(q) \frac{1}{\frac{\mu}{2}}
\]

and from Eqn. (3.24)

\[
\frac{\partial^{2}}{\partial \mu \nu} V_{i} = -\frac{48 \Lambda}{s_{\mu_k}} + \frac{1}{s_{\mu_k}} \left( 1 + C s_{\mu_k} \right) B C - \frac{3}{s_{\mu_k}} \exp(-C s_{\mu_k})
\]
and the Hessian of the penalty term:

\[ \sigma\left(\|\mathbf{q}\|^{-1}\mathbf{I} + \mathbf{q}\mathbf{q}^T / \|\mathbf{q}\|^2\right) \]

For the computation of the Hessian the only additional time-consuming term to evaluate is the symmetric 3 x 3 matrix \( v''_{\alpha'\alpha''} s_{\alpha''} s_{\alpha}^T \). In terms of Euler angles the Hessian differs only in the calculation of the matrices, and obviously there are no penalty terms.

**Comparative Calculations**

Calculations were performed using the modified Newton or quasi-Newton descent methods in combination with quaternions or Euler angles to ascertain the most efficient and reliable method for computing the structure of a defect. Results are reported for the substitutional defect anthracene in naphthalene in which the anthracene and its 20 nearest neighbours (see Chapter 4) were included in the minimization. The results obtained for this system were found to be representative of this type of defect. Since molecular orientations in these systems differ little from those in the pure, perfect crystal it is possible to demonstrate clearly the reduced efficiency and reduced reliability of minimization procedures using Euler angles as the azimuthal angle \( \theta \) decreases from \( 90^\circ \). Unless otherwise stated the procedures followed in these calculations have been used throughout.

In the calculations the environment of molecules chosen to simulate the defect includes all atom-atom interactions within 1 nm of the molecules treated in the minimization. The cycling procedure discussed in the previous sections was used to minimize \( V \) (Eqn. (3.1)) with respect to the translation and orientation variables of each of the selected molecules and was terminated when the potential energy differed between cycles by less than 0.1 kJ mol\(^{-1}\), which corresponds to a difference of 1 in 10\(^5\) (for
the anthracene in naphthalene system \( V \) was approximately \( 2.3 \times 10^3 \text{ kJ mol}^{-1} \). Typically 4-6 cycles were necessary to satisfy this condition. The efficiency of the total minimization was not sensitive to variations in the settings of the parameters which determined the increase in accuracy of the individual molecular minimizations in consecutive cycles. The parametrization of the \((\text{exp-6})\) potential was as in Williams' set IV \(^{[170]}\) and for consistency with the parameter set the position of hydrogen was taken to lie at 0.1027 nm from the carbon nucleus in the experimentally determined carbon-hydrogen bond. Crystallographic inversion symmetry, if present, was retained unless otherwise stated.

For the results reported in this section the quaternion calculations are denoted by \( Q \) and the Euler angle calculations by \( E_\theta \) where the subscript indicates that the body coordinate frames were chosen so that the azimuthal angle \( \theta \) was within \( \pm 5^\circ \) of \( \theta \) for the duration of the calculation. The approximating Hessians of the quasi-Newton scheme were initialized to 20000 I for \( Q \) and 5000 I for \( E_\theta \). The final approximating Hessians were stored at the completion of each cycle and used as the initial estimates in the next cycle.

To gauge the efficiency of each method we plot \( \log_{10} [(V(n) - V_{\min}) / |V_{\min}|] \) at the end of each cycle against the number of 'potential' evaluations '\( n \)', where \( V_{\min} \) is the lowest calculated value of the total intermolecular potential energy. The Newton scheme includes in the 'potential' evaluations the terms \( \nabla_i^2 V_i \) in addition to those required by the quasi-Newton scheme. The results are illustrated in figure 2.

From figure 2 we note that:

i) the Newton scheme in combination with quaternions and \( E_\theta \) are
most efficient.

ii) the quasi-Newton scheme in combination with quaternions takes approximately twice the number of potential evaluations and 40% more computing time than the corresponding Newton method, while it can be seen to be sensitive to small deviations from $\theta = 90^\circ$.

iii) both Newton and quasi-Newton schemes suffer reduced efficiency as the azimuthal angle $\theta$ decreases from $90^\circ$. The quasi-Newton scheme is more sensitive to the changes in $\theta$ than is the Newton scheme.

iv) both schemes exhibit poor and unreliable convergence for $\theta < 10^\circ$.

In addition we note that the quasi-Newton scheme with $E_0$ exhibits a very low rate of convergence which could have terminated prematurely with a lower tolerance, resulting in a value of $V$ approximately 25 kJ mol$^{-1}$ above the actual minimum. The reduced efficiency with decreasing $\theta$ is directly related to the condition number of the Hessian, which for $\mathcal{Q}$ and $E_{90}$ was of the order 10, while for $E_0$ it was $10^6$.

We conclude that the most efficient and reliable method of performing static lattice energy minimizations is to use a modified Newton scheme in combination with quaternions. However, if molecular orientations are expected to change only little during the course of the minimization then the Newton scheme in combination with Euler angles with $\theta \approx 90^\circ$ is an efficient and reliable method. The quasi-Newton scheme in combination with $E_{90}$ is the easiest method to implement and is still relatively efficient, although, since the implementation of the quaternions in this case is only marginally more difficult, and leads to improved performance, it is preferable.
Figure 2

COMPARISON OF THE PERFORMANCE OF THE NEWTON SCHEME 'HESMIN' (-----) AND QUASI-NEWTON SCHEME 'FUNMIN' (------) IN COMBINATION WITH QUATERNIONS 'Q' AND EULER ANGLES 'E' FOR THE SYSTEM ANTHRACENE IN NAPHTHALENE.

($|V_{\text{min}}| \approx 2.3 \times 10^{+3}$ kJ mol$^{-1}$)
CHAPTER 4

POINT DEFECTS: A COMPUTATIONAL STUDY

INTRODUCTION

A detailed study of some simple point defects has been undertaken to determine the potentialities of the method of computation and to obtain an understanding of the effects of lattice relaxation. The experience gained in performing these calculations will permit a more reliable analysis of the results obtained from the calculations on anthracene dimers and related systems (Chapter 5), and those of future studies.

We begin by reviewing the relevant background literature. Related experimental work is also considered in order to illustrate the scope for future applications. Previous calculations are reviewed, and finally, our calculations are reported and discussed.

EXPERIMENTAL BACKGROUND

Point Defects of a Chemical Origin

This type of defect arises when an impurity (i.e. guest) molecule replaces a molecule of a host lattice. In many instances this replacement is well characterised, with the guest adopting one or several orientations. Guest molecules, to varying degrees, will produce disturbances to the surrounding molecules of the host lattice. If the disturbance causes a depression of the transition energies of these host molecules then the energy levels fall below those of the exciton band, and energy trapping may occur [44]. Such disturbed host molecules are called X-traps. For this
reason chemical impurities have been of considerable experimental interest. Albeit there is remarkably little quantitative information on the orientation of guests and the concomitant lattice disturbance which they produce. Most of the quantitative data that have been obtained are from E.S.R. investigations of the triplet state. Since these results are the only source of accurate experimental data with which to compare we must assume that the calculated structure for the guest in its electronic ground state is the same as that in $T_1$. Obviously there will be differences in the intermolecular potential and molecular geometry upon excitation, and since the lifetime of the $T_1$ state is many orders of magnitude greater than the period of a lattice vibration the surrounding lattice has ample time to equilibrate. The assumption of unchanged molecular structure has little justification other than that of practical necessity.

The experimental technique used to determine the guest orientations with which we compare our results is given by Dörner and Schmid [47]. We now give a summary of the general approach to the experimental problem. In these methods the splitting of the components of the triplet state is determined as a function of the angle of rotation of a magnetic field in a chosen crystallographic plane (in order to avoid certain ambiguities of the method data needs to be collected for several crystallographic planes). The form of the secular determinant that describes this splitting is known [108]. The elements of the fine structure tensor, which accounts for the mutual dipolar interaction between the two unpaired spins, to which the discussion is restricted, enter this determinant as parameters to be determined by least squares techniques. The fine structure axes are then determined by diagonalizing the 'fitted' fine structure tensor. In the cases of interest here, e.g. tetracene in anthracene, these axes coincide with the molecular symmetry axes, thus the orientation of the molecule is
determined. Further simplifications arise in these cases since the
$g$-tensor, which relates the splitting of the energy levels to the direction
of the magnetic field in the fine structure frame, is isotropic and thus
its elements enter the secular determinant as a known, or estimated,
multiple of the identity matrix. In less simple cases the elements of this
tensor must also be treated as parameters to be determined.

Before considering the guest orientations we quote as an example the
work of Dörner and Schmid [47] in which the disturbance to a host naphthalene
lattice is determined for the guests 2-fluoro-, 2-chloro- and
2-bromonaphthalene. In these systems the lattice disturbance was found
to increase with increasing substituent size. The largest displacements,
given as angles between the unperturbed host $L$, $M$ and $N$ principal axes,
vide infra, and those in the perturbed orientation $L'$, $M'$ and $N'$, are
found to be $<L'L = 7.2^\circ$, $<M'M = 10.0^\circ$ and $<N'N = 9.5^\circ$, with an error
estimate of $\pm 2^\circ$. Brillante et al [19] in a study of anthracene doped with
2-methylanthracene report polarization ratios which also indicate that the
host molecules adjacent to the guest are not significantly misoriented.

To help systematize the remaining discussion of this section we
consider firstly those guest/host systems in which the guest occupies a
single type of site, and secondly, those in which there are two or more
occupied sites.

Single Guest Sites

Perfect substitution is a concept used in connection with substitutions
involving planar aromatics. In such cases the principal axes of the guest
are coincident with those of the replaced host molecule with no accompanying
lattice distortion. It appears that substitutions of this kind are rare.
We consider as examples tetracene in anthracene, and anthracene in naphthalene. There are few systems involving aromatic hydrocarbons for which quantitative experimental findings are available.

**Tetracene in Anthracene, and Anthracene in Naphthalene**

Ostertag and Wolf [123] reported that an anthracene molecule in a naphthalene host lattice adopts an orientation in which the molecular plane is parallel to that of the replaced host molecule but with a rotation about the anthracene normal axis. This displaces the in-plane axes of the guest with respect to those of the replaced host molecule by an angle of 25°. Chabr et al [30] reported that tetracene enters anthracene with an orientation that is the same as that of the replaced host. The more recent work of Dörner et al [46] shows, contrary to the earlier findings, that there is a small displacement in orientation of the guest away from that of the host. Table 1 gives the orientation of both guests. The values in brackets are those of the host. L, M and N designate the principal axes, in order long(L) and short(M) in-plane directions and normal(N). This axis convention has been adopted throughout this work, even for non-planar molecules. In the latter case the nomenclature is used to label, as it does for the planar aromatics, the principal molecular axes of increasing inertial moment, i.e. \( L < M < N \). Dörner et al [46] show that the error made by Ostertag and Wolf [123] was due to an ambiguity which arose in the E.S.R. least squares fitting procedure.

**Impurity Segregation from Anthracene**

For aromatic hydrocarbons there appears to be no experimental measurement of the enthalpy change that accompanies the replacement of a host molecule by a guest. However, the studies by Sherwood and
TABLE 1
EXPERIMENTAL GUEST ORIENTATIONS [46]

ANTHRACENE ORIENTATION IN A NAPHTHALENE HOST
(Direction Cosines)

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
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<td>-0.1167 [-0.2103]</td>
<td>0.8886 [0.8741]</td>
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<tr>
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<td>-0.8965 [-0.8718]</td>
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<tr>
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<td>0.3584 [0.3143]</td>
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</table>

TETRACENE ORIENTATION IN AN ANTHRACENE HOST
(Direction Cosines)

<table>
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<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
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<td>0.8563 [0.8491]</td>
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<tr>
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</tr>
<tr>
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<td>-0.3891 [-0.4222]</td>
<td>0.4242 [0.4192]</td>
</tr>
</tbody>
</table>

co-workers [36,107,118], and Sloan [147] are very useful. They have studied the
growth of mixed crystals. They ascertained the relative ease with which
certain guests can be incorporated into an anthracene lattice by
measuring the percentage segregation of the guests from melt-grown
crystals. This entails measuring the fraction of guest molecules segregated
to the top of a grown mixed crystal. Ideally the crystals should be grown
slowly, the mixture being stirred so as to approximate closely to
equilibrium conditions [147]. Rapid growth reduces the percentage segregation
while the failure to maintain a homogeneous mixture can result in
non-equilibrium concentrations of the impurity at the growing surface.
Corke et al [36] studied the incorporation of anthraquinone, naphthalene,
tetracene and carbazole as guests in anthracene. The guests were added to
the melt giving concentrations ranging from 21-1300 ppm. The crystals were
grown at 1.5 mm hr\(^{-1}\) without stirring. The following observations were made:

i) The percentage of guest segregated decreased in the series anthraquinone 99%, naphthalene 94%, tetracene 64% and carbazole 2%. There was a similar finding in Sloan's work. This finding can be correlated with the shape of the guest. Carbazole most resembles anthracene and is therefore incorporated readily into the lattice while anthraquinone with its laterally projecting ketone groups fits less readily into the lattice. However, there appears to be no a priori reason why naphthalene should be rejected more readily from the lattice than tetracene.

ii) Carbazole and tetracene doped crystals had a dislocation content which was similar to that of the better pure crystals. For the doped crystals the number of dislocations was of the order 10^4\(-10^6\) cm\(^{-2}\) while for the pure crystals it was 10^5\(-10^6\) cm\(^{-2}\). For naphthalene and anthraquinone doped crystals the dislocation content was much larger. For these crystals it was 10^7\(-10^8\) cm\(^{-2}\) and 10^8\(-10^9\) cm\(^{-2}\) respectively.

iii) Annealing carbazole and tetracene doped crystals resulted in a decrease in dislocation content which appeared in some cases to proceed more rapidly than in the pure crystal. There was no noticeable change in the dislocation content of the anthraquinone and naphthalene doped crystals even on prolonged annealing.

iv) For the growing crystal the impurity and dislocation content were greater in the region of current growth than in the region at which crystallization commenced.
v) There is evidence, particularly for the tetracene guest, that regions of high dislocation content can be associated with the segregation of the impurity from the lattice at high concentrations. There is a related finding by Ferguson [57].

**Solubility**

Kitaigorodsky and Myasnikova [101,102] were the first to observe that two types of solubility were possible in organic molecular crystals. The first kind involves the substitution of host molecules by guest molecules, up to a certain solubility limit, in otherwise perfect regions of host lattice. This is the true solubility. In the second kind guest molecules enter a host lattice and are concentrated in defects in the lattice, such as dislocations, or on boundaries of blocks. This is interblock solubility. The latter kind usually occurs once the true solubility limit has been reached. The thermodynamic aspects of the phenomenon of solubility have been considered [102].

It is useful to note some 'mutual' solubilities of the aromatic hydrocarbons. The following observations have been made:

i) Hochstrasser and Small [89] found that the solubility of phenanthrene in naphthalene was $10^{-5}$ mol/mol (for melt-grown crystals) while with biphenyl as solvent it was $10^{-2}$ mol/mol.

ii) Brillante and Craig [17,18] found that pentacene in anthracene has a solubility not much greater than $10^{-4}$ mol/mol. They also found that pentacene is incorporated more readily into a naphthalene host than an anthracene host. This was rationalized on the basis of a one-for-two substitution. It is clear that a pentacene in naphthalene will encounter repulsive interactions at the L axis.
extremities which would be greater than those experienced in the pure naphthalene lattice while in anthracene a certain free volume would result. We note that lattices appear to tolerate higher than normal repulsions with slight lattice disturbance but will not tolerate free volume. There is another interesting finding reported by Brillante and Craig [18]. They observe that the first layer of pentacene deposited on the surface of an anthracene crystal exhibits an epitaxial relationship to the anthracene substrate but this is lost as the result of aggregation as further layers are deposited.

iii) Sidman [144,145] found that anthracene is a better solvent for tetracene than naphthalene (Ferguson [57] found that the true solubility limit of tetracene in anthracene is \(10^{-4}\) mol/mol). This finding can be rationalized using similar arguments to those that were used for the systems pentacene in anthracene or naphthalene.

**Multiple Guest Sites**

The discussion of this site type can be systematized by adopting the classification scheme of Bridge and Gianneschi [14]. They distinguish three distinct cases:

1) Cases in which slightly different orientations of the guest correspond to different displacements of the neighbouring host molecules. This may occur if the host molecule is not rigid or if the guest is much larger than the host molecule. Examples are phenanthrene in biphenyl, and anthracene in p-terphenyl. These systems have been studied by Hochstrasser and Small [87, 88, 89, 148]. In the former system they found that phenanthrene
occupies two sites separated by a long (L) axis rotation, however, the extent and importance of host distortions could not be determined. More recently, Cullick and Gerkin [45] have shown that below 2K phenanthrene occupies four sites and not two as originally thought. Another example has been observed by Brillante and Craig [18] in studies of anthracene doped with pentacene. Pentacene in substitution occupies three sites. These are thought to differ only by small orientational displacements.

ii) Cases in which the sites result from a guest replacing crystallographically inequivalent host molecules. As examples of this type of site we consider as guests acenaphthylene (Bray and Craig [12]), and α-nitronaphthalene (Myasnikova et al [116]) in a host lattice of acenaphthene. Acenaphthene [50] crystallizes with an orthorhombic unit cell with two crystallographically inequivalent sets of two molecules each. Set I molecules have their principal axes coincident with the crystal axes while set II molecules differ from Set I molecules by having their principal axes displaced slightly about the long (L) axis. In the study made by Bray and Craig [12] acenaphthylene was found to occupy three sites. The substitution of set II molecules is thought to be energetically more favourable. This set of molecules is found to accommodate two configurations of acenaphthylene. These are thought to differ only by a small misalignment. α-nitronaphthalene may occupy four sites in the acenaphthene lattice (neglecting any sites due to the rotation of the nitro group). The stability of the sites was determined by calculation.
iii) Cases in which the host molecules are crystallographically equivalent and differences between the guest sites arise from a large change in orientation of the guest with respect to the lattice. Examples of this type of guest site have been found for 1- (and 2-) amino-, and 1- (and 2-) hydroxyanthracene in anthracene. Since anthracene has an inversion centre these guests can adopt two possible orientations with respect to the lattice. These differ essentially by a $180^\circ$ long axis rotation. In the next section it will become clear that for 2-hydroxyanthracene the situation is not as straightforward as originally thought \([14,20]\) since one or both symmetry allowed sites appear not to be occupied, yet two sites are found.

2-hydroxyanthracene (2-OHA) in Anthracene

2-hydroxyanthracene is a persistent impurity in anthracene even in highly purified samples. It is an efficient energy trap. Bridge and Vincent \([15]\) were the first to identify 2-OHA as impurity in highly purified anthracene and suggested that it probably occupied two sites. Brillante et al \([20]\) confirmed the existence of the two sites whose principal origins are at $24352 \text{ cm}^{-1}(0_8)$ and $24165 \text{ cm}^{-1}(0_9)$. These investigators found only one X-trap. Assuming that the two sites corresponded to the two substitutional sites allowable by symmetry they proceeded to associate the X-trap with the less stable $0_8$ site. This site was interpreted as that which would experience the larger intermolecular repulsions. Using packing calculations Bridge and Gianneschi \([14]\) confirmed this assignment.

Later, Craig and Rajikan \([41]\) reported that the $0_9$ site was photochemically reactive while the $0_8$ site was not. This finding was
disputed by Williams and Clarke [175] but then confirmed by Burland and Thomas [23]. This phenomenon has been termed site selective photochemical change [41]. It is thought that the \( \sigma \) site occurs in a region of disordered or defective lattice such as that found by Parkinson et al [125] or that predicted by Craig et al [40]. At this site the 2-OHA is stereochemically adapted to photoreaction, most likely to form a mixed dimer with anthracene. Thermal activation is required. We report calculations on this system in a later section in order to try and rationalize these observations.

**Vacancies and Self-Diffusion**

Self-diffusion in high perfection and high purity crystals of the rare gases and aromatic hydrocarbons is thought to occur by a single vacancy and/or a divacancy mechanism [26,31]. Which of these is dominant (if either) is not known. The rationalization of the experimental data obtained for the rare gases in terms of one or other of these mechanisms has relied on the results of computational investigations. There have been no similar calculations reported for the aromatic hydrocarbons. The first of these are reported later in this chapter.

The enthalpy of vacancy formation \( \Delta H_{\text{vac}} \) is of central importance to understanding the process of self-diffusion. Nevertheless, there has only been one experimental study giving an accurate value for \( \Delta H_{\text{vac}} \) [31]. This was for krypton for which \( \Delta H_{\text{vac}} \) was found to be 0.7 \( \Delta H_{\text{SUB}} \) (where \( \Delta H_{\text{SUB}} \) is the enthalpy of sublimation of the pure lattice). Most rare gas calculations indicate that \( \Delta H_{\text{vac}} \approx \Delta H_{\text{SUB}} \). Many-body effects have been invoked to account for the difference between the calculated values and the experimental results. However, there are disturbing features of the calculations which should not be overlooked. We now consider the method of
A vacancy is created in the bulk perfect lattice by removing a molecule to the surface. The molecules of the lattice surrounding the vacant site are allowed to relax to positions of minimum energy. \( \Delta H_{\text{vac}} \) is found by adding to the enthalpy of the environment of the vacancy one half of the total interaction energy of a molecule of the perfect lattice to approximate the enthalpy contribution from the molecule which was removed from the bulk and put on the crystal surface, and subtracting this quantity from the total potential energy (i.e. the total enthalpy) of the same molecules of the initial perfect lattice. Clearly there are two questionable features of this method. The first is the arbitrary manner in which the enthalpy contribution of the molecule at the surface is included. The second is that the calculation is done for a vacancy created in the bulk lattice but obviously vacancy formation must take place at an internal or an external surface. We believe that \( \Delta H_{\text{vac}} \) determined experimentally for krypton is reasonable since one would expect that a vacancy would be created more easily at a surface than in the bulk. Thus in part the disagreement between theory and experiment can be understood. However, treating vacancy formation near a surface is not an easy task.

In related calculations Burton and Jura [27] studied other point defects in argon using a pair potential. They found the following:

i) relaxations around small included atoms are qualitatively like those around vacancies, while relaxations around large atoms are opposite in sign to those around vacancies. All relaxations are small. There is a similar finding by Squire and Hoover [149].
ii) The formation of a vacancy next to another defect, such as a smaller or larger guest, is energetically preferred to the formation of an isolated vacancy. The finding that the smaller guest produces this effect is surprising.

We now consider self-diffusion. Radioactive tracer experiments are one way of obtaining an estimate of the diffusion coefficient $D$ for self-diffusion. From the temperature dependence of $D$ the Arrhenius activation enthalpy $\Delta H_{\text{act}}$ for this process can be obtained from:

$$ D = D_0 \exp\left(-\frac{\Delta H_{\text{act}}}{RT}\right) $$

The values of $\Delta H_{\text{act}}$ obtained in this way indicate that the activation enthalpy is approximately $2\Delta H_{\text{SUB}}$ [31] for aromatic hydrocarbons.

Sometimes $\Delta H_{\text{vac}}$ is reported as an activation volume $V^*$ [79]. This volume is given by the pressure derivative of the free energy for self-diffusion $\Delta G_d$, i.e.

$$ V^* = \left[ \frac{\partial (\Delta G_d)}{\partial P} \right]_T $$

In this form the experimental results are difficult to compare with those obtained by calculation since the need to consider molecular orientations makes pressure simulation more difficult than it is for crystals of the rare gases.

For computational purposes $D$ is considered to be proportional to the concentration of vacancies and the rate of vacancy migration i.e.

$$ D \propto \exp\left(-\frac{\Delta H_{\text{vac}}}{RT}\right) \exp\left(-\frac{\Delta H_{\text{mig}}}{RT}\right) $$
The procedure adopted to compute $\Delta H_{\text{mig}}$ (the enthalpy of migration) for the rare gases entailed placing an atom at the mid-point of the 'line' joining the centre of two adjacent unoccupied sites, i.e. the sites from and to which the diffusion 'jump' is to be simulated. The lattice was then allowed to relax to a configuration of minimum energy about the diffusing atom. Values obtained for $\Delta H_{\text{vac}}$ using these procedures have been in agreement with experiment [31]. Although it must be remembered that many approximations have been made in the calculations, and that accurate experimental results are difficult to obtain.

There appears to be only one study of self-diffusion in hydrocarbon molecular crystals. This was the study by Fyfe and Harold-Smith [70]. Their calculations are seriously in error for the reason given by Busing [25].

PREVIOUS CALCULATIONS

In this section we review the static lattice calculations that have been performed on point defects in aromatic hydrocarbon molecular crystals. These are few in number. Most have been performed at an unsophisticated level and in some instances are erroneous. We note the useful related review by Bennett [6] which deals with molecular dynamics and Monte Carlo methods, in addition to static lattice calculations on point defects in non-organic systems.

Single Guest Sites

Ostertag and Wolf [123] reported some general findings from a computational study of anthracene in naphthalene. We were able to obtain further details of their calculations from the Ph.D. thesis of Ostertag [122]. They adopted the following procedure. An environment of naphthalene molecules was formed in which the central molecule was removed and replaced
by an anthracene. The minimum-energy defect structure was found with respect to the centre of mass position and orientation variables of the guest and the 16 nearest neighbours. It is not clear how this was done - we assume that a Newton scheme was applied to the minimization in all variables simultaneously. Inversion symmetry was retained since calculations indicated that off-centre sites were energetically unfavourable. The total potential energy of the guest and 16 neighbours was evaluated using the \((\exp-G)\) potential with Kitaigorodsky's parametrization \([98]\). The potential energy contribution from the remainder of the environment molecules, out to a distance of five lattice spacings, was calculated using a method based on the macroscopic theory of dislocations. In this method the strain energy of the "field" is assumed to decrease elliptically about the guest as the inverse of the distance from the nearest neighbours. The inverse distance dependence appears to be related to the theoretical treatment of "penny-shaped" dislocations, (Nabarro [117]). The harmonic force constants of pure naphthalene are used to calculate this contribution to the total potential energy: it is not clear how this was done.

When the anthracene was put into the lattice in a position of perfect substitution it was found that the defect was less stable than the pure host by \(420 \text{ kJ mol}^{-1}\). Upon allowing full relaxation the energy difference decreased to \(120 \text{ kJ mol}^{-1}\) with small changes in the orientation of the guest and neighbour molecules. The harmonic force constants calculated at the equilibrium defect structure were found to be 5-10 times larger than those of the pure crystal. Other sites were considered in which the anthracene replaced several naphthalenes. Since there was an error in the experimental findings a number of their conclusions are invalid.

We believe, as do Ostertag and Wolf, that the defect energies are too
large. The calculated force constants also are surprisingly large. A particularly strong conclusion drawn by Ostertag and Wolf [123], with which we are in partial agreement only, is that the short interatomic distances encountered in defect situations invalidates the use of potentials parametrized from data collected for equilibrium crystal properties. This conclusion was based on their energetic results, and structural results which were at variance with experiment. Since a number of aspects of the method of calculation are not clear the only explanations that can be offered for the large defect energies and force constants is that perhaps the method of minimization may have been somehow in error or that the macroscopic dislocation theory is not applicable at the molecular level.

Recently, Ramdas [132] reported calculations on anthracene in naphthalene, tetracene in anthracene, and naphthalene in anthracene. His results are in disagreement with ours on a number of points; therefore we shall leave the discussion of this work until a later section.

Multiple Guest Sites

Bray [11] performed molecular packing calculations on acenaphthylene in acenaphthene. He adopted the procedure of minimizing the atom-atom repulsions between the acenaphthylene and the 'rigid' cage of acenaphthene molecules. Using the repulsive part of the (exp-6) potential with the parametrization of Rae and Mason [131] he found that the guest adopts an orientation at each of the crystallographically inequivalent sites that is closely the same as that of the replaced host molecule. However, each crystallographically inequivalent set accommodates only one guest site. This is not in agreement with experiment (see previous sections). Similar calculations were performed by Myasnikova et al [116] on α-nitronaphthalene as a guest in acenaphthalene. Replacement of the set I molecules was found
to lead to the more stable guest site.

Some of the first mixed-crystal packing calculations were performed by Hochstrasser and Small [89]. A particular system that they studied was phenanthrene in biphenyl. In these calculations the phenanthrene was placed into the lattice in a position of "perfect substitution". In principal the procedure was to calculate repulsive potential curves as a function of the angle of rotation about the principal molecular axes of phenanthrene in order to find the minimum-energy orientations. In some instances small displacements of certain neighbours were also considered. They report that the functional form of the repulsive potential curves was extraordinarily sensitive to the choice of the hydrogen repulsion centre in the carbon-hydrogen bond. They conclude from a series of calculations on a number of systems that the assumption of near perfect alignment of the guest and host molecules in aromatic mixed-crystal systems is not generally valid.

Bridge and Gianneschi [14] performed calculations on the two symmetry allowed orientations of 2-OHA in anthracene. In these calculations 2-OHA was placed into the anthracene lattice with its aromatic ring system coincident with that of the replaced host. From this starting position the interaction energy of 2-OHA, in which oxygen is treated as carbon, was minimized with respect to its centre of mass position and orientation variables. The surrounding lattice was held fixed at the experimentally determined equilibrium structure. As stated previously the configurational assignment of Brillante et al [20] was confirmed.
COMPUTATIONAL RESULTS AND DISCUSSION

We report the results of our calculations on pure crystals, on the replacement of a molecule of a host lattice by either a larger or smaller guest, on vacancies, on self-diffusion, and on the packing of 2-OHA in anthracene. This study has enabled us to achieve our stated aims. These were to establish the potentialities of the method of calculation and to obtain an understanding of the effects of lattice relaxation so that a proper analysis of the results of the following photochemical study could be made.

PURE CRYSTALS

As a test of internal consistency we applied the method of computation to pure crystals of naphthalene [37] and anthracene [106], the structures of which were determined by X-ray diffraction at room temperature and 95K respectively. Since these crystal structures were used in the determination of the potential functions they should be well reproduced by the method of computation. Before presenting the results we note that the procedures adopted in the calculations are similar in all subsequent calculations reported in this chapter.

An environment of molecules was chosen, in the manner specified in Chapter 3, so as to include in the minimization the 54 neighbour molecules of the central molecule which are listed in Table 2 and schematically illustrated in figure 1. In the following text when we refer to the 20 nearest neighbours of the central molecule or guest we shall mean the first 20 molecules that are listed in Table 2. In a similar way we shall refer to the 32 and 54 neighbour molecules. Alternatively we may refer to these as the nearest, next nearest, and next next nearest neighbours. As can be
Figure 1. Schematic representation of the energy-minimized environment of anthracene and naphthalene hosts.

O ≡ molecule in ab plane
+
- ≡ molecule above ab plane
-
- ≡ molecule below ab plane
TABLE 2

SITES IN ENERGY-MINIMIZED ENVIRONMENT

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<th>Type in Unit Cell</th>
<th>Site Coordinates</th>
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<tr>
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<tr>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>49</td>
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</tr>
<tr>
<td>50</td>
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<tr>
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<td>0.0</td>
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</tr>
<tr>
<td>53</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>54</td>
<td>1</td>
<td>0.0</td>
</tr>
</tbody>
</table>
seen from figure 1 these neighbours were chosen to form an ellipsoid about the central molecule with the major axis parallel with the molecular $L$ axis.

It was found that the method of calculation when applied to the central molecule and its 20 nearest neighbours reproduced the crystal structures very well (inversion symmetry may be assumed to have been maintained unless otherwise stated). The largest centre of mass displacement occurred in naphthalene. This was of magnitude $3 \times 10^{-3}$ nm. As a measure of the deviation of the molecular orientations from those determined experimentally we have averaged all direction cosines of the principal axes of type 1 molecules (see Table 2). The averaged values are given in Table 3 together with the experimentally determined direction cosines in brackets. The largest deviation from the mean values was $0.4^\circ$ for naphthalene and $0.3^\circ$ for anthracene. Thus the largest deviations from the experimental values were $2.0^\circ - 2.5^\circ$ in several direction angles. It will become apparent later that a knowledge of the magnitude of these displacements will be useful for determining the physical reality of assumed crystallographic models.

Just as the calculated structures of these pure crystals are a test of the accuracy of the potential function, so too is the magnitude of the difference in the potential energy calculated at the experimentally determined structure and that calculated at the energy-minimized structure. We shall refer to this potential energy difference as $\Delta V$ and the total potential energy at the energy-minimized structure as $V_{\text{min}}$ (see Chapter 3).
TABLE 3
CALCULATED AND EXPERIMENTAL PRINCIPAL AXES DIRECTION COSINES FOR NAPHTHALENE AND ANTHRACENE

Naphthalene: Set 1 Orientations

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.4413 [-.4379]</td>
<td>-.1953 [-.2103]</td>
<td>0.8758 [0.8741]</td>
</tr>
<tr>
<td>M</td>
<td>-.2973 [-.3207]</td>
<td>-.8892 [-.8718]</td>
<td>-.3480 [-.3704]</td>
</tr>
<tr>
<td>N</td>
<td>0.8468 [0.8399]</td>
<td>-.4137 [-.4425]</td>
<td>0.3344 [0.3143]</td>
</tr>
</tbody>
</table>

Anthracene: Set 1 Orientations

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.5201 [-.5117]</td>
<td>-.1456 [-.1311]</td>
<td>0.8416 [0.8491]</td>
</tr>
<tr>
<td>M</td>
<td>-.2684 [-.3035]</td>
<td>-.9076 [-.8970]</td>
<td>-.3228 [-.3214]</td>
</tr>
<tr>
<td>N</td>
<td>0.8108 [0.8038]</td>
<td>-.3938 [-.4222]</td>
<td>0.4330 [0.4192]</td>
</tr>
</tbody>
</table>

In Table 4 we give the values of $\Delta V$ obtained for naphthalene and anthracene (using Williams' parametrization [170]) for minimizations including 21, 33 and 55 molecules. Firstly, we note that the magnitude of $\Delta V$ is physically significant. For this reason the defect energies that are

TABLE 4
DIFFERENCE IN POTENTIAL ENERGY BETWEEN THE EXPERIMENTAL AND ENERGY-MINIMIZED STRUCTURES
(Units: kJ mol$^{-1}$)

<table>
<thead>
<tr>
<th>No. of Molecules</th>
<th>Naphthalene</th>
<th>Anthracene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta V$</td>
<td>$\Delta V/</td>
</tr>
<tr>
<td>21</td>
<td>7</td>
<td>2273</td>
</tr>
<tr>
<td>33</td>
<td>11</td>
<td>3477</td>
</tr>
<tr>
<td>55</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
reported in the following sections are obtained by taking the difference of the total potential energy of the defect lattice and that obtained from the analogous relaxation calculation on the pure crystal lattice. Secondly, we note that $\Delta V / |V_{\text{min}}|$ is only 0.4%, and is independent of the number of molecules that are included in the minimization. Therefore, in order to improve on Williams' parametrization of the (exp-6) potential, $\Delta V / |V_{\text{min}}|$ would have to be reduced below 0.4%. This is clearly a very difficult task.

We recall that in Chapter 2 the zero-point vibrational contribution to the Helmholtz free energy was calculated to be 1 kJ mol$^{-1}$ using the Debye approximation. This is 0.5-0.7% of the total potential energy of the pure crystal lattice. Therefore, it seems reasonable to conclude that the attempt to improve the parameters for the (exp-6) potential is pointless without including thermal effects in a proper way. It is clear that the potential which we use is required to contain the effect of zero-point lattice expansion. More disturbing is the fact that the potential also reproduces the room temperature naphthalene crystal structure. Of course this must be so because there were no thermal corrections made to the data for the determination of the potential parameters [170]. Thus thermal effects have been 'included' in the potential in a peculiar way.

Error Parameters

Using the data obtained for anthracene and naphthalene in Table 4 it is easy to obtain the following novel expression for the error $\Delta V$ (Units: kJ mol$^{-1}$):

$$\Delta V \approx N \times \left( 0.135 \times \frac{\text{no. of carbons}}{\text{molecule}} - 0.127 \times \frac{\text{no. of hydrogens}}{\text{molecule}} \right)$$

where $N$ is the total number of molecules included in the minimization. This formula was determined by solving two simultaneous equations using the data for the 21 molecule calculations. It is easily verified that the $\Delta V$
for the other calculations reported in Table 4 are reproduced. When applied to the crystal structure of dianthracene (see Chapter 5) $\Delta V$ was estimated to be 19 for $N = 15$. The calculated value is 16. We propose that it may be possible to use this formula to predict $\Delta V$ for crystal structures of the aromatic hydrocarbons. We can make use of the included thermal effects of the parameters to estimate $\Delta V$ over a wide range of temperature. It may be possible to make estimates of $\Delta V$ to within 20-30%. This has not been thoroughly tested at this time but its potential is obvious. For instance, consider the crystal structure of 1,2-di-(9-anthryl)ethane photodimer, see figure 6 of Chapter 5. For this crystal $\Delta V$ is estimated to be 26 for $N = 21$, we report in Chapter 5 that $\Delta V$ calculated is 2-3 times larger than this value. It will be concluded that a discrepancy of this magnitude between $\Delta V$ estimated and $\Delta V$ calculated gives an indication that the crystal structure is abnormal in some way. In the 1,2-di-(9-anthryl)ethane case there is a very good reason for this which will be discussed later.

Thus we propose that the (exp-6) potential, with Williams' parametrization, may be used to calculate $\Delta V$ for an assumed crystallographic model and compared with that estimated by the given formula. If a significant difference exists between the two, i.e. the difference is 2 or 3 times $\Delta V$, then we may conclude that that model is suspect and further investigation should be undertaken.

Test of Currently Available Parameter Sets

Similar calculations to those reported in Table 4 were performed on naphthalene using commonly used (exp-6) parameter sets. For all of these calculations the C-H bond length was increased to 0.108 nm. The results are listed in Table 5. Clearly Williams' parameter set IV [170] is better (see also Table 4) and is thus retained for all future calculations. The calculated structures were found to be similar for all parameter sets. Similar results were found for anthracene.
TABLE 5

POTENTIAL ENERGY VARIATIONS $\Delta V$ CALCULATED FOR NAPHTHALENE USING STANDARD PARAMETER SETS
(Units: kJ mol$^{-1}$)

| Parameter Set                        | $\Delta V$ | $|V_{\text{min}}|$ | $\Delta V / |V_{\text{min}}|$ (%) |
|--------------------------------------|------------|-------------------|------------------------|
| Williams Set IV [170]                | 11         | 2238              | 0.5                    |
| Williams (exp-6-1) Set II [172]      | 17         | 2400              | 0.7                    |
| Mirskaya et al [110]                 | 20         | 2003              | 1.0                    |
| Warshel and Karplus [164]            | 21         | 2635              | 0.8                    |
| Kitaigorodsky [98]                   | 34         | 2186              | 1.6                    |

HOST MOLECULE REPLACED BY A LARGER IMPURITY

We consider the systems tetracene in anthracene and anthracene in naphthalene. In both the central molecule of the environment described in the preceding section was removed and replaced by the guest. The guest was placed in the lattice in each case with the orientation that it had in its own crystal lattice i.e. the atomic position coordinates were transferred directly from the guest crystal system to that of the host. This procedure is justified since the tetracene L, M and N axes make angles of $16^\circ$, $6^\circ$ and $17^\circ$ respectively with the same axes of anthracene [113]; thus the orientation of tetracene is not too different from that of anthracene. Similarly, anthracene is placed into naphthalene. Survey calculations showed that the centre of mass of each guest was situated at the coordinate origin. Therefore, inversion symmetry was maintained.
1. Tetracene in Anthracene

A series of calculations was performed to assess the effect, and extent, of lattice relaxation about the tetracene. In the first calculation the total potential energy of the lattice was minimized with respect to the orientation variables of tetracene alone. In the subsequent calculations the lattice surrounding the tetracene was permitted to relax to a varying extent. Calculations were made in which 20, 32 and 54 neighbour molecules were included in the minimization. The defect energies, i.e. enthalpies of mixing, are listed in Table 6. It is clear that without lattice relaxation the enthalpy of mixing is very large. Relaxation significantly reduces it.

TABLE 6

ENTHALPY OF MIXING FOR TETRACENE IN ANTHRACENE
(Units: kJ mol\(^{-1}\))

<table>
<thead>
<tr>
<th>Calculation</th>
<th>(V_{\text{anthracene}} - V_{\text{defect}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid Lattice</td>
<td>171</td>
</tr>
<tr>
<td>20 neighbours</td>
<td>25</td>
</tr>
<tr>
<td>32 neighbours</td>
<td>17</td>
</tr>
<tr>
<td>54 neighbours</td>
<td>15</td>
</tr>
<tr>
<td>20 neighbours (290K anthracene structure)</td>
<td>4</td>
</tr>
</tbody>
</table>

However, it is necessary to include next nearest neighbours in the minimization if a convergence is to be obtained. It is found from the largest calculation that the interaction energy of tetracene is 17 kJ mol\(^{-1}\) more stable than the replaced anthracene while the environment is destabilized by 32 kJ mol\(^{-1}\). This accounts for the 15 kJ mol\(^{-1}\) reported. Relaxation of the nearest neighbours leaves a repulsive interaction between the tetracene and the 1-2 pair of neighbours of 1 kJ mol\(^{-1}\).
Further relaxation decreases this interaction to $-0.5 \text{ kJ mol}^{-1}$. The analogous interaction in pure anthracene is $-4 \text{ kJ mol}^{-1}$. We note (Table 6) that the enthalpy of mixing decreases by $21 \text{ kJ mol}^{-1}$ when the 290K anthracene crystal structure is used.

We give the orientation of the guest in Table 7 for each calculation in the series. It can be seen that without relaxation the guest adopts an orientation that is close to that which is experimentally observed, Table 1. On including the 20 nearest neighbours better agreement with experiment is found. Further relaxation marginally alters this orientation.

In Table 8 we list the centre of mass displacements in each calculation. We note the relatively large displacement of the neighbour molecule at 001. The magnitude of its displacement vector is at its largest 0.04 nm and is essentially directed along the c crystallographic axis. The inclusion of next, and next next nearest neighbours allows the nearest neighbours to undergo further displacement e.g. consider molecules 1 and 4. While some of the next nearest neighbours experience significant displacements, e.g. consider molecules 25, 29 and 32; the displacements of the next next neighbours are smaller.

The largest change in orientation of a neighbour molecule occurs for the 3-4 symmetry-related pair. Table 9 gives the orientation of these molecules and illustrates the effect on the molecular orientation by allowing the various degrees of lattice relaxation. It can be seen that the inclusion of next, and next next nearest neighbours has very little bearing on the orientation of these molecules. It is important to note that the largest displacement in a direction cosine of a principal axis is $7^\circ$. Table 10 gives the orientation of the 1-2 symmetry-related pair of molecules. In Table 11 we give the relationship of the principal axes of
### TABLE 7
CALCULATED ORIENTATION OF TETRACENE IN ANTHRACENE  
(Principal Axis Direction Cosines)*

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>L</strong></td>
<td>-.5133 (0.8°)</td>
<td>-.1730 (3.0°)</td>
<td>0.8406 (1.7°)</td>
</tr>
<tr>
<td><strong>M</strong></td>
<td>-.2371 (2.7°)</td>
<td>-.9128 (0.0°)</td>
<td>-.3327 (2.2°)</td>
</tr>
<tr>
<td><strong>N</strong></td>
<td>0.8248 (0.8°)</td>
<td>-.3700 (1.2°)</td>
<td>0.4275 (0.2°)</td>
</tr>
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</table>

<table>
<thead>
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<th>c'</th>
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<tbody>
<tr>
<td><strong>L</strong></td>
<td>-.5060 (0.3°)</td>
<td>-.1298 (0.5°)</td>
<td>0.8527 (0.4°)</td>
</tr>
<tr>
<td><strong>M</strong></td>
<td>-.2571 (1.5°)</td>
<td>-.9210 (1.0°)</td>
<td>-.2928 (0.2°)</td>
</tr>
<tr>
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<td>0.8233 (0.6°)</td>
<td>-.3674 (1.3°)</td>
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</table>

<table>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>L</strong></td>
<td>-.5156 (0.9°)</td>
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</tr>
<tr>
<td><strong>M</strong></td>
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<td>-.9253 (1.8°)</td>
<td>-.2809 (0.9°)</td>
</tr>
<tr>
<td><strong>N</strong></td>
<td>0.8180 (0.0°)</td>
<td>-.3612 (1.7°)</td>
<td>0.4476 (1.5°)</td>
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</tbody>
</table>

<table>
<thead>
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<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>L</strong></td>
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<td>-.1167 (0.3°)</td>
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</tr>
<tr>
<td><strong>M</strong></td>
<td>-.2601 (1.3°)</td>
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<td>-.2828 (0.8°)</td>
</tr>
<tr>
<td><strong>N</strong></td>
<td>0.8190 (0.2°)</td>
<td>-.3661 (1.4°)</td>
<td>0.4418 (1.0°)</td>
</tr>
</tbody>
</table>

* Values in brackets give the magnitude of the displacement from the experimental values.
TABLE 8

CENTRE OF MASS DISPLACEMENTS OF TETRACENE NEIGHBOURS
(Units: nm)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Neighbours Relaxed</th>
<th>Neighbours Relaxed</th>
<th>Neighbours Relaxed</th>
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<tbody>
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<td>a</td>
<td>b</td>
<td>c'</td>
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<td>-.01</td>
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<td>-.01</td>
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<td></td>
<td></td>
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<td>0.03</td>
</tr>
<tr>
<td>4</td>
<td>0.0</td>
<td>-.01</td>
<td>0.02</td>
</tr>
<tr>
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<td>0.01</td>
<td>-.01</td>
<td>-.01</td>
</tr>
<tr>
<td>11</td>
<td>-.01</td>
<td>0.0</td>
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<tr>
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</tr>
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<td>0.01</td>
<td>0.03</td>
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<td>19</td>
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</tr>
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<td>0.0</td>
<td>0.01</td>
</tr>
<tr>
<td>29</td>
<td>-.01</td>
<td>0.01</td>
<td>0.0</td>
</tr>
<tr>
<td>32</td>
<td>-.01</td>
<td>-.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>
### TABLE 9

**ORIENTATION OF THE 3-4 SYMMETRY-RELATED PAIR OF ANTHRACENE MOLECULES ADJACENT TO TETRACENE**

(Principal Axes Direction Cosines)*

![Image](https://via.placeholder.com/150)

<table>
<thead>
<tr>
<th>Neighbours Relaxed</th>
<th>a (°)</th>
<th>b (°)</th>
<th>c' (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 Neighbours Relaxed</td>
<td>0.5581 (3.2°)</td>
<td>-.1934 (3.7°)</td>
<td>-.8069 (4.4°)</td>
</tr>
<tr>
<td></td>
<td>- .1711 (8.0°)</td>
<td>0.9248 (4.0°)</td>
<td>-.3399 (1.1°)</td>
</tr>
<tr>
<td></td>
<td>0.8119 (0.8°)</td>
<td>0.3278 (6.0°)</td>
<td>0.4830 (4.0°)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Neighbours Relaxed</th>
<th>a (°)</th>
<th>b (°)</th>
<th>c' (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32 Neighbours Relaxed</td>
<td>0.5549 (3.0°)</td>
<td>-.1720 (2.4°)</td>
<td>-.8140 (3.7°)</td>
</tr>
<tr>
<td></td>
<td>- .1913 (6.8°)</td>
<td>0.9258 (4.0°)</td>
<td>-.3261 (0.3°)</td>
</tr>
<tr>
<td></td>
<td>0.8096 (0.6°)</td>
<td>0.3367 (5.4°)</td>
<td>0.4808 (4.0°)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Neighbours Relaxed</th>
<th>a (°)</th>
<th>b (°)</th>
<th>c' (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>54 Neighbours Relaxed</td>
<td>0.5586 (3.3°)</td>
<td>-.1775 (2.7°)</td>
<td>-.8102 (4.1°)</td>
</tr>
<tr>
<td></td>
<td>- .1882 (6.9°)</td>
<td>0.9242 (3.9°)</td>
<td>-.3322 (0.7°)</td>
</tr>
<tr>
<td></td>
<td>0.8078 (0.4°)</td>
<td>0.3380 (5.3°)</td>
<td>0.4829 (4.2°)</td>
</tr>
</tbody>
</table>

* Values in brackets give the magnitude of the displacements from the pure crystal values.
TABLE 10

ORIENTATION OF THE 1-2 SYMMETRY-RELATED PAIR OF ANTHRACENE MOLECULES ADJACENT TO TETRACENE (Principal Axes Direction Cosines)*

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.4700 (2.7°)</td>
<td>-.1971 (3.9°)</td>
<td>0.8604 (1.2°)</td>
</tr>
<tr>
<td>M</td>
<td>-.2813 (1.5°)</td>
<td>-.8905 (0.7°)</td>
<td>-.3577 (2.2°)</td>
</tr>
<tr>
<td>N</td>
<td>0.8366 (3.3°)</td>
<td>-.4102 (0.9°)</td>
<td>0.3631 (3.4°)</td>
</tr>
</tbody>
</table>

* Values in brackets give the magnitude of the displacements from the pure crystal values.

TABLE 11

RELATIONSHIP OF GUEST AND DISPLACED NEIGHBOUR MOLECULE PRINCIPAL AXES (L',M',N') TO THOSE OF THE PURE HOST (L,M,N)

**Tetracene/anthracene**

<table>
<thead>
<tr>
<th></th>
<th>L'</th>
<th>M'</th>
<th>N'</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6°</td>
<td>3.8°</td>
<td>3.7°</td>
<td></td>
</tr>
</tbody>
</table>

**3-4 Symmetry-Related Anthracene Pair**

<table>
<thead>
<tr>
<th></th>
<th>L'</th>
<th>M'</th>
<th>N'</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5°</td>
<td>6.8°</td>
<td>6.2°</td>
<td></td>
</tr>
</tbody>
</table>

**1-2 Symmetry-Related Anthracene Pair**

<table>
<thead>
<tr>
<th></th>
<th>L'</th>
<th>M'</th>
<th>N'</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5°</td>
<td>2.5°</td>
<td>3.7°</td>
<td></td>
</tr>
</tbody>
</table>
the tetracene, 1-2 and 3-4 symmetry-related molecules to those of the pure, perfect host.

To illustrate the effect that lattice relaxation has on the localized mode frequencies we list in Table 12 the tetracene frequencies calculated by Method B of Appendix B. The principal components of each localized eigenvector are denoted by $L_R$, $M_R$, and $N_R$ for librations about the principal inertial axes, and $L_T$, $M_T$, and $N_T$ for translations along those axes. The frequencies calculated for the rigid lattice show how unrealistic the structure is. Relaxation significantly reduces the frequencies as it does the energy of the defect. Again the effect diminishes as the number of molecules in the minimization increases. As can be seen, the frequencies are in general higher than those of the pure lattice.

Finally, we consider atom-atom distances in the pure and defect-lattices. In the pure anthracene lattice the central molecule has 38 atom-atom contacts with its 20 nearest neighbours which are less than 0.3 nm. Of these the shortest is 0.25 nm. With the same neighbour in the fully relaxed lattice the tetracene has 62 such contacts. Of these the shortest is 0.23 nm. There are, however, 12 atom-atom contacts which are less than 0.25 nm. All of these are hydrogen-hydrogen contacts.

2. Anthracene in Naphthalene

A series of calculations similar to those reported for tetracene in anthracene was carried out for anthracene in naphthalene. The findings for both systems are similar. The room temperature naphthalene crystal structure has been used for the host lattice. In Table 13 we list the enthalpy of mixing ($\Delta H_{mix}$) for each calculation.
### TABLE 12

**LOCALIZED FREQUENCIES OF OSCILLATION**

**OF TETRACENE GUEST**

(Units: cm⁻¹)

<table>
<thead>
<tr>
<th>Rigid Lattice</th>
<th>20 Neighbours Relaxed</th>
<th>32 Neighbours Relaxed</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type</strong></td>
<td><strong>λ</strong></td>
<td><strong>Type</strong></td>
</tr>
<tr>
<td>Mₐ</td>
<td>259</td>
<td>Lₐ</td>
</tr>
<tr>
<td>Lₐ</td>
<td>182</td>
<td>Mₐ</td>
</tr>
<tr>
<td>Nₜ</td>
<td>173</td>
<td>Nₜ</td>
</tr>
<tr>
<td>Lₜ</td>
<td>108</td>
<td>Mₜ</td>
</tr>
<tr>
<td>Nₐ</td>
<td>105</td>
<td>Nₐ</td>
</tr>
<tr>
<td>Mₜ</td>
<td>85</td>
<td>Lₜ</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>54 Neighbours Relaxed</th>
<th>Pure Anthracene (95K)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type</strong></td>
<td><strong>λ</strong></td>
</tr>
<tr>
<td>Lₐ</td>
<td>128</td>
</tr>
<tr>
<td>Mₐ</td>
<td>120</td>
</tr>
<tr>
<td>Nₜ</td>
<td>101</td>
</tr>
<tr>
<td>Mₜ</td>
<td>65</td>
</tr>
<tr>
<td>Nₐ</td>
<td>64</td>
</tr>
<tr>
<td>Lₜ</td>
<td>42</td>
</tr>
</tbody>
</table>

* The subscripts R and T indicate a libration and a translation respectively. Thus Mₐ indicates that the eigenvector is principally an M axis libration.
### TABLE 13

**ENTHALPY OF MIXING FOR ANTHRACENE IN NAPHTHALENE**

(Units: kJ mol\(^{-1}\))

<table>
<thead>
<tr>
<th>Calculation</th>
<th>(V_{\text{naphthalene}} - V_{\text{defect}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid Lattice</td>
<td>118</td>
</tr>
<tr>
<td>20 Neighbours</td>
<td>1</td>
</tr>
<tr>
<td>32 Neighbours</td>
<td>-4</td>
</tr>
<tr>
<td>20 Neighbours</td>
<td>11</td>
</tr>
<tr>
<td>C-H bond length = 0.108 nm</td>
<td></td>
</tr>
<tr>
<td>32 Neighbours</td>
<td>4</td>
</tr>
<tr>
<td>C-H bond length = 0.108 nm</td>
<td></td>
</tr>
<tr>
<td>20 Neighbours</td>
<td>37</td>
</tr>
<tr>
<td>theoretically calculated structure</td>
<td></td>
</tr>
</tbody>
</table>

For the energetics a similar pattern to that found for tetracene in anthracene is observed. Without relaxation the energy of the defect is very large. Relaxation reduces this energy difference considerably, however, unlike the tetracene/anthracene system the defect is found to be more stable than the pure host. Since this result is surprising we consider the effect of small changes in the molecular geometry and the crystal structure on \(\Delta H_{\text{mix}}\). It is shown in Table 13 that upon increasing the carbon-hydrogen bond length to 0.108 nm the defect becomes less stable than the pure host but this energy difference is still small i.e. 4 kJ mol\(^{-1}\). On repeating the energy minimization for the 20 nearest neighbours using the theoretically calculated OK "phononless" structure the energy difference increases to 37 kJ mol\(^{-1}\). The calculated* structure had cell dimensions \(a = 0.78\) (\(\Delta a = -0.04\)), \(b = 0.58\) (\(\Delta b = -0.02\)), and \(c = 0.85\) (\(\Delta c = -0.01\)), with \(\beta = 120.9^\circ\) (\(\Delta \beta = -2^\circ\)). The large change in the 'a' direction was found in a number of calculations using different parameter sets. Thus the energy* This calculation was performed using a computer program written by Dr G.S. Pawley.
differences are seen to be very sensitive to small changes in both the carbon-hydrogen bond length and the crystal structure.

We must consider the enthalpy of the defect calculated using the room temperature naphthalene crystal structure as an approximation to the enthalpy at this temperature. As such this introduces the interesting possibility that the incorporation of anthracene into the naphthalene lattice is entropy-controlled. It was shown in Chapter 2 that at room temperature the entropy contribution to the Helmholtz free energy of a hypothetical molecular crystal was of the order of $-10 \text{ kJ mol}^{-1}$. For anthracene and naphthalene we estimate that this is 5-10% of the total potential energy of the lattice. For the defect lattice the entropy contribution must be less than this, i.e. less negative.

We can estimate crudely the vibrational contribution to the free energy mixing by using a simple Cell Model calculation (remembering that the configurational entropy contributes a negligible amount to the free energy) (see Huntington et al [90]). In this model the free energy of the crystal is assumed to be given as a sum over one-molecule free-energy functions which are evaluated for each molecule in a cage of its neighbour molecules. These are held fixed in their experimentally determined or calculated equilibrium positions. The vibrational motion of the molecule in the cage is calculated in the harmonic approximation and the frequencies so obtained are used to evaluate the sum over normal mode frequencies (Eqn.(2.2)). The error introduced by the neglect of correlated motion can be assumed to cancel to a large extent when the difference between the host and guest one-molecule free energy functions is taken. We make the additional assumption that only this difference needs to be evaluated, i.e. the contribution from the guest's neighbours is ignored. For anthracene in naphthalene at
approximately 300K the calculated vibrational frequencies are 113, 109, 88, 61, 46, 40 cm\(^{-1}\) while for pure naphthalene they are 88, 68, 68, 47, 42, 38 cm\(^{-1}\). Using these values the vibrational contribution to the pure crystal Helmholtz free energy is found to be -20 kJ mol\(^{-1}\) while that for the defect is found to be -15 kJ mol\(^{-1}\). The former value is twice as large as that calculated using the Debye approximation. Therefore we need to add 5 kJ mol\(^{-1}\) to our calculated defect energy. The defect is now destabilized by the small amount of 1 kJ mol\(^{-1}\). Similar contributions from the most perturbed of the guest's neighbours would still further increase the free energy of mixing.

Without lattice relaxation anthracene is found to adopt an orientation that is close to that which is experimentally determined. As before, relaxation causes the orientation to change slightly and the agreement with experiment is improved. The orientations are given in Table 14. It is also found that the orientation adopted by anthracene in the theoretically calculated "phononless" naphthalene lattice is close to that observed experimentally but the agreement tends to be slightly worse than that calculated for the experimentally determined naphthalene crystal structure.

As in the tetracene study the largest angular displacements occur for the 1-2 and 3-4 symmetry-related lattice molecules. Table 15 gives the orientations of these molecules when all nearest neighbours are included in the minimization. For a comparison we also give the orientation of the 1-2 symmetry-related pair obtained in the analogous calculation using the theoretically calculated naphthalene crystal structure. In Table 16 we list the centre of mass displacements found when the next nearest neighbours included in the minimization. As is shown the next nearest neighbours are displaced significantly from their pure crystal equilibrium positions.
TABLE 14
ORIENTATION OF ANTHRACENE GUEST
IN NAPHTHALENE
(Principal Axes Direction Cosines)*

Guest in Rigid Lattice

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.4188</td>
<td>-.1940</td>
<td>0.8871</td>
</tr>
<tr>
<td></td>
<td>(1.6°)</td>
<td>(4.5°)</td>
<td>(0.2°)</td>
</tr>
<tr>
<td>M</td>
<td>-.2649</td>
<td>-.9084</td>
<td>-.3236</td>
</tr>
<tr>
<td></td>
<td>(4.3°)</td>
<td>(1.6°)</td>
<td>(2.2°)</td>
</tr>
<tr>
<td>N</td>
<td>0.8686</td>
<td>-.3705</td>
<td>0.3290</td>
</tr>
<tr>
<td></td>
<td>(4.2°)</td>
<td>(3.6°)</td>
<td>(1.8°)</td>
</tr>
</tbody>
</table>

20 Neighbours Relaxed

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.4191</td>
<td>-.1438</td>
<td>0.8965</td>
</tr>
<tr>
<td></td>
<td>(1.6°)</td>
<td>(1.6°)</td>
<td>(1.0°)</td>
</tr>
<tr>
<td>M</td>
<td>-.2789</td>
<td>-.9192</td>
<td>-.2779</td>
</tr>
<tr>
<td></td>
<td>(3.5°)</td>
<td>(3.1°)</td>
<td>(0.6°)</td>
</tr>
<tr>
<td>N</td>
<td>0.8640</td>
<td>-.3665</td>
<td>0.3452</td>
</tr>
<tr>
<td></td>
<td>(3.7°)</td>
<td>(3.8°)</td>
<td>(0.8°)</td>
</tr>
</tbody>
</table>

20 Neighbours Relaxed using Theoretically Calculated Host Crystal Structure

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.3700</td>
<td>-.1153</td>
<td>0.9219</td>
</tr>
<tr>
<td></td>
<td>(4.7°)</td>
<td>(0.1°)</td>
<td>(4.5°)</td>
</tr>
<tr>
<td>M</td>
<td>-.3121</td>
<td>-.9192</td>
<td>-.2402</td>
</tr>
<tr>
<td></td>
<td>(1.5°)</td>
<td>(3.1°)</td>
<td>(2.8°)</td>
</tr>
<tr>
<td>N</td>
<td>0.8750</td>
<td>-.3766</td>
<td>0.3041</td>
</tr>
<tr>
<td></td>
<td>(4.9°)</td>
<td>(3.2°)</td>
<td>(3.3°)</td>
</tr>
</tbody>
</table>

* Values in brackets give the magnitude of the displacement from the experimental values.
<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.3449 (5.8°)</td>
<td>-.2571 (2.6°)</td>
<td>0.9027 (3.7°)</td>
</tr>
<tr>
<td>M</td>
<td>-.3184 (0.0°)</td>
<td>-.8727 (0.2°)</td>
<td>-.3702 (0.2°)</td>
</tr>
<tr>
<td>N</td>
<td>0.8830 (4.9°)</td>
<td>-.4151 (1.8°)</td>
<td>0.2191 (5.6°)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.4900 (3.3°)</td>
<td>0.2138 (0.1°)</td>
<td>0.8451 (3.1°)</td>
</tr>
<tr>
<td>M</td>
<td>0.1965 (7.3°)</td>
<td>-.9174 (5.9°)</td>
<td>0.3460 (1.7°)</td>
</tr>
<tr>
<td>N</td>
<td>0.8493 (1.0°)</td>
<td>0.3356 (6.7°)</td>
<td>0.4076 (5.8°)</td>
</tr>
</tbody>
</table>

* Values in brackets give the magnitude of the displacement from the pure crystal values.

Displacement of 1-2 Symmetry-Related Pair of Host Naphthalenes in the Theoretically Calculated Lattice

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.3215 (4.8°)</td>
<td>-.2792 (4.4°)</td>
<td>0.9048 (1.5°)</td>
</tr>
<tr>
<td>M</td>
<td>-.3238 (1.0°)</td>
<td>-.8656 (2.7°)</td>
<td>-.3821 (2.5°)</td>
</tr>
<tr>
<td>N</td>
<td>0.8898 (3.0°)</td>
<td>-.4158 (0.3°)</td>
<td>0.1879 (6.1°)</td>
</tr>
</tbody>
</table>
TABLE 16
HOST NAPHTHALENE CENTRE OF MASS
DISPLACEMENTS ADJACENT TO AN
ANTHRACENE GUEST

<table>
<thead>
<tr>
<th>Neighbour Molecule</th>
<th>Displacement (nm)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c'</td>
</tr>
<tr>
<td>1</td>
<td>-.02</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td>0.01</td>
<td>-.02</td>
</tr>
<tr>
<td>5</td>
<td>0.0</td>
<td>-.01</td>
<td>-.01</td>
</tr>
<tr>
<td>25</td>
<td>-.01</td>
<td>0.0</td>
<td>0.01</td>
</tr>
<tr>
<td>30</td>
<td>0.01</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>32</td>
<td>-.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

VACANCIES

A vacancy was created in the 95K lattice of anthracene and in naphthalene by removing the central molecule from the previously described environment of molecules. In both cases the 20 nearest neighbours were permitted to relax about the vacancy. The minimization commenced from the experimentally determined positions. It was found that the neighbour molecules do not move to occupy the free volume. There are only small changes in orientations and positions of the centre of mass. Table 17 lists the largest of these displacements. There is a tendency for the molecules nearest the vacancy to move outwards from the vacancy while those farthest away (e.g. the molecule at 001) tend to move inwards toward the vacancy. Somewhat surprising is the finding for anthracene that the largest angular displacements occur for the molecules at the lattice sites 0±1 0. We note that the calculations presented here are of the traditional bulk lattice type rather than surface simulation calculations as was proposed earlier.
**TABLE 17**

**LARGEST DISPLACEMENTS FOR NAPHTHALENE**

**MOLECULES ADJACENT TO A VACANCY**

<table>
<thead>
<tr>
<th>Principle Axes Direction Cosines* of 9-10 Symmetry-Related Pair</th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.4249 (0.9°)</td>
<td>0.1828 (1.8°)</td>
<td>0.8866 (1.6°)</td>
</tr>
<tr>
<td>M</td>
<td>0.2854 (2.0°)</td>
<td>-.9024 (3.9°)</td>
<td>0.3228 (3.1°)</td>
</tr>
<tr>
<td>N</td>
<td>0.8591 (2.1°)</td>
<td>0.3902 (3.3°)</td>
<td>0.3313 (1.0°)</td>
</tr>
</tbody>
</table>

**Centre of Mass Displacement of the 9(-10) Symmetry-Related Pair**

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>-.01</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**LARGEST DISPLACEMENTS FOR ANTHRACENE**

**MOLECULES ADJACENT TO A VACANCY**

<table>
<thead>
<tr>
<th>Principal Axes Direction Cosines* of 11-12 Symmetry-Related Pair</th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.5223 (0.8°)</td>
<td>-.1424 (0.7°)</td>
<td>0.8408 (1.0°)</td>
</tr>
<tr>
<td>M</td>
<td>-.2446 (3.6°)</td>
<td>-.9195 (3.2°)</td>
<td>-.3077 (0.8°)</td>
</tr>
<tr>
<td>N</td>
<td>0.8169 (1.3°)</td>
<td>-.3664 (3.6°)</td>
<td>0.4454 (1.8°)</td>
</tr>
</tbody>
</table>

* Values in brackets give the magnitude of the displacement from the experimental values.
As noted before, the enthalpy of formation of a vacancy can only be calculated by assuming an averaged interaction of a molecule at a surface. We prefer not to do this because of the uncertainties involved, but instead report the change in enthalpy of the environment of the vacancy. It is found that this enthalpy is $1.5 - 3.0 \text{ kJ mol}^{-1}$ more stable than the same molecules in the pure, perfect crystal. This result was found for the experimentally determined crystal structures, the theoretically calculated OK structure, and structures in which the carbon-hydrogen bond length was increased to 0.108 nm.

As a test of the stability of the lattice structure surrounding the vacancy we displaced the molecule at 001 into the cavity by 0.2 nm and repeated the minimization. The displaced molecule returned to the position close to that which it occupies in the pure, perfect crystal.

Divacancies were created in the 95K anthracene lattice by removing the molecule at the origin and the molecule at the lattice site 001 or -0.5 0.5 0.0. The lattice was allowed to relax about the 'hole' in the usual way without inversion symmetry being retained. In both cases the orientational and centre of mass displacements of the respective 32 and 31 nearest neighbours of the divacancy were found to be small. The lattice structure remains essentially the same as that in the perfect crystal.

**A LARGER GUEST MOLECULE ADJACENT TO A VACANCY**

An alternative mode of entry of a guest into a lattice is for it to occupy a site adjacent to a vacancy. We consider tetracene as a guest adjacent to a vacancy at the lattice site 001 in anthracene. We find that the orientation adopted by tetracene is close to that observed experimentally. All nearest neighbours of the tetracene and the vacancy were allowed to relax. The tetracene orientation is given in Table 18. The tetracene is
TABLE 18
TETRACENE ORIENTATION ADJACENT TO A VACANCY

AT 001 IN ANTHRACENE
(Principal Axes Direction Cosines)*

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.5613  (4.0°)</td>
<td>-.0910  (1.8°)</td>
<td>0.8226  (3.6°)</td>
</tr>
<tr>
<td>M</td>
<td>-.2428  (2.3°)</td>
<td>-.9321  (2.9°)</td>
<td>-.2688  (1.6°)</td>
</tr>
<tr>
<td>N</td>
<td>0.7912  (2.5°)</td>
<td>-.3506  (2.4°)</td>
<td>0.5011  (5.0°)</td>
</tr>
</tbody>
</table>

* Values in brackets give the magnitude of the displacement from the experimentally observed values.

now displaced from the site origin by (-.08,0.0,0.11)nm. This translational freedom allows the tetracene to lower its interaction energy by 12 kJ mol$^{-1}$. The enthalpy of formation of this defect is found to be lower by 25 kJ mol$^{-1}$ than that required to form a vacancy in the pure anthracene lattice.

HOST MOLECULE REPLACED BY A SMALLER GUEST

In this section we report the results of calculations on host lattices of anthracene and naphthalene containing smaller guest. In the calculations the usual procedure of removing a host molecule and replacing it by the guest is followed. However, the cavity is searched in these cases to find the stable guest sites. To carry out the search the cage molecules surrounding the guest are held rigid. Only if the guest is found to occupy a site with its centre of mass coincident with the coordinate, or site, origin is inversion symmetry maintained in the relaxation calculations. We consider naphthalene or benzene in anthracene (at 95K), and benzene in naphthalene.
1. **Naphthalene in Anthracene**

Naphthalene was placed into the anthracene lattice at the site origin with the same orientation as the replaced anthracene. It was found that the naphthalene moves from the origin to occupy one of two inversion-related sites. Without allowing relaxation of the lattice the naphthalene occupies a site displaced by \( a = 0.05 \), \( b = 0.01 \), and \( c' = -0.08 \) (nm) with an orientation close to that of the replaced anthracene, Table 19. Upon allowing the 20 nearest neighbours to relax there is only small change in the position (\( a=0.04, b=0.01, \) and \( c'=-0.08 \) (nm)) and orientation of the naphthalene, Table 19. There are only small changes in the position and orientation of the neighbour molecules. The naphthalene site is illustrated in figure 2.

**TABLE 19**

**ORIENTATION OF NAPHTHALENE IN ANTHRACENE**

**WITHOUT LATTICE RELAXATION**

(Principal Axes Direction Cosines)*

<table>
<thead>
<tr>
<th></th>
<th>( a )</th>
<th>( b )</th>
<th>( c' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-0.5257 (1.0°)</td>
<td>-0.1674 (2.1°)</td>
<td>0.8340 (1.7°)</td>
</tr>
<tr>
<td>M</td>
<td>-0.2659 (2.4°)</td>
<td>-0.8990 (0.4°)</td>
<td>-0.3480 (1.6°)</td>
</tr>
<tr>
<td>N</td>
<td>0.8081 (0.4°)</td>
<td>-0.4047 (1.2°)</td>
<td>0.4281 (0.7°)</td>
</tr>
</tbody>
</table>

**ORIENTATION OF NAPHTHALENE IN ANTHRACENE**

**WITH LATTICE RELAXATION**

<table>
<thead>
<tr>
<th></th>
<th>( a )</th>
<th>( b )</th>
<th>( c' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-0.5264 (1.0°)</td>
<td>-0.1674 (2.1°)</td>
<td>0.8336 (1.7°)</td>
</tr>
<tr>
<td>M</td>
<td>-0.2776 (1.7°)</td>
<td>-0.8928 (0.4°)</td>
<td>-0.3546 (2.1°)</td>
</tr>
<tr>
<td>N</td>
<td>0.8036 (0.0°)</td>
<td>-0.4181 (0.3°)</td>
<td>0.4235 (0.4°)</td>
</tr>
</tbody>
</table>

* Values in brackets give the magnitude of the displacement from the anthracene experimental values.
Figure 2: Equilibrium position of naphthalene in anthracene crystal, shown in relation to the displaced anthracene molecule.
Without lattice relaxation the potential energy of this system is found to be 55.5 kJ mol\(^{-1}\) above that of the pure crystal. Relaxation reduces the energy difference marginally to 55.0 kJ mol\(^{-1}\). We have computed the barrier to the interconversion of the two sites by placing the naphthalene at the site origin, holding the centre of mass fixed and allowing the guest orientational freedom only. When the 20 nearest neighbours are also allowed to relax the barrier is found to be 2 kJ mol\(^{-1}\). Without relaxation of the lattice at the saddle point the barrier is found to be 16 kJ mol\(^{-1}\). In the first instance the naphthalene is assumed to pass along a trajectory from one site to the other at a velocity which is low enough for the lattice to equilibrate at each point. In the second the naphthalene is assumed to undergo an instantaneous 'jump' over the barrier. It is clear that the barrier height will depend on the 'jump' velocity.

At the minimum-energy position at the site origin, i.e. at the top of the barrier, the naphthalene is found to have an orientation significantly displaced from that of the replaced anthracene. This orientation is given in Table 20.

<table>
<thead>
<tr>
<th>TABLE 20</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ORIENTATION OF NAPHTHALENE AT</strong></td>
</tr>
<tr>
<td><strong>THE SADDLE POINT IN ANTHRACENE</strong></td>
</tr>
<tr>
<td>(Principal Axes Direction Cosines)*</td>
</tr>
</tbody>
</table>
| &nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&n...
2. Benzene in Anthracene

We report a brief study of the mixed crystal benzene in anthracene. In these calculations an idealized geometry was used for benzene in which the carbons were placed at the vertices of a regular hexagonal of side 0.1397 nm. For this system two sites for benzene were found. One is origin-centred while the other is displaced from the origin. The latter is related by inversion to a third site. These are illustrated in figure 3 and the orientations of both are given in Table 21. We define the $X'$ principal axis as that which passes through the mid-point of a carbon-carbon bond, and the $X''$ principal axis as that which passes along a carbon-hydrogen bond. The angle between the normal axis of the benzene and the normal axis of anthracene is 2° for the origin-centred site and 1° for the displaced site. Neighbour displacements are small.

**TABLE 21**

BENZENE SITES IN ANTHRACENE

(Principal Axes Direction Cosines)

<table>
<thead>
<tr>
<th>Origin-Centred Site</th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>X'</td>
<td>0.4617</td>
<td>0.8866</td>
<td>0.0288</td>
</tr>
<tr>
<td>X''</td>
<td>-0.4057</td>
<td>0.1822</td>
<td>0.8956</td>
</tr>
<tr>
<td>N</td>
<td>0.7888</td>
<td>-0.4252</td>
<td>0.4438</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Displaced Site</th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>X'</td>
<td>0.5027</td>
<td>0.8613</td>
<td>-0.0735</td>
</tr>
<tr>
<td>X''</td>
<td>-0.3392</td>
<td>0.2747</td>
<td>0.8997</td>
</tr>
<tr>
<td>N</td>
<td>0.7951</td>
<td>-0.4274</td>
<td>0.4302</td>
</tr>
</tbody>
</table>

Centre of Mass Displacement

(Units: nm)

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.11</td>
<td>0.02</td>
<td>0.19</td>
</tr>
</tbody>
</table>
Figure 3. Benzene sites in Anthracene host.
The origin-centred site is found to be less stable than the displaced site by approximately 2 kJ mol$^{-1}$ while the potential energy of the lattice is approximately 110 kJ mol$^{-1}$ above that of the pure crystal.

3. Benzene in Naphthalene

A brief study was also made of the mixed crystal benzene in naphthalene. Surprisingly, benzene is found to occupy two sites. Again there is an origin-centred site and two inversion related displaced sites. The orientation of benzene at each of these sites is given in Table 22 and is illustrated in figure 4. For the displaced site the centre of mass position coordinates are $a = -0.04$, $b = -0.02$, and $c' = 0.08$ (nm). The normal axis of benzene and the normal axis of anthracene make angles of 5° and 0° for the origin-centre and displaced sites respectively. Both sites are essentially equi-energetic (the displaced site is marginally more stable). The potential energy of the lattice is 48 kJ mol$^{-1}$ above that of the pure lattice. Again neighbour displacements are small.

<table>
<thead>
<tr>
<th>TABLE 22</th>
</tr>
</thead>
<tbody>
<tr>
<td>BENZENE SITES IN NAPHTHALENE</td>
</tr>
<tr>
<td>(Principal Axes Direction Cosines)</td>
</tr>
</tbody>
</table>

**Origin-Centred Site**

| X'    | 0.4102 | 0.8742 | 0.2597 |
| X''   | -0.3166| -0.1306| 0.9395 |
| N     | 0.8553 | -0.4677| 0.2232 |

**Displaced Site**

| X'    | 0.4965 | 0.8624 | -0.0983 |
| X''   | -0.2226| 0.2359 | 0.9459  |
| N     | 0.8390 | -0.4478| 0.3091  |
Figure 4. Benzene sites in Naphthalene host.
REJECTION OF VOIDS FROM CRYSTAL LATTICES

We recall that pentacene has been found to be incorporated more readily into naphthalene than it is into anthracene. Such observations have led us to infer that host lattices more readily reject guest molecules which produce voids, if substitutionally incorporated into the lattice, than those that are oversized and produce lattice distortions. We have seen that creating voids significantly raises the potential energy of the lattice, moreso than that of an oversized guest. Thus we can correlate these larger enthalpy differences with the tendency to reject voids. However, we have always considered that the guest was initially at infinite and the displaced host molecules removed to infinity. A more realistic model would be to put all displaced host molecules, and guest molecules in their initial positions, on the crystal surface, and then calculate the enthalpy differences. In this case if the defect is still considered to be in the bulk it can be argued that the enthalpy of mixing for tetracene in anthracene should increase while the enthalpy of mixing for naphthalene in anthracene should decrease. It is clear that until more accurate experimental information becomes available and calculations incorporating surface effects are attempted final conclusions on the creation of voids cannot be drawn. Nevertheless we can correlate the experimental observations with the results of our calculations.

2-OHA IN ANTHRACENE

We recall from the introductory remarks that 2-OHA is found to occupy two sites in anthracene: one site is photoreactive ($0_\text{r}$) and the other photostable ($0_\text{p}$). We investigate 2-OHA in substitution in anthracene to find if the symmetry-allowed configurations can be correlated with the experimental findings. This work is essentially an extension of that
reported by Bridge and Gianneschi [14].

2-OHA Molecular Geometry

In order to be consistent with the host crystal structure, anthracene at 95K, we have generated an idealized 2-OHA molecule from Mason's averaged bond lengths and bond angles assuming a C-O-H bond angle of 109° and a carbon-oxygen bond length of 0.136 nm. The total potential energy of interaction of an idealized anthracene molecule is found to differ by 0.5 kJ mol⁻¹ from that calculated for the experimentally determined structure. The hydroxyl proton has been treated as an aromatic proton throughout, with its assumed interaction centre lying at 0.1 nm from the oxygen. Figure 5 illustrates the four possible intramolecular configurations of 2-OHA. In some calculations the hydroxyl proton was rotated out of the molecular plane by either ±10°.

Potential Parameter Set

Since oxygen interactions with carbon and hydrogen now need to be considered we undertook a survey of a number of parameter sets to test their reliability. We required that the parameter sets produce, for each configuration illustrated in figure 5, a total interaction energy of the molecule of 2-OHA, with its anthracene environment, above that of the pure crystal. It was found that the energy of the H1 configuration was close to that of the pure crystal and thus was used as the main criterion for selection. In the survey calculations oxygen was treated as if it were carbon using Williams' parameter set, and as nitrogen using the parameter sets of Reynolds [136] (without electrostatic interactions), and Righini and Califano [138]. Calculations were also performed using parameters for the carbon, hydrogen and oxygen mixed interactions obtained by applying
FIGURE 5: 2 POSSIBLE LATTICE ORIENTATIONS OF THE C-O BOND, AND THE EXTREME POSITIONS OF -OH PROTONS, IN 2-HYDROXYANTHRACENE
combining rules [105] to the parameters of Williams and Kitaigorodsky et al [100] or Scott and Scheraga [143]. The results obtained using these parameter sets are listed in Table 23. It was found that the parameter set of Righini and Califano [138] was the only one for which the H1 conformation could be calculated to be less stable than the pure crystal. Hence this parameter set was adopted for the full series of calculations. However, all parameter sets produced similar structures. This is shown in Table 24 for the H1 configuration where we give the direction cosines of the 2-OHA normal axis, and the centre of mass displacement. In all calculations we have made the further simplifying assumption that hydrogen bonding is not important. Although we note the determining influence of hydrogen bonding on the crystal structures of phenol [72] and β-naphthol [167].

Results

For each configuration illustrated in figure 5 we permitted 2-OHA and its 20 nearest neighbours to relax to positions of minimum energy in the usual way. Figure 6 illustrates the optimum positions of the four planar 2-OHA configurations. Table 25 summarizes the results and gives the molecular orientation and centre of mass displacement for the in-plane H1 configuration. By comparison with Table 3 it can be seen that there is only a small orientational displacement of the 2-OHA away from the orientation of the replaced host. Only small centre of mass and orientational displacements of the nearest neighbours occur. The neighbour displacements are all smaller than the largest displacements found for tetracene in anthracene. This is true for each configuration of 2-OHA, even those in which the hydroxyl proton is rotated out of the molecular by 10°. The out of plane displacement of the hydroxyl proton raised the total potential energy of the lattice in all cases with very little asymmetry in each potential curve about the in-plane configuration.
### TABLE 23
SURVEY OF PARAMETER SETS FOR 2-OHA CALCULATIONS

RESULTS FOR THE H1 CONFIGURATION

<table>
<thead>
<tr>
<th>Parameter Set*</th>
<th>( V_{2-OHA} - V_{pure} ) (Units: kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Williams</td>
<td>-4</td>
</tr>
<tr>
<td>0 Ëœ C</td>
<td></td>
</tr>
<tr>
<td>Reynolds</td>
<td>-1</td>
</tr>
<tr>
<td>0 Ëœ N</td>
<td></td>
</tr>
<tr>
<td>Righini and Califano</td>
<td>+8</td>
</tr>
<tr>
<td>0 Ëœ N</td>
<td></td>
</tr>
<tr>
<td>Williams + Kitaigorodsky</td>
<td>-4</td>
</tr>
<tr>
<td>Williams + Scott and Scheraga</td>
<td>-12</td>
</tr>
</tbody>
</table>

### TABLE 24
2-OHA H1 POSITION AND ORIENTATION - PARAMETER SET COMPARISON

<table>
<thead>
<tr>
<th>Parameter Set</th>
<th>N axis direction cosines</th>
<th>Centre of Mass Displacement (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Williams Ëœ C</td>
<td>0.8158</td>
<td>-.3895</td>
</tr>
<tr>
<td>Reynolds Ëœ N</td>
<td>0.8167</td>
<td>-.3822</td>
</tr>
<tr>
<td>Righini and Califano Ëœ N</td>
<td>0.8149</td>
<td>-.3857</td>
</tr>
<tr>
<td>Williams + Kitaigorodsky</td>
<td>0.8200</td>
<td>-.3829</td>
</tr>
<tr>
<td>Williams + Scott and Scheraga</td>
<td>0.8181</td>
<td>-.3885</td>
</tr>
</tbody>
</table>

* Ëœ means equivalent to.
Figure 6. Position of 2-OHA relative to anthracene.
TABLE 25
2-OHA CONFIGURATIONAL ENERGIES RELATIVE TO PURE ANTHRACENE

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>3</td>
</tr>
<tr>
<td>H2</td>
<td>8</td>
</tr>
<tr>
<td>H3</td>
<td>10</td>
</tr>
<tr>
<td>H4</td>
<td>11</td>
</tr>
</tbody>
</table>

Principal Axes Direction Cosines for the Anthracene

Nucleus of 2-OHA in Anthracene: H1 Configuration

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.503</td>
<td>-.127</td>
<td>0.855</td>
</tr>
<tr>
<td>M</td>
<td>-.282</td>
<td>-.911</td>
<td>-.302</td>
</tr>
<tr>
<td>N</td>
<td>0.8199</td>
<td>-.3876</td>
<td>0.4213</td>
</tr>
</tbody>
</table>

2-OHA Centre of Mass Displacement:

H1 Configuration

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-.01</td>
<td>-.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The molecular displacements found in these calculations seem too small to account for the molecular reorientation that must precede photochemical reaction since the structure of the defect is similar to that of the photochemically stable bulk perfect crystal. Thus we conclude that the photochemically reactive 2-OHA site occurs at a dislocation or some point of crystalline imperfection, while the photochemically stable 2-OHA site may be substitutional with configuration H1.
SELF-DIFFUSION

We report the results of a preliminary study of self-diffusion in anthracene and naphthalene. Diffusion in a selected crystallographic direction is simulated by making the molecule at the coordinate origin follow a reaction coordinate through the lattice to a chosen unoccupied site. The approximate enthalpies of migration which are calculated for each reaction coordinate are then used to estimate, in the usual way, the enthalpy of activation for self-diffusion.

Saddle Point Location

Two methods of locating the saddle point(s) which separate the stable lattice structures can be used. Firstly, there is a modified conjugate gradient scheme by Sinclair and Fletcher [146]. As the name implies the method requires only the computation of the first derivatives of the potential energy; a knowledge of the direction of the line joining the two stable configurations is the only initial information that is required. Secondly, there is the method of reaction coordinates [6]. This method requires the calculation of particular functions of the position and orientation variables of the lattice molecules (i.e. reaction coordinates) which will cause the lattice to pass from one stable configuration, through a saddle point, to another stable configuration when at each value of the reaction coordinate, between those for the stable configurations, the remaining molecular variables are varied for minimum-energy. The method is complicated. There is no guarantee that a particular reaction coordinate will produce the lowest barrier between the stable sites - all possibilities must be examined. This is not easy since the reaction coordinates themselves are difficult to formulate. Once a reaction coordinate has been formulated it should be checked for hysteresis of the reaction path in the neighbourhood of the
saddle point [6]. The reaction path can be thought of in a manner similar to that of trajectories in phase space in statistical mechanics. If there are \( N \) variables describing the configuration of the lattice, \( M \) of which compose the reaction coordinate, then the minimum-energy lattice configuration at a particular value of the reaction coordinate can be represented by a vector in the \((N-M)\) dimensional subspace. The trajectory that the ends of the vectors map out as the reaction coordinate is varied between its values at each stable configuration is the reaction path. Clearly the first method is the better one to implement for the location of saddle points but it seems that simple diffusion profiles are not obtainable. However, for the purposes of this work we have chosen the latter and proceeded to use simple reaction coordinates to obtain estimates of the enthalpy of migration. The method of reaction coordinates has the advantage of giving qualitative information on the shape of barriers. We have not examined the reaction coordinates for hysteresis.

**Method of Computation**

The computation was done in the following way. An environment of molecules was constructed with a vacancy either at the lattice site 001 or 010 in an anthracene (at 95K) or naphthalene lattice. The molecule at the origin was then made to traverse a trajectory toward either of the vacant sites. At selected points along [001] or [010] the total intermolecular potential energy was minimized with respect to the orientation and translation variables of the diffusing molecule subject to the constraint that either the \( c' \) or \( b \) component of the centre of mass position vector \( \mathbf{r} \) remains constant, i.e. our reaction coordinates are \( \mathbf{r} \cdot \mathbf{k} \) and \( \mathbf{r} \cdot \mathbf{j} \). We chose these reaction coordinates for simplicity. In the lattice relaxation calculations the 32 nearest lattice molecules to the diffusing molecule
and the vacancy are included in the minimization. These are all listed in Table 2.

Results

The results of this brief study are illustrated in figure 7. It can be seen that the enthalpy of migration is of the order of $40-60 \text{ kJ mol}^{-1}$ for the unrelaxed lattices while relaxation reduces the height of the barrier by approximately $20 \text{ kJ mol}^{-1}$. If we include the enthalpy of formation of a vacancy, which is estimated by calculation to be equal to the enthalpy of sublimation, then for anthracene ($\Delta H_{\text{SUB}} \approx 100 \text{ kJ mol}^{-1}$) and for naphthalene ($\Delta H_{\text{SUB}} \approx 70 \text{ kJ mol}^{-1}$) the enthalpy of activation for self-diffusion is approximately $130 \text{ kJ mol}^{-1}$ and $90 \text{ kJ mol}^{-1}$ respectively. These estimates are clearly much less than those found by experiment. The activation enthalpies calculated in this way are approximately 1.3 times $\Delta H_{\text{SUB}}$. If we use as the enthalpy of vacancy formation that which was experimentally obtained for krypton then the activation enthalpy for self-diffusion is found to be approximately equal to $\Delta H_{\text{SUB}}$.

To come to terms with this discrepancy other aspects of the calculations need to be considered. Firstly, the shape of the barrier is seen to depend on the trajectory followed. There is a departure from the simple Arrhenius barrier shape for diffusion along [001] while that along [010] is Arrhenius in nature. We recall that these trajectories are dependent on the reaction coordinate; and further, due to time limitations not all calculations could be completed therefore conclusive remarks cannot be made. However, the calculations do show that there is anisotropy in the barriers to diffusion, principally in the barrier shape. Secondly, the potential functions that have been used in these calculations were derived from data collected for equilibrium conditions, therefore, we can expect that the region of the
Self-diffusion in anthracene (95K structure) 'along' [010]

Self-diffusion in 95°K anthracene 'along' [001].

Self-diffusion in naphthalene 'along' [001] (room temperature structure).
potential well is 'accurately' determined compared to that of the repulsive part. Thus sampling of the repulsive part during the process of diffusion can be expected to introduce errors. Although from Table 26 we see that the number of atom-atom distances that are less than 0.3 nm is less in the central region (i.e. $c' = 0.4-0.5$ nm) of the trajectory than at the end of points. The number of atom-atom distances less than 0.25 nm, which can be thought of as being unusual for anthracene, are very few. Thus we infer that the barrier to self-diffusion along [001] is determined by only 2 or 3 atom-atom contacts.

**TABLE 26**

**SELF-DIFFUSION IN ANTHRACENE ALONG [001]**

: CHECK OF ATOM-ATOM DISTANCES

(Units: nm)

<table>
<thead>
<tr>
<th>Distance along $c'$</th>
<th>No. atom-atom distances &lt; .3 nm</th>
<th>No. atom-atom distances &lt; .25 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>44</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>38</td>
<td>2</td>
</tr>
<tr>
<td>0.2</td>
<td>42</td>
<td>1</td>
</tr>
<tr>
<td>0.3</td>
<td>43</td>
<td>3</td>
</tr>
<tr>
<td>0.4</td>
<td>36</td>
<td>3</td>
</tr>
<tr>
<td>0.5</td>
<td>35</td>
<td>2</td>
</tr>
<tr>
<td>0.6</td>
<td>45</td>
<td>3</td>
</tr>
<tr>
<td>0.7</td>
<td>39</td>
<td>2</td>
</tr>
<tr>
<td>0.8</td>
<td>38</td>
<td>2</td>
</tr>
</tbody>
</table>

To conclude this section we give the paths followed by the diffusing anthracene molecule along [001] and [010], Table 27. In the former case the path followed in the relaxed lattice is given. As might be expected the orientation of the diffusing molecule changes little from that in the perfect lattice for diffusion along [001] but changes markedly for diffusion
potential well is 'accurately' determined compared to that of the repulsive part. Thus sampling of the repulsive part during the process of diffusion can be expected to introduce errors. Although from Table 26 we see that the number of atom-atom distances that are less than 0.3 nm is less in the central region (i.e. $c' = 0.4-0.5$ nm) of the trajectory than at the end of points. The number of atom-atom distances less than 0.25 nm, which can be thought of as being unusual for anthracene, are very few. Thus we infer that the barrier to self-diffusion along [001] is determined by only 2 or 3 atom-atom contacts.

**TABLE 26**

**SELF-DIFFUSION IN ANTHRACENE ALONG [001]**

<table>
<thead>
<tr>
<th>Distance along $c'$</th>
<th>No. atom-atom distances $&lt; .3$ nm</th>
<th>No. atom-atom distances $&lt; .25$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>44</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>38</td>
<td>2</td>
</tr>
<tr>
<td>0.2</td>
<td>42</td>
<td>1</td>
</tr>
<tr>
<td>0.3</td>
<td>43</td>
<td>3</td>
</tr>
<tr>
<td>0.4</td>
<td>36</td>
<td>3</td>
</tr>
<tr>
<td>0.5</td>
<td>35</td>
<td>2</td>
</tr>
<tr>
<td>0.6</td>
<td>45</td>
<td>3</td>
</tr>
<tr>
<td>0.7</td>
<td>39</td>
<td>2</td>
</tr>
<tr>
<td>0.8</td>
<td>38</td>
<td>2</td>
</tr>
</tbody>
</table>

To conclude this section we give the paths followed by the diffusing anthracene molecule along [001] and [010], Table 27. In the former case the path followed in the relaxed lattice is given. As might be expected the orientation of the diffusing molecule changes little from that in the perfect lattice for diffusion along [001] but changes markedly for diffusion
TABLE 27
PATHS FOLLOWED BY ANTHRACENE
BETWEEN LATTICE SITES IN SELF-DIFFUSION CALCULATIONS

a) Diffusion along [001]

<table>
<thead>
<tr>
<th>( r \cdot k ) (nm)</th>
<th>Orientation (Principal Axes Direction Cosines)*</th>
<th>Centre of Mass Position (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r \cdot k ) (nm)</td>
<td>( a )</td>
<td>( b )</td>
</tr>
<tr>
<td>0.0</td>
<td>-0.52(1°)</td>
<td>-0.14(1°)</td>
</tr>
<tr>
<td>M</td>
<td>-0.27(1°)</td>
<td>-0.91(1°)</td>
</tr>
<tr>
<td>N</td>
<td>0.81(1°)</td>
<td>-0.40(1°)</td>
</tr>
<tr>
<td>0.2</td>
<td>-0.60(6°)</td>
<td>-0.11(1°)</td>
</tr>
<tr>
<td>0.77(3°)</td>
<td>-0.34(5°)</td>
<td>0.54(8°)</td>
</tr>
<tr>
<td>0.62(8°)</td>
<td>0.08(12°)</td>
<td>0.78(7°)</td>
</tr>
<tr>
<td>-0.29(1°)</td>
<td>-0.95(8°)</td>
<td>-0.13(11°)</td>
</tr>
<tr>
<td>0.73(6°)</td>
<td>-0.30(7°)</td>
<td>0.61(13°)</td>
</tr>
</tbody>
</table>

** 'a' axis component of 'c' projection onto the 'c' axis.

b) Diffusion along [010]

<table>
<thead>
<tr>
<th>( r \cdot k ) (nm)</th>
<th>Orientation (Principal Axes Direction Cosines)</th>
<th>Centre of Mass Position (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r \cdot k ) (nm)</td>
<td>( a )</td>
<td>( b )</td>
</tr>
<tr>
<td>0.1</td>
<td>-0.53(1°)</td>
<td>-0.04(5°)</td>
</tr>
<tr>
<td>M</td>
<td>-0.09(13°)</td>
<td>-0.99(18°)</td>
</tr>
<tr>
<td>N</td>
<td>0.84(4°)</td>
<td>-0.13(17°)</td>
</tr>
<tr>
<td>0.2</td>
<td>-0.34(11°)</td>
<td>-0.68(35°)</td>
</tr>
<tr>
<td>0.37(40°)</td>
<td>-0.74(16°)</td>
<td>-0.57(16°)</td>
</tr>
<tr>
<td>0.86(6°)</td>
<td>0.05(28°)</td>
<td>0.50(5°)</td>
</tr>
<tr>
<td>0.3</td>
<td>-0.49(1°)</td>
<td>-0.25(7°)</td>
</tr>
<tr>
<td>-0.08(14°)</td>
<td>-0.08(14°)</td>
<td>-0.08(14°)</td>
</tr>
<tr>
<td>(1°)†</td>
<td>(22°)</td>
<td>(1°)</td>
</tr>
<tr>
<td>0.34(40°)</td>
<td>-0.94(6°)</td>
<td>-0.08(14°)</td>
</tr>
<tr>
<td>(2°)</td>
<td>(6°)</td>
<td>(23°)</td>
</tr>
<tr>
<td>0.80(0°)</td>
<td>0.25(40°)</td>
<td>0.55(9°)</td>
</tr>
<tr>
<td>(0°)</td>
<td>(10°)</td>
<td>(9°)</td>
</tr>
</tbody>
</table>

* Values in brackets give the magnitude of the displacements from the experimental values for the molecule at the coordinate origin.
† Second values in brackets give the magnitude of the displacement from the experimental values for the molecule at the lattice site 0.5 0.5 0.0.
along [010]. At the mid-point of the latter path the diffusing molecule has an orientation similar to that of the lattice molecules at $-0.5 \ 0.5 \ 0.0$ and $0.5 \ 0.5 \ 0.0$ between which it is passing. In both cases the displacements of the centre of mass from the c and b crystallographic axes are small.

**SUMMARY**

The principal findings of the calculations reported in the previous sections may be summarized as follows:

i) Lattice relaxation is of major importance in calculating the enthalpy of mixing of crystals in which a host molecule is replaced by a larger guest. For these systems the reduction in the strain energy can be very large. Lattice relaxation is essentially unimportant, both energetically and structurally, for guest molecules smaller than the replaced host molecule. Although, if energy barriers to the interconversion between guest sites are to be calculated lattice relaxation may produce significant changes in the magnitude of the barrier.

ii) For guests larger than the replaced host molecule, e.g. tetracene in anthracene, the orientation adopted by the guest in the rigid host is close to that which is experimentally observed; lattice relaxation improves this agreement slightly.

iii) In most cases studied lattice relaxations were found to be small. This is in agreement with the findings of the calculations on the rare gases, and the few experimental data available on X-traps.

iv) For guests larger than the replaced host molecule the magnitude
of the enthalpy of mixing is found to be sensitive to small changes in the carbon-hydrogen bond length and small changes in crystal structure [9]. This is understandable since small changes in the short atom-atom distances found in the defect lattice will produce larger energetic changes than will similar changes in the pure lattice. Therefore, we suggest that for results to be reproducible care must be taken to standardize the carbon-hydrogen bond length.

v) For over-sized guests it seems that convergence of the enthalpy of mixing can only be obtained by including next nearest neighbours in the potential energy minimization.

vi) For the systems tetracene in anthracene, and naphthalene in anthracene the relative magnitudes of the calculated enthalpies of mixing are in agreement with the measured segregation coefficients, i.e. it is easier to put tetracene into an anthracene lattice, $\Delta H_{mix} \approx 15 \text{ kJ mol}^{-1}$, than it is to put naphthalene into an anthracene lattice, $\Delta H_{mix} \approx 55 \text{ kJ mol}^{-1}$. These results are also in agreement with the experimental observations that suggest that guests which leave voids upon substitution are less readily incorporated into the host lattice than are those guests that 'over-fill' the available volume and produce lattice distortions, e.g. we recall the example of pentacene in anthracene or naphthalene hosts. It is tempting to speculate by associating these findings with guest solubilities. For example a guest with a solubility of $10^{-4}$ mol/mol in a solvent such as anthracene can be crudely expected to have a distribution over the host lattice which corresponds to one guest per cube of side 15-20 unit cells.
This is quite remarkable and illustrates a subtlety of nature. We suggest that for systems such as tetracene in anthracene which have relatively small enthalpies of mixing and produce lattice distortions, then the guest solubility is entropy controlled. While for systems such as naphthalene in anthracene which have relatively large enthalpies of mixing, and produce little lattice distortion, then the guest solubility is enthalpy controlled.

vii) The structure of the lattice surrounding a mono- or divacancy is little changed from that of the bulk perfect lattice.

viii) A vacancy adjacent to an 'over-sized' guest is more stable than an isolated vacancy, at least for the structure considered in this work.

ix) 'Under-sized' guest molecules may exhibit multiple potential minima when incorporated substitutionally into a lattice. These may or may not be related by symmetry.

x) The example of 2-OHA in anthracene shows that symmetry arguments alone may not be adequate to explain experimental results. This impurity system poses fundamental problems concerning the mode of incorporation of guests into host lattices.

xi) While values for $\Delta H_{\text{act}}$ for self-diffusion may be inaccurate because of the theoretical difficulties involved in treating surfaces it seems that the type of calculations presented here may be useful in studying anisotropy in self- and mutual diffusion.

We conclude this chapter with a brief examination of work reported by Ramdas [132] on the systems tetracene in anthracene, anthracene in naphthalene,
and naphthalene in anthracene. There are a number of points on which his and our results disagree. We consider several errors which we believe he has made. Firstly, naphthalene in anthracene is reported to have an origin-centred site. At our level of calculation we found that this was a saddle point. This seems reasonable when one considers figures 2 and 4. The naphthalene moved from this site even without lattice relaxation to one of the two inversion-related sites. Secondly, the enthalpies of mixing reported for naphthalene in anthracene, and tetracene in anthracene are not in agreement with the experimentally measured segregation coefficients, our calculations are. The error in this case is rather serious since it is found by experiment that naphthalene is almost completely rejected from the anthracene lattice at high dilution; according to Ramdas naphthalene in anthracene is considerably more stable than pure anthracene. Thirdly, the enthalpy of mixing of anthracene in naphthalene is not in agreement with our result. It is difficult to ascertain why there is this discrepancy because Ramdas has not given the full details of his calculations. We can only assume that part of the discrepancy can be attributed to the very small environment of molecules used in the calculations in combination with electrostatic terms in the potential which are known to be very long range and sensitive to incomplete environments. We think that there may be a similar error in other reported work [133] but it is difficult to tell because the details of the calculations have again not been given.
CHAPTER 5

THE RÔLE OF LATTICE CONSTRAINTS IN THE PHOTOCHEMISTRY OF BRIDGED ANTHRACENES AND RELATED SYSTEMS

INTRODUCTION

In this chapter the computational method is extended to the study of certain ground state conformational problems which have arisen from photochemical investigations into the behaviour of anthracene dimers \((\text{A}\,\text{A})\) in a host lattice of dianthracene, i.e. di-para-anthracene \((\text{A}\,\text{A}_2)\), and alkane-bridged bichromophoric molecules in host lattices of their photodimers. In particular we shall be concerned with 1, 2-di-(9-anthryl)ethane \((\text{AEA})\) in a host lattice of its photodimer \((\text{CAEA})\), see figure 1. The purpose of the calculations is to complement the experimental work and act as a guide in the interpretation of the observations.

NATURE OF THE CONFORMATIONAL PROBLEM

Highly purified single crystals of \(\text{A}\,\text{A}_2\) and \(\text{CAEA}\) when irradiated with light of a particular wavelength at low temperatures produce the photocleaved molecules \(\text{A}\,\text{A}\) and \(\text{AEA}\) respectively. These may be considered to be either isolated in otherwise perfect regions of the host lattice or in aggregates in regions of disrupted lattice. The wavelength of the irradiating light and the period of irradiation determine which condition prevails; weakly absorbed light and short periods of irradiation produce the former condition whereas strongly absorbed light and longer periods of irradiation produce the latter.

The photocleaved molecules that are produced in isolation adopt specific conformations which result from the constraints imposed by the host lattice.
Figure 1. Photodimer of 1,2-di-(9-anthryl) ethane.
It is the nature of these conformations which the computational study is intended to elucidate.

**STRUCTURE IN SOLID STATE PHOTOCHEMISTRY**

In this section a brief review is given of the historical development of the important concepts connecting structure and reactivity in the solid state. These concepts form a basis for the work to be reported. This review is followed by an account of the experimental work performed on A\textsubscript{1}A in A\textsubscript{2}, and AEA in CAEA.

It appears that the expansion of spectroscopic investigations into phenomena occurring in molecular crystals was initiated by the discovery of the pyrene excimer by Förster and Kasper\textsuperscript{[69]} in 1954. Shortly after this discovery Ferguson\textsuperscript{[58]} observed excimer emission from pyrene single crystals. This phenomenon was then investigated by Stevens\textsuperscript{[151]} who proceeded to correlate the spectroscopic data collected from a number of aromatic hydrocarbons with their observed crystal structures. This work is well-known but because of its importance the salient points are briefly noted. Stevens observed the following:

1) molecules such as naphthalene\textsuperscript{[37]}, anthracene\textsuperscript{[106]}, phenanthrene\textsuperscript{[159]} and chrysene\textsuperscript{[24]} do not exhibit excimer emission from the bulk perfect crystal. This behaviour is attributed to the packing arrangement in which adjacent molecules adopt an almost 'orthogonal' configuration. The necessary overlap of the molecular planes required for the formation of an excimer is not permitted, as shown in structure (a) of figure 2. Although it is now equally well-known\textsuperscript{[176]} that excimer emission from crystalline anthracene is possible at dislocations where the molecules can adopt a
packing arrangement which permits favourable molecular overlap.

ii) disc-shaped molecules such as pyrene [29], perylene [28,84] (the \(\alpha\)-form), and 1, 12-benzperylenes [159] exhibit excimer emission. This is attributed to the packing arrangement in the pure crystal where there is substantial overlap of the molecular planes, as shown in structure (b) of figure 2.

iii) oval-shaped molecules such as coronene [56] and ovalene [85] pack in a column arrangement which also permits significant overlap of the molecular planes and thus is correlated with the observed excimer emission, see structure (c) of figure 2.

In 1965 Schmidt and co-workers [73] expounded the principle of topochemical preformation in which it was proposed that "reaction in the solid state occurs with a minimum amount of atomic or molecular movement", the products of certain solid state reactions being determined by the geometry of the reactant lattice, i.e. by the orientation and distance of separation of the respective photoreactive molecular segments of adjacent molecules. This is illustrated in figure 3 for the now classic example of topochemical behaviour - the \((\alpha,\beta,\gamma)\) polymorphs of substituted trans-cinnamic acid. A comprehensive treatment of topochemistry is given in the recent review by Thomas et al [153].

Non-topochemical behaviour was observed by Craig and Sarti-Fantoni [42] in a study of the photodimerization of crystalline 9-cyanoanthracene. The product expected from an analysis of the crystal structure [129] is the 'head-to-head' or cis photodimer, however it is found that, as in solution, the 'head-to-tail' or trans photodimer is formed. This phenomenon was explained by assuming that the photoreaction takes place at a dislocation
**Figure 2.** Schematic representation of three types of crystal lattice adopted by aromatic hydrocarbons viewed along the molecular planes.

- **α-type**
  \[ d > 5.5 \text{Å} \]

- **γ-type**
  \[ d = 4.8 - 5.2 \text{Å} \]

- **β-type**
  \[ d = 3.8 - 4.2 \text{Å} \]

**Figure 3.** Reactivity in (α, β, γ)-polymorphs of substituted trans-cinnamic acid.

(d = crystallographic axial length)
where the molecules can adopt the mutual orientation necessary for the production of the trans photodimer.

The concepts discussed above form an important part of the study of the photodimerization of anthracene. This problem has been of interest for many years. The need to define the reaction pathway precisely for this reaction has led to the development of solid state experimental techniques for isolating the anthracene pair and restricting their motion. It was in the course of such studies that the conformational problem of interest here arose. The technique for isolating anthracene dimers in the solid state was developed by Ferguson, Chandross and McRae [33,34,35,59]. The method developed originally (and still used) involves the preparation of a dilute solution of $A_2$ in methylcyclohexane, cooling it to liquid nitrogen temperatures and then cleaving the $A_2$ molecules (which are predominantly in isolation) by irradiating the rigid glass with light of wavelength 254nm. The dimers produced in this manner are constrained by the matrix to adopt a conformation which is close to being perfectly eclipsed. The study of the effects of temperature are however hampered, since warming, and thus softening of the glass, allows the anthracenes to adopt many slightly different conformations [62]. This problem was overcome by preparing the anthracenes in situ in a $A_2$ crystal by the photocleavage of a $A_2$ molecule [60]. In order to define the conformational preferences of the anthracenes even more precisely their motion was further restricted by the imposition of an alkane bridge. This technique led to the studies of AEA in CAEA [2,65,66,67].

**EXPERIMENTAL OBSERVATIONS: A•A IN A₂, AND AEA IN CAEA**

The experimental work performed on A•A in A₂, and AEA in CAEA is now reviewed in order to provide a framework within which to undertake the computational study. To begin, the salient features of the pure crystal
structures of A2 and CAEA are noted.

Pure Crystal Structures

Dianthracene crystallizes in the space group $P_{bca}$ with four molecules in the unit cell [48] (figure 4). The cell has dimensions: $a = 0.827\text{nm}$, $b = 1.208\text{nm}$, and $c = 1.885\text{nm}$. The structure was determined by X-ray diffraction at room temperature. There is no report of disorder. The principal inertial axes of A2 are illustrated in figure 5.

The crystal structure of CAEA has been determined by X-ray diffraction at room temperature [2], the structure is illustrated in figure 6. Since CAEA is unstable at room temperature and upon exposure to X-rays difficulties were experienced in the structure determination; however it was found to refine in the space group $P2_1$ with the two molecules in the unit cell placed at the lattice points 000 and 044. These points act as pseudo-inversion centres for the anthracene moieties. The structure is considered not to be disordered at the unit cell level but domains of $P_c$ space group symmetry may be present. This conclusion was drawn from the observation of reflections contravening the glide extinction and the screw axis extinction. The final choice of the $P2_1$ space group was made on a simple statistical analysis of the collected data [139]. Thus the screw-diad and the pseudo-inversion centre may not be exact symmetry elements even though they were imposed in the refinement, however, departures are thought to be very small [139]. There is no estimate of the proportion of each domain that may be present. The unit cell was found to have dimensions: $a = 1.0095\text{nm}$, $b = 1.2471\text{nm}$, and $c = 0.8340\text{nm}$ with $\beta = 111.20^\circ$.

A·A in A2 - Experimental

Irradiation of A2 single crystals with 254nm light at 10 K for a
Figure 4: Dianthracene crystal structure

Figure 5. Projection of a A₂ molecule along the molecular N axis.
Figure 6. CAEA Crystal Structure
period of several minutes photolyzes the A₂ molecules producing anthracene dimers in concentrations not exceeding 0.1M for depths up to 1 micron below the crystal surface [60]. The dimers absorb at 254nm and react to reform A₂ but because the quantum yield for the photodimerization is essentially zero at this temperature continued irradiation simply results in an increase in the concentration of the dimers.

Ferguson and Mau [60] found that two conformations of A·A in A₂ could be produced depending on the period of irradiation. The conformation of interest in this work exhibits red excimer emission and is produced in isolation from other anthracene pairs in otherwise perfect regions of crystal. This conformation was initially thought to be perfectly eclipsed - the so-called sandwich conformation. The other conformation of A·A exhibits green excimer emission and is formed in regions of disrupted lattice, thus it is not considered.

From the temperature dependence of φ_D and φ_F (the quantum yield for fluorescence) it was found that an Arrhenius activation energy of 600 cm⁻¹ (530 cm⁻¹ for perdeutero - anthracene) was required before the anthracenes would photodimerize to reform A₂. This unusually large value (which corresponds to approximately 800 K) was tentatively explained in terms of the energy required to excite a combination of physically reasonable ground state internal modes of appropriate frequency under the assumption that in the excited state the modes and frequency are little changed. Similar values for the thermal barrier to photodimerization and photocyclization of 1-(9-anthryl)-3-(1-naphthyl)-propane (ANP) have been measured [61,63]. In this work [61,63] the barrier was interpreted as being due to the energy required to transform the molecule of ANP from a non-eclipsed to an eclipsed conformation whence reaction can occur. The views held by the authors
regarding the rôle of the cage molecules is that the cage exerts a dominating influence on the facility with which the aromatic moieties may move, upon excitation, to the more favourable sandwich conformation. This view is in contradistinction to that held earlier [62].

Further investigations by Ferguson and Miller [64] into the effects of molecular structure and environment on the photodimerization of substituted anthracenes confirmed that the red excimer emitting anthracene dimer was not perfectly eclipsed and that the barrier to photodimerization was a measure of the energy required to displace molecules of the cage as necessary in order to attain the perfectly eclipsed conformation. However the quantum yield for photodimerization of 9-substituted anthracenes, prepared in an analogous manner to A·A, is unity over the temperature range 6-300 K. This is interpreted as indicating that the 9-substituted anthracenes adopt a perfectly eclipsed conformation upon photocleavage.

AEA in CAEA - Experimental

The most recent paper [2] of a series [65,66,67] on the photochemistry and photophysics of AEA and CAEA contains all the relevant information for this computational study. It is reported that the molecule of AEA in isolation in CAEA adopts four conformations, two are non-fluorescent and two are fluorescent. The following characteristics of the non-fluorescent species were observed:

i) the two conformations originate from different sets of molecules: they are labelled \( P_1 \) and \( P_2 \).

ii) the site \( P_1 \) is assigned "to dissociated molecules which retain the orientation of the photoisomer" i.e. the dissociation does not displace the molecule far from the eclipsed conformation.
iii) the site $P_2$ is assigned to a conformation which also has the anthracene moieties eclipsed but the whole molecule is rotated about an axis normal to the (100) face by 7 or 8 degrees toward the $c$ axis, see figure 6.

iv) both conformations have the anthracene moieties asymmetrically displaced from planarity.

v) there is no barrier to photocyclization.

The following characteristics are observed for the fluorescent conformations:

i) they correspond to two different conformations of the one molecule.

ii) the conformations are thought to result, in the first case, from a long axis relative displacement of the anthracenes accompanied by a partial return to the planar anthracene configuration, and in the second case, a similar displacement occurs but in addition there is a small rotation about the central bridging carbon-carbon bond.

iii) there is a thermal barrier to photoisomerization which is difficult to measure.

These observations on the systems $A\cdot A$ in $A_2$, and AEA in CAEA will be in part clarified in the next section.

**AEA in Solution**

An aspect of the work of Hayashi et al [81,82,83] on the photophysics of anthracenophanes and 1,2-di-(9-anthryl)ethane in solution is relevant to the work reported here. They observe the formation of an excimer of AEA at
room temperature which is interpreted as being due to a conformation which
is partially overlapped and related to the fully eclipsed conformation by a
rotation about the central carbon-carbon bridging bond. This conformation
is of interest because of the results obtained from AEA free molecule
calculations which are reported in a later section.

METHOD OF CALCULATION

The method employed in the study of the point defect problems in
Chapter 4 is now extended to treat the situation in which there are two
guest molecules, or a single guest molecule with certain internal degrees
of freedom. The method of computation of the equilibrium structure of AEA
will be detailed later. In order to avoid repetition several procedures
which are used throughout this work are outlined in this section and hence
will not be referred to again.

In all calculations, except where otherwise stated, the position of
hydrogen in the experimentally determined carbon-hydrogen bond has been
standardized to 0.1027nm for aromatic protons and 0.104nm for aliphatic
protons, with the exception of the aromatic protons of A₂. These were
standardized to 0.103nm because the A₂ atomic position coordinates were
averaged, vide infra. In all calculations the molecular geometry of
anthracene was taken from the averaged data of Mason[106]. This also
applies to the anthracene moieties of AEA since the molecular geometry is
not known, vide infra. In the lattice relaxation calculations the
environment of molecules used includes all atom-atom contacts less than
1.0nm with the central molecule or guest, and the neighbour molecules which
are specified in each section. All atom-atom sums were truncated at 1.0nm.

The pure crystal packing calculations in which the total potential
energy of the crystal is minimized with respect to the displacements in the
unit cell parameters and molecular position and/or orientation variables,
subject to the constraint of an appropriate space group symmetry, were
performed with the computer program CRASH which was written by Dr G.S. Pawley.
This program was also used to calculate phonon frequencies. All other
calculations were performed with our computer program - OVID.

Williams' aromatic parameter set IV [170] was used in all calculations
even though aliphatic protons are present in the systems studied. This was
done to preserve continuity with the earlier calculations. The use of a
mixed aromatic-aliphatic parameter set [171] is expected only marginally to
alter the structures reported here. Thus for instance consider Table 1 in
which Williams' mixed parameter set IV [171] is compared to the set used in
these calculations.

\[
V(R) = -\frac{A}{R^6} + B \exp(-CR)
\]
(Units: kJ mol\(^{-1}\) and nm)

**TABLE 1**

<table>
<thead>
<tr>
<th>Parameter Type</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic Parameter Set IV [170]</td>
<td></td>
</tr>
<tr>
<td>(A_{CC})</td>
<td>(2238 \times 10^{-6})</td>
</tr>
<tr>
<td>(B_{CC})</td>
<td>(31.2 \times 10^{4})</td>
</tr>
<tr>
<td>(C_{CC})</td>
<td>(36.0)</td>
</tr>
<tr>
<td>(A_{CH})</td>
<td>(582 \times 10^{-6})</td>
</tr>
<tr>
<td>(B_{CH})</td>
<td>(3.94 \times 10^{6})</td>
</tr>
<tr>
<td>(C_{CH})</td>
<td>(36.7)</td>
</tr>
<tr>
<td>(A_{HH})</td>
<td>(151 \times 10^{-6})</td>
</tr>
<tr>
<td>(B_{HH})</td>
<td>(1.67 \times 10^{4})</td>
</tr>
<tr>
<td>(C_{HH})</td>
<td>(37.4)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter Type</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed Aromatic-Aliphatic Parameter Set IV [171]</td>
<td></td>
</tr>
<tr>
<td>(A_{CC})</td>
<td>(2377 \times 10^{-6})</td>
</tr>
<tr>
<td>(B_{CC})</td>
<td>(35 \times 10^{4})</td>
</tr>
<tr>
<td>(C_{CC})</td>
<td>(36.0)</td>
</tr>
<tr>
<td>(A_{CH})</td>
<td>(523 \times 10^{-6})</td>
</tr>
<tr>
<td>(B_{CH})</td>
<td>(3.7 \times 10^{6})</td>
</tr>
<tr>
<td>(C_{CH})</td>
<td>(36.7)</td>
</tr>
<tr>
<td>(A_{HH})</td>
<td>(114 \times 10^{-6})</td>
</tr>
<tr>
<td>(B_{HH})</td>
<td>(1.1 \times 10^{4})</td>
</tr>
<tr>
<td>(C_{HH})</td>
<td>(37.4)</td>
</tr>
</tbody>
</table>
The repulsive part of both potentials is almost identical, from which follows the conclusion regarding structural similarity. While the inevitable energy differences which accompany changes of parameter sets are of concern the particular differences between these two parameter sets seem unlikely to alter the conclusions made in this chapter.

COMPUTATIONAL RESULTS AND DISCUSSION

A·A IN A₂

Calculations on the conformation adopted by a pair of anthracene molecules formed in situ by the photocleavage of a molecule of A₂ in a A₂ single crystal show that in the ground state the two anthracene molecules are related by the inversion centre at an origin at the site from which they were cleaved, with the molecular planes parallel and slightly displaced from the eclipsed position. Somewhat surprising is the result that the total intermolecular potential energy of the anthracene pair is lower than that of the pure host lattice. These results are correlated with the observations and conclusions of Ferguson et al [60, 64].

DETAILS OF THE CALCULATIONS

Pure Crystal Calculation

A calculation was performed on the pure crystal structure of A₂ in which the unit cell dimensions and the molecular orientation were permitted to vary, subject to the constraint of P₁bc₃ space group symmetry, so as to minimize the total intermolecular potential energy of the lattice. The initial structure used in the calculation was taken from experiment; however because the reported atomic position coordinates are not of high precision they were averaged to give exact mmm symmetry. The molecular geometry is illustrated in figure 7.
Figure 7. $A_2$ molecular geometry in projection along 'a'.
It was found that the molecular orientation changed by less than 1° in the angular displacements about the a, b and c crystal-fixed axes, and only small displacements occurred in the unit cell dimensions:
\[ \Delta a = -0.02\text{nm}, \quad \Delta b = -0.01\text{nm}, \quad \text{and} \quad \Delta c = +0.01\text{nm}. \]
Since there has been no measurement of the thermal expansion of crystalline \( A_2 \) it is simply concluded that these changes are normal for aromatic hydrocarbons studied with atom-atom potentials. Phonon frequencies calculated at several values of the wave vector indicate that the minimum energy structure is stable. Therefore it would appear that the room temperature P\(_{\text{bca}}\) structure of \( A_2 \) persists into the régime of low temperatures with little change. This conclusion is in agreement with the spectroscopic observations of Ferguson and Mau [60]. Finally, the calculated heat of sublimation of \( A_2 \) is 143 kJ mol\(^{-1}\) which is a plausible result when one considers that the experimentally determined heat of sublimation of coronene [160] is 147 kJ mol\(^{-1}\).

**Pure Crystal Relaxation Calculation**

The investigation of the conformation of the anthracene pair is treated in an analogous manner to that of a single guest molecule replacing a host molecule. Using the experimentally determined unit cell dimensions an environment of molecules forming a pure \( A_2 \) lattice is constructed so as to include the 14 nearest neighbours of the central molecule, these are listed in Table 2. The molecular types are defined in Table 3 in terms of the symmetry relationship to the origin-centred molecule (figure 4). The minimum energy conformation of the central molecule and its specified neighbours is found by applying the technique developed in Chapter 3. Inversion symmetry was maintained, the resultant energy is used in the comparison with the results obtained for the dimer system. It is found that
## TABLE 2

**A₂ LATTICE SITES INCLUDED IN THE RELAXATION CALCULATIONS**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Type</th>
<th>Position in reduced units</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>a</strong></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
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</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-1.0</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>-0.5</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>-0.5</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>-0.5</td>
</tr>
<tr>
<td>9</td>
<td>4</td>
<td>-0.5</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>0.0</td>
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<tr>
<td>12</td>
<td>3</td>
<td>0.0</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>0.0</td>
</tr>
<tr>
<td>14</td>
<td>3</td>
<td>0.0</td>
</tr>
</tbody>
</table>

## TABLE 3

**SYMMETRY TYPES IN DIANTHRACENE ENVIRONMENT**

<table>
<thead>
<tr>
<th>Type</th>
<th>Rotation</th>
<th>Translation (reduced units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[1 0 0; 0 -1 0; 0 0 -1]</td>
<td>[0.5; 0.5; 0.0]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>glide along b</td>
</tr>
<tr>
<td>2</td>
<td>[1 0 0; 0 -1 0; 0 0 1]</td>
<td>[0.0; 0.5; 0.5]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>glide along c</td>
</tr>
<tr>
<td>3</td>
<td>[1 0 0; 0 1 0; 0 0 -1]</td>
<td>[0.5; 0.0; 0.5]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>glide along a</td>
</tr>
</tbody>
</table>
the structural variations are small. For example Table 4 gives the direction cosines of the principal axes of the central molecule before and after minimization.

**A·A in A₂ - Rigid Lattice Calculations**

In the calculations on the system A·A in A₂, the central molecule of A₂ was removed from the environment of molecules described and replaced by two anthracenes which were put into the lattice in a conformation selected with respect to the principal axes of the removed molecule of A₂ as if it were occupying the site (figures 4 and 7, and Table 4). The 'cavity' was then systematically searched for stable conformations of the dimer before embarking on the longer lattice relaxation calculations. The results of the calculations in Chapter 4 showed that the minimum energy conformation of a guest in an unrelaxed host lattice is structurally similar to that in the relaxed lattice; thus such a preliminary search avoids duplication of effort in longer calculations. All the grid points used to sample the regions of the cage are schematically illustrated in figure 8.

The minimization from each grid point converged to the same conformation of the dimer in which the anthracenes have their molecular planes displaced from the eclipsed conformation, yet parallel and related by the inversion centre with a perpendicular distance of separation between the planes of 0.347nm, as in figure 9(a). The direction cosines of the anthracene principal axes and the coordinates of a centre of mass are given in Table 5. The interaction energy between the anthracenes is approximately -52 kJ mol⁻¹ while the total interaction energy of the dimer is -300 kJ mol⁻¹, or 20 kJ mol⁻¹ more stable than the replaced host molecule (Table 7). This result will be discussed presently.
### TABLE 4

**PRINCIPAL AXES OF $A_2$ BEFORE MINIMIZATION**

(Direction cosines)

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.164</td>
<td>-.349</td>
<td>-.923</td>
</tr>
<tr>
<td>M</td>
<td>-.736</td>
<td>0.666</td>
<td>-.121</td>
</tr>
<tr>
<td>N</td>
<td>0.657</td>
<td>0.659</td>
<td>-.366</td>
</tr>
</tbody>
</table>

**PRINCIPAL AXES OF $A_2$ AFTER MINIMIZATION**

(Direction cosines)

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.175</td>
<td>-.381</td>
<td>-.908</td>
</tr>
<tr>
<td>M</td>
<td>-.724</td>
<td>0.675</td>
<td>-.144</td>
</tr>
<tr>
<td>N</td>
<td>0.667</td>
<td>0.632</td>
<td>-.394</td>
</tr>
</tbody>
</table>
### TABLE 5

**PRINCIPAL AXES OF ANTHRACENES WITHOUT LATTICE RELAXATION**

(direction cosines)

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.167</td>
<td>0.458</td>
<td>0.873</td>
</tr>
<tr>
<td>M</td>
<td>0.680</td>
<td>0.587</td>
<td>-0.439</td>
</tr>
<tr>
<td>N</td>
<td>-0.714</td>
<td>0.667</td>
<td>-0.213</td>
</tr>
</tbody>
</table>

**CENTRE OF MASS POSITION COORDINATES (nm)**

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-0.14</td>
<td>0.12</td>
<td>0.01</td>
</tr>
</tbody>
</table>

### TABLE 6

**PRINCIPAL AXES OF ANTHRACENES AFTER LATTICE RELAXATION**

(direction cosines)

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.181</td>
<td>0.476</td>
<td>0.861</td>
</tr>
<tr>
<td>M</td>
<td>0.674</td>
<td>0.577</td>
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</tr>
<tr>
<td>N</td>
<td>-0.716</td>
<td>0.664</td>
<td>-0.216</td>
</tr>
</tbody>
</table>

**CENTRE OF MASS POSITION COORDINATES (nm)**

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-0.14</td>
<td>0.11</td>
<td>0.0</td>
</tr>
</tbody>
</table>
### TABLE 7

**CONFORMATIONAL ENERGIES**

(Units: kJ mol\(^{-1}\) and nm)

<table>
<thead>
<tr>
<th>Crystal</th>
<th>C-H Bond Length (AR/AL)</th>
<th>A·A Interaction E at R minimum</th>
<th>UΔE</th>
<th>RΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.T.</td>
<td>0.1027/0.104</td>
<td>-52</td>
<td>20</td>
<td>29</td>
</tr>
<tr>
<td>R.T.</td>
<td>0.108 /0.109</td>
<td>-52</td>
<td>13</td>
<td>20</td>
</tr>
<tr>
<td>C.S.</td>
<td>0.1027/0.104</td>
<td>-52</td>
<td>8</td>
<td>26</td>
</tr>
</tbody>
</table>

**Code**

- R.T. \(\equiv\) Room temperature crystal structure
- C.S. \(\equiv\) Calculated crystal structure
- AR \(\equiv\) Aromatic C-H bond length
- AL \(\equiv\) Aliphatic C-H bond length
- U \(\equiv\) Unrelaxed lattice
- R \(\equiv\) Relaxed lattice
- \(\Delta E\) \(\equiv\) \(E_{\text{pure lattice}} - E_{\text{A·A/A}}\)

### TABLE 8

**ANTHRACENE - NEIGHBOUR INTERACTION ENERGIES**

(Energies: kJ mol\(^{-1}\))

<table>
<thead>
<tr>
<th>Neighbour Molecule</th>
<th>Anthracene</th>
<th>Dianthracene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dispersion</td>
<td>Repulsion</td>
</tr>
<tr>
<td>2</td>
<td>-35</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>-38</td>
<td>17</td>
</tr>
<tr>
<td>4</td>
<td>-25</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>-59</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>-17</td>
<td>12</td>
</tr>
<tr>
<td>9</td>
<td>-17</td>
<td>10</td>
</tr>
<tr>
<td>11</td>
<td>-12</td>
<td>6</td>
</tr>
</tbody>
</table>
Grid point search: $A \cdot A$ in $A_2$

where $\bigcirc$ denotes the centre of mass of an anthracene below the LN plane, and

- the centre of mass above the LN plane.

(Molecular planes are parallel and separated by 0.3 nm, with the anthracene $L$ and $M$ axes parallel to the $A_2$ $L$ and $N$ axes respectively, see also Figures 4 and 7).

(L' = anthracene $L$ axes)

(This conformation was not possible because of small atom–atom distances)

(Inversion symmetry was not maintained)

**Figure 8.**
a) Relative Displacement of Anthracenes without Lattice Relaxation (distances in nm)

b) Relative Displacement of Anthracenes with Lattice Relaxation (distances in nm)

Figure 9.
A·A in A2 - Relaxation Calculations

The calculations were then extended to investigate the effect of lattice relaxation. In these calculations inversion symmetry was retained since the results of the grid point search indicated that the anthracenes were so related. The minimization was performed as usual with the cycling procedure being discontinued when the total intermolecular potential energy between cycles differed by less than 0.1 kJ mol\(^{-1}\). The calculations reveal that the dimer system increases its stability by only 9 kJ mol\(^{-1}\), with very small changes to the conformation of the anthracenes found in the rigid lattice (Table 7 and figures 9 and 10). The orientation and centre of mass of an anthracene are given in Table 6. The molecular planes which are now separated by a perpendicular distance of separation of 0.348 nm tend to adopt a conformation in which the projection of the carbon atoms of one molecule on to the plane of the other is such that a projected carbon lies in the middle of a carbon-carbon bond, and not in an asymmetrical position as in the rigid lattice calculation. The mutual interaction energy of the anthracenes decreases marginally and there is little displacement in either translation or orientation of the cage molecules.

Since the calculations indicate that the dimer system is thermodynamically more stable than the pure A\(_2\) host lattice, additional calculations were performed to test the sensitivity of this energy difference to variations in molecular geometry or crystal structure. Upon increasing the aromatic and aliphatic carbon-hydrogen bond lengths to 0.108 nm and 0.109 nm respectively the energy difference for the relaxed lattice increased to 20 kJ mol\(^{-1}\); when the theoretically calculated A\(_2\) crystal structure was used this energy difference only increased to 26 kJ mol\(^{-1}\), (Table 7). The structures were similar for all calculations.
Figure 10. A·A Conformation with respect to the A₂ Molecule
DISCUSSION

The two principal findings of the experimental investigation of A\textsuperscript{1}A in A\textsubscript{2} are that in the ground electronic state the anthracenes adopt a partially eclipsed conformation and that in the excimer state there is an abnormally large thermal barrier which must be surmounted before photodimerization can occur [60]. This barrier is interpreted as the energy required to overcome the repulsions of the neighbouring lattice molecules as the anthracenes move from the partially eclipsed to the perfectly eclipsed conformation [64]. These findings are now correlated with the results of the calculations.

The calculated conformation of the dimer is in agreement with the experimental observations as is evident from the results reported in the previous section, although the possibility that the anthracenes are displaced from planarity cannot be discounted. However the calculated thermodynamic state enthalpy difference cannot be directly compared with the experimentally determined barrier height in the excimer state although it may be concluded from the calculations that a considerable increase in the internal energy of the dimer system must accompany the transformation to the pure A\textsubscript{2} lattice. This change in internal energy may in part contribute to the measured thermal barrier.

Since this thermodynamic state enthalpy difference is perhaps unexpected it has been considered with some caution, particularly after the findings of the previous chapter where it was shown that the energy (enthalpy) differences calculated by the method of atom-atom potentials are very sensitive to changes in molecular geometry or crystal structure. The results listed in Table 7 show that the enthalpy difference is not due to the choice of molecular geometry, crystal structure nor the process of
lattice relaxation.

The calculations illuminated other features of the photocleavage. At the minimum energy A•A conformation in the relaxed lattice it is found that the total potential energy (enthalpy) of the environment is less than the same molecules in the pure $A_2$ lattice by approximately $5-10 \text{kJ mol}^{-1}$, whereas the anthracenes experience an enhanced attraction in the 'cavity' over that of the replaced host molecule. This latter effect is illustrated by considering the attractive and repulsive contributions to the total potential energy of $A_2$ and A•A in the two situations. In the pure lattice the approximate decomposition is $-437 \text{kJ mol}^{-1}$ and $156 \text{kJ mol}^{-1}$, and in the dimer system it is $-542 \text{kJ mol}^{-1}$ and $226 \text{kJ mol}^{-1}$, so while the anthracenes experience a larger repulsive interaction than does the $A_2$ molecule they experience an even larger attractive interaction. Therefore the transformation from the dimer system to the pure $A_2$ lattice is not one of increased repulsion but rather of markedly decreased attraction.

Table 8 lists some interaction energies of the anthracene which lies predominantly to the negative side of the bc plane in figure 4. It is interesting to note that the total interaction energy of the anthracene pair which is $-316 \text{kJ mol}^{-1}$ lies almost midway between the interaction energy of the $A_2$ molecule, $-280 \text{kJ mol}^{-1}$, and that of the two anthracenes in the $P2_1/a$ cell, $-380 \text{kJ mol}^{-1}$.

Returning to the structural aspect, a consideration of Tables 4 and 6, and figures 4, 9 and 10 will lead to the conclusion that in order for the anthracenes to adopt the perfectly eclipsed conformation which is aligned with the $A_2$ molecule that has been replaced, they must not only translate relative to each other in their L and M directions but they must also rotate slightly ($\approx 5^\circ$) about their N axes.
In conclusion, the atom-atom potential method calculates a conformation of the anthracene pair in the A₂ lattice which is in agreement with the experimental findings. The state enthalpy difference between the dimer system and the pure lattice is difficult to predict because of the inherent sensitivity of the method of calculation but it appears to be large and associated with increased attraction in the dimer system rather than a diminution of repulsive interactions.

AEA IN CAEA

The calculations are now extended to the system in which a molecule of 1,2-di-(9-anthryl)ethane replaces a molecule in the lattice of its photodimer CAEA. The calculations corroborate the experimental finding that domains belonging to the space groups P₂₁ and Pₑ may be present. It is also found that each domain may contain isolated disordered molecules which in conjunction with the molecule of the ordered lattices result in the production of three conformations of AEA. Two AEA conformations in each domain may be associated with the experimentally observed fluorescent species and the other to the non-fluorescent species P₁. The fluorescent conformations of each domain, and similarly the non-fluorescent conformations, differ by little and thus are likely to have overlapping absorption and emission spectra which precludes their separation by experiment. The conformations which have been found by calculation appear not to be associated with the experimentally observed P₂ site. Suggestions of the nature of this species are given. Of course it may be possible that some of the calculated conformations either are not present or are present in varying concentrations.

In the Pₑ domain the two fluorescent sites can be associated with a dissociated molecule of the ordered lattice, and the non-fluorescent site
to an isolated disordered molecule. In the \( \text{P}_{2}\_1 \) domain the non-fluorescent species can be associated with a molecule of the ordered lattice and the two fluorescent species with an isolated disordered molecule.

METHOD OF COMPUTATION

The method of calculation reported in Chapters 3 and 4 is further extended to treat this problem in which a selected number of intramolecular variables is included in the minimization. In these calculations the Newton scheme Hesmin is used to minimize the potential energy of the rigid, lattice molecules while the quasi-Newton scheme Funmin is used to minimize the potential energy of AEA. In the following sections the intramolecular potential and the minimization method are expounded.

The Potential Energy

The potential energy of a molecule in a conformation close to equilibrium can be expanded in terms of a set of internal displacement coordinates [16], the empirical ('force') constants which appear in such expansions can be evaluated for a class of molecule by least squares fitting of theoretical expressions for molecular properties dependent on the potential and its derivatives to spectroscopic and thermodynamic data [165]. For molecular conformations far from equilibrium the assumption must be made that these empirical potentials still model the essential features of the Born-Oppenheimer surface; in addition, for functions of a subset of internal variables the assumption must be made that minima of this function correspond closely to the minima on the actual surface.

The expansion chosen for AEA uses a small subset of the total number of possible internal coordinates which appear in the Urey-Bradley force field. The energy contribution by the omitted variables is assumed either to remain
constant for each conformation or to have little effect on the chosen representation of the potential energy surface. The variables selected include the rotations about the three bridging ethane bonds, the angular displacement from the c-c-c tetrahedral angle of the methylene groups and the out-of-plane displacement of the two aromatic ring systems i.e. the displacement corresponding to the so-called 'butterfly' mode. In the following discussion these variables will be designated by the symbols \( \theta_i \), \( \phi_i \) and \( \psi_i \) respectively, where the subscript will be used to distinguish between the variables within a set. The intramolecular potential energy may then be written as

\[
V_{\text{INTRA}} = V_{\text{NB}}(\theta, \phi, \psi) + V_{\text{AG}}(\phi) + V_{\text{AR}}(\psi)
\]  

(5.1)

where \( V_{\text{NB}} \) is the total non-bonded interaction energy, and \( V_{\text{AG}} \) and \( V_{\text{AR}} \) are the potential energies corresponding to distortions of the tetrahedral angle and the out-of-plane displacement of the aromatic rings respectively.

\( V_{\text{NB}} \) is evaluated in the usual manner using the Buckingham (exp-6) potential with Williams' parametrization. The interactions between atoms within an aromatic ring system or methylene group are neglected. Any changes in the potential energy caused by distortions of these groups are assumed to appear in \( V_{\text{AG}} \) and \( V_{\text{AR}} \). These are given by harmonic potentials with force constants of 130 and 500kJ mol\(^{-1}\)rad\(^{-2}\) respectively.

The potential constants are taken from the work of Warshel and Lifson[165] and from the anthracene free-molecule 'butterfly' mode frequency which is usually taken to be 90cm\(^{-1}\) (the calculated moment of inertia of a half anthracene about the M symmetry axis is 5.6amu nm\(^2\)). As will be shown presently the non-bonded interactions so dominate the molecular conformation in the free molecule state and solid state that the choice of force constants basically alters the total energy only and not the optimum molecular
conformation.

**Coordinate Manipulation**

Consider figure 11 in which the molecule of AEA has an arbitrary orientation with respect to the laboratory axes $x$, $y$ and $z$. In the crystal lattice the entire molecule has three orientational and three translational degrees of freedom. However these displacements can no longer be taken with respect to rotations about, and translations of, the centre of mass. In the calculations the rotations and translations of the whole molecule are taken about, and with respect to, the point labelled $P_1$.

In order to place the following developments in perspective the sequence of operations performed in the computation of the total inter- and intra-molecular potential energy and its derivatives is outlined. Firstly, the initial set of coordinates of the molecule of AEA are taken and the intra-molecular manipulations to be described are carried out; secondly, the rotations and translations of the molecule as a whole are then implemented, and finally the total potential energy and potential derivatives are evaluated. This sequence of events is important for the method of minimization.

A rotation about a general axis $\mathbf{P}_{nm}$ with the sense $n$ to $m$ can be performed simply and elegantly using quaternions. This is achieved in the following manner: we translate all atoms so that the atom $\mathbf{P}_n$ is coincident with the origin $0$ of the laboratory frame, determine the vector $\mathbf{P}_{nm}$ and normalize it. In the notation of Chapter 3 this axis may then be labelled $\mathbf{u}_0$. A rotation about it by $\omega$ degrees can be associated with the quaternion

$$ q = (\cos \frac{\omega}{2}, \sin \frac{\omega}{2} \mathbf{u}_0^T)\mathbf{T}, $$

a left handed rotation being produced by the rotation matrix $\mathbf{R}(q)$ ($= \mathbf{A}$ of Eqn. (3.8)). Following each rotation all
Figure II. AEA Intramolecular Variables
the atoms of AEA are translated so that the point \( P_n \) is coincident with its original position, and the sequence is then repeated for the next rotation.

Rotations about the bridging bonds are simple: (see figure 11 for the sense of the rotation axes) we translate \( P_n \) to 0, determine \( q \) and thus \( R(q) \) and then operate on the appropriate set of coordinates. These have been conventionally taken to be those to the right of \( P_m \) in figure 11, with the rotation matrix ordered so that a positive angle \( \omega \) produces a right-handed screw rotation. For angular displacements of the \( sp^3 \) tetrahedral angle the required manipulation is only marginally more difficult. Consider the angle formed by the atoms \( P_2P_1P_3 \). The rotation axis is normal to the plane formed by these three atoms and is chosen to be given by the cross-product \( P_{12} \times P_{13} \). Following normalisation the above procedure is implemented. The rotation matrix is arranged so that a positive angle \( \omega \) produces an increase in the valence angle when the rotation matrix operates on the coordinates to the left of \( P_1 \) in figure 11. This operation does not correspond to the actual angle bending mode since the distances between the protons bound to \( P_1 \) and the carbon atom \( P_3 \) remain invariant, however, for small angular displacements (to which the later work is restricted) it may be anticipated that the errors introduced by this technique will be no larger than those from the omitted internal coordinates. A consideration of figure 11 will lead to the conclusion that this technique of varying the valence angle is the most realistic way of modelling the valence angle bend subject to the condition that the point \( P_1 \) must remain invariant to any intramolecular operation.

The displacements of the aromatic rings from planarity are easily produced by following the procedures outlined above except with the obvious need to displace one half of the ring system by \( +\omega \) and the other half by \(-\omega \).
The convention has been adopted that a positive sign for $\omega$ indicates that the ring has been opened outward from the other aromatic ring.

**Derivatives of the Intramolecular Potential**

The only term in Eqn. (5.1) that presents any difficulty in the calculation of the potential derivatives with respect to the set of variables $\{\theta, \phi, \psi\}$ is the derivative of $V_{NB}$, the remaining terms being trivial. Since the quasi-Newton scheme is used to minimize the potential energy of AEA only the first derivatives are required.

Consider

$$V_{NB}(\omega_1) = \sum_k \sum_{\ell} v_{k\ell}(\omega_1)$$

where

$$v_{k\ell}(\omega_1) = \frac{A}{(R_{k\ell}(\omega_1))^6} + B \exp(-CR_{k\ell}(\omega_1))$$

(5.2)

$\omega_1$ is the $i$-th internal coordinate,

$k$ labels the atoms of which the position is dependent on $\omega_1$,

$\ell$ labels the atoms of which the position is independent of $\omega_1$,

$R_{k\ell}(\omega_1)$ is the distance of separation of atoms $k$ and $\ell$ with the displacement vector $R_{k\ell}$ having the sense $\ell$ to $k$.

The subscripts $k$ and $\ell$ have been omitted from the constants $A$, $B$ and $C$.

As in the earlier work the following substitution is made for convenience:

$$\rho_{k\ell} = \frac{1}{2} \|R_{k\ell}(\omega_1)\|^2$$
Upon taking the derivative of Eqn. (5.2) with respect to $\omega_i$, we obtain

$$
\frac{\partial v_{k\ell}(\omega_i)}{\partial \omega_i} = \left[ \frac{6A}{(R_{k\ell}(\omega_i))^3} - \frac{BC}{R_{k\ell}(\omega_i)} \exp(-CR_{k\ell}(\omega_i)) \right] 
$$

$$
\cdot \frac{\partial R_{k\ell}(\omega_i)}{\partial \omega_i} 
$$

$$
= v_{k\ell}^T R_{k\ell}(\omega_i) \cdot \frac{\partial R_{k\ell}(\omega_i)}{\partial \omega_i} 
$$

where vectors are by convention taken to be written in columns.

Now

$$
R_{k\ell}(\omega_i) = r_k(\omega_i) - r_{\ell} 
$$

where $r_k$ is the atomic position vector of atom $k$ (and similarly for $r_{\ell}$) in the laboratory coordinate frame. Therefore we may write

$$
F_k(\omega_i) = F_{p1} + A(q') \cdot F_{p1k}(\omega_i) 
$$

with $A(q')$ the 'rigid' body rotation matrix for the rotation about the atom $p_1$. This is represented by the quaternion $q'$. At this point we remember that the intra- and intermolecular operations have been performed; thus for the calculation of the derivatives we consider the set of transformed coordinates as a new initial set with the values of the internal and external displacement variables set to zero. Therefore

$$
\frac{\partial R_{k\ell}(\omega_i)}{\partial \omega_i} = \frac{\partial r_{p1k}(\omega_i)}{\partial \omega_i} \quad \text{(since } A(q') = I) 
$$

$$
= \left. \frac{\partial R(\omega_i)}{\partial \omega_i} \right|_{\omega_i=0} \cdot r_{p1k} 
$$

(5.3)

where $r_{p1k}$ is the vector joining atoms $p_1$ and $k$ and the matrix has
been written as a function of the rotation angle rather than the associated quaternion. From Eqns. (3.11) the derivative appearing in Eqn. (5.3) is found to be given by

\[
\begin{align*}
\frac{\partial R(\omega_i)}{\partial \omega_i} & \bigg|_{\omega_i = 0} = \begin{pmatrix}
0 & \zeta_0 & -\eta_0 \\
-\zeta_0 & 0 & \xi_0 \\
\eta_0 & -\xi_0 & 0
\end{pmatrix}
\end{align*}
\]

Since \( \frac{\partial R_k^l(\omega_i)}{\partial \omega_i} \) is in fact independent of the subscript \( k \), then for each atom \( k \) the sum \( \sum_k v_k^l R_k^l(\omega_i) \) must be evaluated and the inner product with expression in Eqn. (5.3) taken at the completion of the summation. The total derivative with respect to \( \omega_i \) is then given by summing over \( k \).

For the bending of the aromatic rings \( \frac{\partial R(-\omega_i)}{\partial \omega_i} \bigg|_{\omega_i = 0} \) is simply given by \(-R'\). The calculation of the derivatives is then straightforward but care must be taken to include only those interactions \( v_k^l(\omega_i) \) which contribute to the derivative.

Free Molecule Calculations on the Conformation of AEA

Calculations have been performed on AEA as a free molecule to test the reliability of the program. The results are listed in Table 9. In part (i) of the Table the molecule of AEA is held in the eclipsed conformation and calculations are performed in which only the \( sp^3 \) angle-bending (\( \phi \)) and ring-bending (\( \psi \)) variables have been considered. Sections (a) and (b) illustrate the expected behaviour upon variation of the force constants in \( V_{AG} \) and \( V_{AR} \). Section (c) yields a structure anticipated from the results of sections (a) and (b) when the minimization is carried out simultaneously in the variables \( \phi \) and \( \psi \).

By allowing for a variation in the angles of rotation about the
been written as a function of the rotation angle rather than the associated quaternion. From Eqns. (3.11) the derivative appearing in Eqn. (5.3) is found to be given by

\[ R' = \frac{\partial R(\omega_i)}{\partial \omega_i} \bigg|_{\omega_i=0} = \begin{bmatrix} 0 & \zeta_0 & -\eta_0 \\ -\zeta_0 & 0 & \xi_0 \\ \eta_0 & -\xi_0 & 0 \end{bmatrix} \]

Since \( \frac{\partial R_{kl}(\omega_i)}{\partial \omega_i} \) is in fact independent of the subscript \( k \), then for each atom \( k \) the sum \( \sum_k v_k R_{kl}(\omega_i) \) must be evaluated and the inner product with expression in Eqn. (5.3) taken at the completion of the summation. The total derivative with respect to \( \omega_i \) is then given by summing over \( k \).

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By allowing for a variation in the angles of rotation about the
TABLE 9

FREE MOLECULE CALCULATIONS
(Units: Energy(E): kJ mol\(^{-1}\); Force constant(k): kJ mol\(^{-1}\) rad\(^{-2}\); angles: degrees)

i) Eclipsed conformation.
   a) sp\(^3\) angle bending variables
      \[
      \begin{array}{ccc}
      \hline
      k & E & \phi \\
      0 & 39.8 & +11.8 \\
      65 & 42.4 & +10.8 \\
      130 & 44.5 & +10.0 \\
      260 & 48.2 & +9.1 \\
      \hline
      \end{array}
      \]
   b) ring bending variables
      \[
      \begin{array}{ccc}
      k & E & \psi \\
      0 & 51.8 & 6.7 \\
      250 & 54.9 & 6.0 \\
      500 & 57.4 & 5.5 \\
      1000 & 61.5 & 4.9 \\
      \hline
      \end{array}
      \]
   c) sp\(^3\) angle bending and ring bending variables
      \[
      \begin{array}{ccc}
      k & E & \phi, \psi \\
      130/500 & 41.6 & +7.2, +2.3 \\
      \hline
      \end{array}
      \]

ii) Rotations about the bridging ethane bonds.
    \[
    \begin{array}{cccc}
    E & \theta_1 & \theta_2 & \theta_3 \\
    23.6 & -6.6 & 77.1 & -6.6 \\
    \end{array}
    \]

iii) Full minimization.
    a) Energy = 18.8 (k:130/500)
        Bond rotations: \( \theta_1 = -3.9 \), \( \theta_2 = 70.0 \), \( \theta_3 = -3.9 \)
        Angle bending: \( \phi_1 = +5.8 \), \( \phi_2 = +5.8 \)
        Ring bending: \( \psi_1 = -4.0 \), \( \psi_2 = -4.0 \)
    b) Energy = 20.3 (k:130/1000)
        Bond rotations: \( \theta_1 = -3.9 \), \( \theta_2 = 69.1 \), \( \theta_3 = -3.9 \)
        Angle bending: \( \phi_1 = +4.5 \), \( \phi_2 = +4.5 \)
        Ring bending: \( \psi_1 = -2.3 \), \( \psi_2 = -2.3 \)
bridging bonds a substantial reduction in the potential energy can be achieved, see part (ii) of Table 9. A further reduction, although much smaller, is realized by minimizing in the 7 variables, as shown in part (iii); however this leads to an 'inward' bending of the anthracene moieties by 4°. Increasing the ring-bending force constant to 1000 kJ mol⁻¹ rad⁻² reduces this inward bending by approximately 2° with the expected decrease in the φ. Figure 12 illustrates the free-molecule equilibrium conformation of AEA. The atomic position coordinates used are discussed below.

In these (and all following) calculations potential curves for each variable support the conclusion that the calculated conformation is a minimum. As well, at the minimum, all variables are given a small asymmetrical displacement and the calculation is then repeated to test for convergence to a saddle point. It should be noted that in the free-molecule calculations the quasi-Newton scheme converges very easily to a saddle point.

MOLECULAR GEOMETRY OF AEA AND CAEA

The carbon-carbon bond lengths of the ethane bridge in the idealized structure of AEA were taken to be 0.154nm [130]. The length of the bonds to the anthracenes and the central bridging bond are probably closer to 0.152nm and 0.158nm respectively [157,161], however, these small differences are unlikely to alter significantly the results reported in this section. The methylene protons were placed at the vertices of a regular tetrahedron.

The reported molecular geometry of CAEA as determined by X-ray diffraction has one unusual feature. This is the length of the bond from the bridging carbons to the anthracene moieties. It is 0.1442nm. Normally such a carbon-carbon single bond would be expected to be approximately
Figure 12. AEA Free molecule Minimum-energy Conformation
0.15nm in length as was found for the related molecule bi(anthracene-9,10-dimethylene) photoisomer [49]. The short bond length could in part be due to the constraints imposed in the crystallographic refinement.

DETAILS OF THE CALCULATIONS

Since the crystallographic analysis strongly indicated that the CAEA lattice had a pseudo-inversion centre, and that domains of space group $P_c$ and $P2_1$ could be present, calculations on both space groups were performed. The results of the calculations on the $P_c$ lattice are given first, and in detail, while the results of the analogous calculations on the $P2_1$ lattice are reported only briefly since they are very similar. All calculations have been performed for the molecule of AEA placed at the origin of the laboratory coordinate frame in figure 6 (to which repeated reference is necessary).

$P_c$ SPACE GROUP CALCULATIONS

Pure Crystal Calculations

A calculation starting at the experimentally determined structure of CAEA [2] (i.e. using the $P2_1$ data with the appropriate change of symmetry) was performed to find the minimum-energy $P_c$ cell. Small displacements only were found for the monoclinic angle ($<0.1^\circ$), components of the centre of mass position vector ($<0.01\text{nm}$), orientation variables ($<3^\circ$) and the unit cell dimensions: $\Delta a = -0.03\text{nm}$, $\Delta b = -0.02\text{nm}$, and $\Delta c = -0.01\text{nm}$. The displacement $\Delta a$ is less than that found for naphthalene (Chapter 4). Phonon frequencies calculated at the energy-minimized structure indicate that it is stable. These results are in agreement with the observations of Anderson et al [2] who report no abnormal behaviour of the CAEA crystal over the temperature range 10-300 K. Finally, the heat of sublimation is calculated to be 159 kJ mol$^{-1}$ which is a lowering in the interaction energy.
of a molecule by approximately 16 kJ mol\(^{-1}\) from that which is calculated at the experimentally determined structure. This energy decrease is twice that found in the analogous calculation on dianthracene which is observed to be similar to the energy changes in other studied systems.

**Pure Crystal Relaxation Calculation**

The investigation of the experimentally determined pure crystal structure of \(\text{PcCAEA}\) (i.e. approximated with the \(\text{P2}_1\) data) were then extended by enlarging the environment of molecules in the usual manner so as to include the lattice sites listed in Table 10. The total potential energy \(V\) was then minimized with respect to the orientation and translation variables of the central molecule and its specified neighbours. The cycling procedure was terminated in this and all succeeding calculations when \(V\) differed by less than 0.5 kJ mol\(^{-1}\) between cycles.

The minimization lowered \(V\) by 67 kJ mol\(^{-1}\) which is much larger than in similar calculations on naphthalene: \(\Delta V = 7\) kJ mol\(^{-1}\); anthracene: \(\Delta V = 13\) kJ mol\(^{-1}\), and dianthracene: \(\Delta V = 16\) kJ mol\(^{-1}\). This result suggests that the packing is "loose" i.e. the molecules do not occupy the full volume which is expected from the X-ray analysis. This conclusion is supported by the finding that the change in molecular orientation is as large as \(3^\circ\) in the direction cosines of the principal axes (Table 11) which is larger than any change observed in all the other pure crystal systems studied in the course of this work. If one considers that a guest molecule larger than a replaced host molecule displaces certain of its neighbours by \(7^\circ\) in the direction cosines of their principal axes then perhaps the displacements found for CAEA are significant.
TABLE 10
ENERGY MINIMIZED SITES IN THE STUDY OF AEA IN CAEA

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Lattice Site</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-1.0</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td>0.0</td>
<td>-1.0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.0</td>
<td>1.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.0</td>
<td>-1.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.0</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>8</td>
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<td>-0.5</td>
<td>-0.5</td>
<td></td>
</tr>
<tr>
<td>9</td>
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<td>0.5</td>
<td>-0.5</td>
<td></td>
</tr>
<tr>
<td>10</td>
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<td>0.5</td>
<td></td>
</tr>
<tr>
<td>11</td>
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<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>-1.0</td>
<td>-0.5</td>
<td>-0.5</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1.0</td>
<td>-0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>-1.0</td>
<td>0.5</td>
<td>-0.5</td>
<td></td>
</tr>
<tr>
<td>15</td>
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<td>0.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>-1.0</td>
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<td>-1.0</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>-1.0</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>1.0</td>
<td>-0.5</td>
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<tr>
<td>19</td>
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<td>-0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1.0</td>
<td>0.5</td>
<td>-0.5</td>
<td></td>
</tr>
</tbody>
</table>
### Table 11

(a) **PRINCIPAL AXES OF CAEA BEFORE MINIMIZATION**

(direction cosines)

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-0.970</td>
<td>0.151</td>
<td>-0.193</td>
</tr>
<tr>
<td>M</td>
<td>-0.243</td>
<td>-0.677</td>
<td>0.694</td>
</tr>
<tr>
<td>N</td>
<td>-0.026</td>
<td>0.720</td>
<td>0.693</td>
</tr>
</tbody>
</table>

(b) **PRINCIPAL AXES OF CAEA AFTER MINIMIZATION**

(direction cosines)

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L'</td>
<td>-0.965(1°)</td>
<td>0.205(3°)</td>
<td>-0.162(2°)</td>
</tr>
<tr>
<td>M'</td>
<td>-0.260(1°)</td>
<td>-0.700(2°)</td>
<td>0.666(2°)</td>
</tr>
<tr>
<td>N'</td>
<td>0.023(3°)</td>
<td>0.685(3°)</td>
<td>0.729(3°)</td>
</tr>
</tbody>
</table>

1 See figure 1.

2 Values in brackets give the magnitude of the angular variation between (a) and (b).

(c) **COMPONENTS OF NEW AXES IN INITIAL FRAME**

<table>
<thead>
<tr>
<th></th>
<th>L'</th>
<th>M'</th>
<th>N'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.998</td>
<td>0.018</td>
<td>-0.060</td>
</tr>
<tr>
<td>M</td>
<td>-0.017</td>
<td>0.998</td>
<td>0.037</td>
</tr>
<tr>
<td>N</td>
<td>0.060</td>
<td>-0.036</td>
<td>0.998</td>
</tr>
</tbody>
</table>
When it is recalled that there is no observation of anomalous thermal motion, or disorder at the unit cell level, and that the screw-diad of the reported structure may not be exact, and also that a c glide fits the scattering data almost as well as the screw-diad, it can be concluded that the calculations reflect the slight errors in the assumed crystallographic model. The anomalously large energy reductions found in these calculations indicate that the energetic results of the following sections should be treated cautiously.

AEA in a Ordered $P_c$ CAEA Lattice

Despite the findings of the last section the reported crystal structure of CAEA was used to study the conformations adopted by AEA. In the calculations the central molecule in the specified environment was removed from the lattice and replaced by a molecule of AEA in an eclipsed conformation, and with the ethane bridge located in the same position as that of the host molecule. The molecule of AEA was put into the lattice in the principal inertial frame of the replaced host molecule as if it was occupying the site. The substitution is made in such a way as to ensure that similar axes i.e. the $L$, $M$ and $N$ axes of both molecules are parallel and close to coincidence. The purpose of the following calculations is to find the possible conformations of the molecule of AEA and describe their internal geometry and relationship to the host molecule from which they originate, and then examine the consequences of these findings for the reported crystal structure. The precise location of the molecule of AEA will not be given although it is available.

Grid Point Search

As in the study of $A\cdot A$ in $A_2$ the 'cavity' was searched for starting
conformations before commencing the longer calculations. The simplest way to undertake the grid search is to displace one anthracene moiety relative to the other by a rotation about the central bridging carbon-carbon bond, first in one sense and then in the other. The two grid points obtained in this manner are expected to lead to different local minima since it is known from the AEA free molecule calculations that the intramolecular potential will tend to produce such displacements. From these grid points two distinct sites of minimum energy could indeed be found. These can be labelled in terms of the sense of rotation about the central bridging bond: site A is obtained by a positive rotation (see the section dealing with the definition of the intramolecular variables) and site B by a negative rotation. A more detailed description will be given presently.

Search for the Experimentally Determined AEA Conformations

Attempts were made to locate a minimum corresponding to that suggested by Anderson et al [2] in which the anthracene moieties are displaced relative to each other in the long axis direction. This site is different from those labelled A and B. This search was difficult because the entire molecule of AEA needs to be appropriately oriented and positioned (a grid point search in 10 dimensions is required). All attempts to find this minimum failed because either the atom-atom contacts were too close or else the minimization simply converged to one of the above-mentioned sites. An exhaustive search could not be made because the potential energy and its derivatives are very time consuming to evaluate ($\approx$10-15 sec) and up to 100 minimization steps were in some instances required to locate a minimum. (it is hoped that in future this process may be made more efficient by re-initializing the approximating Hessian $S^{-1}$ to a multiple of the identity matrix after a selected number of steps - this would then give essentially
steepest descent - and thus overcome the problem of the build up of round-off errors in $g^{-1}$. It is concluded that at this level of calculation only the sites A and B exist in the ordered lattice of $P_c$ CAEA.

**Details of the Calculations on Sites A and B**

Calculations at three levels of complexity were performed on each of the sites. In the first calculation the host lattice was held rigid and the minimum energy conformation of AEA was found with respect to the displacements in the seven external variables and the rotations about the bridging ethane bonds. In the second calculation the lattice was again held rigid and the minimization performed with respect to all internal and external variables of AEA starting at the minimum energy conformation determined in the first calculation. The third calculation was a repetition of the second except that the 20 nearest neighbour molecules were permitted freedom to relax about the molecule of AEA. In this calculation the starting position was the conformation determined in the second. The characteristics for the sites A and B are listed in Tables 12 and 13 respectively, with the molecular conformations found from the third calculation being illustrated in figure 13.

There are several points which should be noted about the technique of minimization and the nature of the conformations:

i) the calculations of the first type produce two conformations of AEA widely separated in terms of the angle of rotation about the central bridging bond i.e. $\theta_2$. The inclusion of the extra internal degrees of freedom in the calculations of the second and third type result in a much smaller separation.
ii) lattice relaxation has only a small effect on the internal conformation of AEA but has a large effect on the total potential energy.

iii) the anthracene moieties are asymmetrically displaced from planarity, as shown by the values of the variables $\psi_1$ and $\psi_2$ in Tables 12 and 13.

iv) the lattice acts to constrain the molecule of AEA in a near eclipsed conformation in which the $sp^3$ bridging angle is also constrained to be close to the tetrahedral value or is slightly compressed.

v) the two sites are calculated to be equi-energetic in the lattice relaxation calculation, however, in the second calculation site B is found to be more stable than site A by approximately 10 kJ mol$^{-1}$.

vi) there are only small displacements in translation and orientation of the nearest neighbours.

vii) the orientational displacements of the whole molecule are small and the translational displacements are less than 0.02nm.

A further calculation was performed on site A in which the ring-bending force constant was increased by 50% in order to examine the importance of this term in the determination of the molecular conformation. Little change was found. The results again indicated that the conformation is predominantly determined by the non-bonded interactions.
### TABLE 12
**SITE A - P<sub>c</sub> LATTICE**

#### INTRAMOLECULAR CONFORMATION

(Units: degrees)

<table>
<thead>
<tr>
<th>Calculation</th>
<th>θ₁</th>
<th>θ₂</th>
<th>θ₃</th>
<th>φ₁</th>
<th>φ₂</th>
<th>ψ₁</th>
<th>ψ₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid Lattice (1)</td>
<td>-4</td>
<td>27</td>
<td>-3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rigid Lattice (2)</td>
<td>0</td>
<td>6</td>
<td>3</td>
<td>-3</td>
<td>-3</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>Relaxed Lattice (3)</td>
<td>1</td>
<td>4</td>
<td>3</td>
<td>-1</td>
<td>0</td>
<td>9</td>
<td>5</td>
</tr>
</tbody>
</table>

#### ENERGIES

(Units: kJ mol⁻¹)

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Intramolecular</th>
<th>Intermolecular</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Harmonic</td>
<td>Dispersion</td>
</tr>
<tr>
<td>Rigid Lattice (1)</td>
<td>-</td>
<td>-171</td>
</tr>
<tr>
<td>Rigid Lattice (2)</td>
<td>11</td>
<td>-146</td>
</tr>
<tr>
<td>Relaxed Lattice (3)</td>
<td>8</td>
<td>-137</td>
</tr>
<tr>
<td>Pure CAEA</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Total potential energy = -4602 kJ mol⁻¹.

#### CENTRE OF MASS DISPLACEMENTS OF NEAREST NEIGHBOURS

(Units: nm)

<table>
<thead>
<tr>
<th>Neighbour Molecule</th>
<th>a</th>
<th>b</th>
<th>c'</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>2</td>
<td>-.01</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>0.01</td>
<td>0.0</td>
<td>0.01</td>
</tr>
<tr>
<td>8</td>
<td>0.0</td>
<td>-.02</td>
<td>0.0</td>
</tr>
<tr>
<td>10</td>
<td>-.01</td>
<td>-.02</td>
<td>0.0</td>
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</tbody>
</table>

#### LARGEST ANGULAR DISPLACEMENT - NEIGHBOUR MOLECULE 9

**EXPERIMENTALLY DETERMINED ORIENTATION (direction cosines)**

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.970</td>
<td>0.151</td>
</tr>
<tr>
<td>M</td>
<td>-0.243</td>
<td>0.677</td>
</tr>
<tr>
<td>N</td>
<td>-0.026</td>
<td>-0.720</td>
</tr>
</tbody>
</table>

**ORIENTATION IN RELAXED LATTICE (direction cosines)**

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.971</td>
<td>0.155</td>
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<tr>
<td>M</td>
<td>-0.237</td>
<td>0.734</td>
</tr>
<tr>
<td>N</td>
<td>-0.036</td>
<td>-0.662</td>
</tr>
</tbody>
</table>
TABLE 13
SITE B - P\(_c\) LATTICE

<table>
<thead>
<tr>
<th>Calculation</th>
<th>(\theta_1)</th>
<th>(\theta_2)</th>
<th>(\theta_3)</th>
<th>(\phi_1)</th>
<th>(\phi_2)</th>
<th>(\psi_1)</th>
<th>(\psi_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid Lattice (1)</td>
<td>9</td>
<td>-30</td>
<td>12</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rigid Lattice (2)</td>
<td>5</td>
<td>-12</td>
<td>9</td>
<td>-2</td>
<td>-2</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>Relaxed Lattice (3)</td>
<td>4</td>
<td>-12</td>
<td>8</td>
<td>-1</td>
<td>-1</td>
<td>8</td>
<td>7</td>
</tr>
</tbody>
</table>

**ENERGIES**
(Unit: kJ mol\(^{-1}\))

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Intramolecular</th>
<th>Intermolecular</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Harmonic</td>
<td>Dispersion</td>
</tr>
<tr>
<td>Rigid Lattice (1)</td>
<td>-</td>
<td>-167</td>
</tr>
<tr>
<td>Rigid Lattice (2)</td>
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<td>-140</td>
</tr>
<tr>
<td>Relaxed Lattice (3)</td>
<td>9</td>
<td>-133</td>
</tr>
<tr>
<td>Pure CAEA</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Total potential energy = -4603 kJ mol\(^{-1}\).

**CENTRE OF MASS DISPLACEMENTS OF NEAREST NEIGHBOURS**
(Unit: nm)

<table>
<thead>
<tr>
<th>Neighbour Molecule</th>
<th>a</th>
<th>b</th>
<th>c'</th>
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<tbody>
<tr>
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<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>-.01</td>
<td>0.01</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
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<td>0.01</td>
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<td>8</td>
<td>0.01</td>
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<tr>
<td>10</td>
<td>-.01</td>
<td>-.01</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**LARGEST ANGULAR DISPLACEMENT - NEIGHBOUR MOLECULE 16**

<table>
<thead>
<tr>
<th>EXPERIMENTALLY DETERMINED ORIENTATION (direction cosines)</th>
<th>ORIENTATION IN RELAXED LATTICE (direction cosines)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>L</td>
<td>0.970</td>
</tr>
<tr>
<td>M</td>
<td>0.243</td>
</tr>
<tr>
<td>N</td>
<td>-.026</td>
</tr>
</tbody>
</table>
Figure 13. AEA in Ordered $P_c$ CAEA Site A

AEA in Ordered $P_c$ CAEA Site B

Figure 13. AEA in Disordered $P_c$ CAEA
Sites A and B - Conclusions

The conclusion can be drawn that the molecules of the pure, perfect bulk lattice of $P_c$ CAEA permit only two conformations of AEA. These are equi-energetic and are displaced from the eclipsed conformation by rotations in opposite senses about the central bridging bond. We note the disturbing feature that lattice relaxation causes site A to adopt a nearly eclipsed conformation. This will be considered later. The sites are thus correlated with the two fluorescent conformations observed by Anderson et al [2].

Disordered $P_c$ CAEA

Since the pure ordered lattice of CAEA allows only two conformations of AEA, a molecule of CAEA was inverted at a lattice site and calculations performed to test the stability of this packing arrangement and that of the concomitant AEA conformations.

The atomic position coordinates of the molecule of CAEA were obtained in their principal inertial frame, inverted, and put back into the lattice with respect to the original principal frame. The total potential energy of the lattice was then minimized with respect to the position and orientation variables of this molecule and the specified twenty nearest neighbours in the usual manner. The total intermolecular potential energy of the disordered lattice was found to be only 1 kJ mol$^{-1}$ less stable than the ordered lattice. This energy difference is probably an underestimate and would be expected to increase if the calculation were to be repeated using a low temperature structure for CAEA. Since the X-ray analysis indicates that the lattice is not disordered at the unit cell level it appears then from energetic considerations that the lattice may contain
isolated disordered molecules. The orientation of the disordered molecule is little changed from that at the ordered site.

**AEA in a Disordered P_c CAEA Lattice**

AEA was then placed into the CAEA lattice in an analogous manner to that described in the preceding section except in this instance it was reflected in the CAEA LM plane. The 'cavity' was then searched as before for local minima. The minimization converged from the two grid points to the same conformation in which the anthracene moieties are essentially eclipsed. The results of the calculations are given in Table 14 and the molecular conformation found in the full relaxation calculation is illustrated in figure 13. This conformation retains the same orientation as the host molecule from which it was obtained and as might be expected it is energetically much less stable than the sites found in the ordered lattice ($\Delta V \approx 30$ kJ mol$^{-1}$). This site appears to be associated with the experimentally observed P$_1$ site [2].

**P2$_1$ SPACE GROUP CALCULATIONS**

**Pure Crystal Calculations**

A calculation starting at the experimentally determined structure of CAEA [2] was performed to find the minimum-energy P$_2_1$ cell. Small displacements only were found for the monoclinic angle (<0.1°), components of the centre of mass position vector (<0.01nm), orientation variables (<2.5°) and the unit cell dimensions: $\Delta a = -.02$nm, $\Delta b = -.01$nm, and $\Delta c = -.01$nm. Again such displacements are normal for this type of calculation. Phonon frequencies calculated at several values of the wave vector indicate that the calculated structure is stable. Finally, the heat of sublimation is calculated to be 157 kJ mol$^{-1}$ which is almost the same
TABLE 14

AEA IN THE DISORDERED P$_{c}$ LATTICE

INTRAMOLECULAR CONFORMATION
(Units: degrees)

<table>
<thead>
<tr>
<th>Calculation</th>
<th>$\theta_1$</th>
<th>$\theta_2$</th>
<th>$\theta_3$</th>
<th>$\phi_1$</th>
<th>$\phi_2$</th>
<th>$\psi_1$</th>
<th>$\psi_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid Lattice (2)</td>
<td>-2</td>
<td>0</td>
<td>-2</td>
<td>-7</td>
<td>-2</td>
<td>13</td>
<td>6</td>
</tr>
<tr>
<td>Relaxed Lattice (3)</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>-4</td>
<td>-1</td>
<td>10</td>
<td>6</td>
</tr>
</tbody>
</table>

ENERGIES
(Units: kJ mol$^{-1}$)

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Intramolecular</th>
<th>Intermolecular</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Harmonic</td>
<td>Dispersion</td>
</tr>
<tr>
<td>Rigid Lattice (2)</td>
<td>16</td>
<td>-154</td>
</tr>
<tr>
<td>Relaxed Lattice (3)</td>
<td>11</td>
<td>-141</td>
</tr>
<tr>
<td>Disordered CAEA</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Total potential energy = -4572 kJ mol$^{-1}$.

CENTRE OF MASS DISPLACEMENTS OF NEAREST NEIGHBOURS
(Units: nm)

<table>
<thead>
<tr>
<th>Neighbour Molecule</th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
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<tr>
<td>3</td>
<td>0.01</td>
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</tr>
<tr>
<td>9</td>
<td>0.01</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>10</td>
<td>-0.02</td>
<td>-0.03</td>
<td>0.01</td>
</tr>
</tbody>
</table>
as that calculated for the $P_c$ structure. There is an unusually large 16 kJ mol$^{-1}$ decrease in the molecular interaction energy from that which is calculated at the experimentally determined structure.

**Pure Crystal Relaxation Calculation**

The lattice relaxation technique when applied to the pure crystal produces a large lowering of the total potential energy: $\Delta V = 82$ kJ mol$^{-1}$. This is interpreted as indicating that the packing in the reported $P2_1$ structure is 'loose' and reflects the small errors in the assumed crystallographic model. We note that $\Delta V$ for the $P2_1$ calculations is larger than that found in the $P_c$ calculation. This result is a little surprising, however, because of the difficulties experienced with the crystallographic structure determination there perhaps is no a priori reason for expecting the converse result.

**AEA in a Ordered $P2_1$ CAEA Lattice**

AEA was put into the ordered $P2_1$ lattice and the 'cavity' searched in an analogous manner to that described for the $P_c$ lattice. It was found that only one conformation of AEA could be accommodated by the lattice. It should be noted that by holding the anthracenes planar two minima are found. These can be described in terms of the angle of rotation about the central bridging bond. One has a rotation of $+31^\circ$ and the other a rotation of $-12^\circ$. The first conformation has a rather small stabilization energy of $-31$ kJ mol$^{-1}$ while the second conformation rests in a positive potential well with total potential energy of 60 kJ mol$^{-1}$. Both of these conformations give the same site upon including the remaining internal variables in the minimization. The results obtained for this site are listed in Table 15 and the conformation from the full relaxation
The comparison between this site and the disordered \( P_c \) AEA site is somewhat obscured by the particular manner in which the calculations were performed. However, the application of the \( c \) glide to the disordered \( P_c \) molecule at the origin of the coordinate axes in figure 6, i.e. the molecule labelled 1, will clarify the situation. A consideration of figures 6 and 11, and Tables 14, 15 and 16 will reveal that the anthracene moiety adjacent to the neighbouring ethane bridge is displaced most from planarity, and is accompanied by a compression of the related \( sp^3 \) valence angle i.e. \( \psi_2 \) and \( \phi_2 \) for the ordered \( P_{21} \) lattice molecule. The molecular conformation and orientation are essentially the same at both sites, and thus must be almost indistinguishable experimentally. Although the total potential energy of AEA at both sites is practically the same, the sum over the twenty nearest neighbours favours the disordered \( P_c \) site (Tables 14 and 15), however this energy difference is probably not accurate for the reasons given earlier.

AEA in a Disordered \( P_{21} \) CAEA Latice

The presence of disorder in the \( P_{21} \) lattice is treated in an analogous manner to the disordered \( P_c \) lattice. As might have been anticipated there are two conformations of AEA which are almost indistinguishable from the two 'fluorescent' sites in the ordered \( P_c \) lattice. The results for both sites are listed in Tables 16 and 17, and their conformations obtained from the lattice relaxation calculations are given in figure 14. The conformation labelled \( A' \) is similar to conformation \( A \) reported earlier (in the relaxation calculation site \( A' \) adopts a near eclipsed conformation as reported for site \( A \)), and similarly for \( B' \) and \( B \), Table 19 lists the direction cosines of the principal axes of AEA in each
### TABLE 15

**AEA IN THE ORDERED P2₁ LATTICE**

#### INTRAMOLECULAR CONFORMATION

(Units: degrees)

<table>
<thead>
<tr>
<th>Calculation</th>
<th>θ₁</th>
<th>θ₂</th>
<th>θ₃</th>
<th>φ₁</th>
<th>φ₂</th>
<th>ψ₁</th>
<th>ψ₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid Lattice (2)</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>-3</td>
<td>-6</td>
<td>6</td>
<td>13</td>
</tr>
<tr>
<td>Relaxed Lattice (3)</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-3</td>
<td>6</td>
<td>10</td>
</tr>
</tbody>
</table>

#### ENERGIES

(Units: kJ mol⁻¹)

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Intramolecular</th>
<th>Intermolecular</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Harmonic</td>
<td>Dispersion</td>
</tr>
<tr>
<td>Rigid Lattice (2)</td>
<td>16</td>
<td>-156</td>
</tr>
<tr>
<td>Relaxed Lattice (3)</td>
<td>11</td>
<td>-141</td>
</tr>
<tr>
<td>Pure CAEA</td>
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<td>-</td>
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</tbody>
</table>

Total potential energy = -4555 kJ mol⁻¹.

#### CENTRE OF MASS DISPLACEMENTS OF NEAREST NEIGHBOURS

(Units: nm)

<table>
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<tr>
<th>Neighbour Molecule</th>
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<th>c'</th>
</tr>
</thead>
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<td>0.0</td>
<td>0.01</td>
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<tr>
<td>2</td>
<td>-0.01</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.02</td>
</tr>
<tr>
<td>4</td>
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</tr>
<tr>
<td>17</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.01</td>
</tr>
<tr>
<td>18</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.01</td>
</tr>
</tbody>
</table>
TABLE 16

PRINCIPAL AXES OF AEA IN THE DISORDERED P_0 LATTICE
(direction cosines)

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-.979</td>
<td>-.164</td>
<td>0.118</td>
</tr>
<tr>
<td>M</td>
<td>0.201</td>
<td>0.714</td>
<td>-.671</td>
</tr>
<tr>
<td>N</td>
<td>0.026</td>
<td>0.681</td>
<td>0.732</td>
</tr>
</tbody>
</table>

PRINCIPAL AXES OF AEA IN THE ORDERED P_2_1 LATTICE
(direction cosines)

<table>
<thead>
<tr>
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<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.977</td>
<td>-.171</td>
<td>0.125</td>
</tr>
<tr>
<td>M</td>
<td>0.209</td>
<td>0.701</td>
<td>-.681</td>
</tr>
<tr>
<td>N</td>
<td>0.029</td>
<td>0.692</td>
<td>0.721</td>
</tr>
</tbody>
</table>
TABLE 17

SITE A' IN THE DISORDERED P2₁ LATTICE

INTRAMOLECULAR CONFORMATION

(Units: degrees)

<table>
<thead>
<tr>
<th>Calculation</th>
<th>θ₁</th>
<th>θ₂</th>
<th>θ₃</th>
<th>φ₁</th>
<th>φ₂</th>
<th>Ψ₁</th>
<th>Ψ₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid Lattice (2)</td>
<td>-3</td>
<td>-6</td>
<td>0</td>
<td>-3</td>
<td>-2</td>
<td>5</td>
<td>11</td>
</tr>
<tr>
<td>Relaxed Lattice (3)</td>
<td>-3</td>
<td>-2</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>6</td>
<td>9</td>
</tr>
</tbody>
</table>

ENERGIES

(Units: kJ mol⁻¹)

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Intramolecular</th>
<th>Intermolecular</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Harmonic</td>
<td>Dispersion</td>
</tr>
<tr>
<td>Rigid Lattice (2)</td>
<td>12</td>
<td>-146</td>
</tr>
<tr>
<td>Relaxed Lattice (3)</td>
<td>9</td>
<td>-137</td>
</tr>
<tr>
<td>Pure CAEA</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Total potential energy = -4574 kJ mol⁻¹.

CENTRE OF MASS DISPLACEMENT OF NEAREST NEIGHBOURS

(Units: nm)

<table>
<thead>
<tr>
<th>Neighbour Molecule</th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.02</td>
<td>0.0</td>
<td>0.01</td>
</tr>
<tr>
<td>3</td>
<td>-0.02</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>0.01</td>
<td>0.01</td>
<td>-0.01</td>
</tr>
<tr>
<td>10</td>
<td>-0.01</td>
<td>-0.02</td>
<td>-0.01</td>
</tr>
<tr>
<td>13</td>
<td>-0.01</td>
<td>0.0</td>
<td>-0.02</td>
</tr>
<tr>
<td>16</td>
<td>0.01</td>
<td>0.0</td>
<td>0.01</td>
</tr>
</tbody>
</table>
### TABLE 18

SITE B' IN THE DISORDERED P2₁ LATTICE

#### INTRAMOLECULAR CONFORMATION

(Units: degrees)

<table>
<thead>
<tr>
<th>Calculation</th>
<th>θ₁</th>
<th>θ₂</th>
<th>θ₃</th>
<th>φ₁</th>
<th>φ₂</th>
<th>Ψ₁</th>
<th>Ψ₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid Lattice (2)</td>
<td>-9</td>
<td>11</td>
<td>-4</td>
<td>-3</td>
<td>-1</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Relaxed Lattice (3)</td>
<td>-8</td>
<td>14</td>
<td>-4</td>
<td>0</td>
<td>-1</td>
<td>7</td>
<td>9</td>
</tr>
</tbody>
</table>

#### ENERGIES

(Units: kJ mol⁻¹)

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Intramolecular</th>
<th>Intermolecular</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Harmonic</td>
<td>Dispersion</td>
</tr>
<tr>
<td>Rigid Lattice (2)</td>
<td>12</td>
<td>-140</td>
</tr>
<tr>
<td>Relaxed Lattice (3)</td>
<td>9</td>
<td>-132</td>
</tr>
<tr>
<td>Disordered CAEA</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Total potential energy = -4578 kJ mol⁻¹.

#### CENTRE OF MASS DISPLACEMENT OF NEAREST NEIGHBOURS

(Units: nm)

<table>
<thead>
<tr>
<th>Neighbour Molecule</th>
<th>a</th>
<th>b</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.01</td>
<td>0.0</td>
<td>0.01</td>
</tr>
<tr>
<td>3</td>
<td>-.01</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>0.01</td>
<td>0.01</td>
<td>-.01</td>
</tr>
<tr>
<td>10</td>
<td>-.02</td>
<td>-.02</td>
<td>0.0</td>
</tr>
<tr>
<td>15</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>
TABLE 19

ORIENTATION OF NON-ECLIPSED CONFORMATIONS OF AEA IN P_c AND DISORDERED P2_1 CAEA
(direction cosines of principal axes)

<table>
<thead>
<tr>
<th>SITE A</th>
<th>P_c Lattice</th>
<th>P2_1 Lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>&quot;L&quot;</td>
<td>0.990</td>
<td>-0.138</td>
</tr>
<tr>
<td>&quot;M&quot;</td>
<td>0.111</td>
<td>0.715</td>
</tr>
<tr>
<td>&quot;N&quot;</td>
<td>0.084</td>
<td>0.686</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SITE B</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c'</td>
<td>a</td>
<td>b</td>
<td>c'</td>
</tr>
<tr>
<td>&quot;L&quot;</td>
<td>-0.930</td>
<td>0.225</td>
<td>-0.292</td>
<td>&quot;L&quot;</td>
<td>-0.900</td>
<td>0.257</td>
</tr>
<tr>
<td>&quot;M&quot;</td>
<td>-0.368</td>
<td>-0.603</td>
<td>0.708</td>
<td>&quot;M&quot;</td>
<td>-0.435</td>
<td>-0.586</td>
</tr>
<tr>
<td>&quot;N&quot;</td>
<td>-0.017</td>
<td>0.765</td>
<td>0.644</td>
<td>&quot;N&quot;</td>
<td>-0.031</td>
<td>0.769</td>
</tr>
</tbody>
</table>

(N.B. The principal moments of inertia are similar for the corresponding conformations.)
Fig. 14. AEA in Disordered P2₁ CAEA Site A'
of the four conformations. As in the previous section it is found that the individual interaction energies of the photocleaved molecules in both sites are similar to those calculated in the ordered $P_c$ lattice, however the contribution to the total potential energy of the lattice favours the $P_c$ conformations.

It was found that the pure disordered lattice is more stable by 1 kJ mol$^{-1}$ than the pure, ordered lattice. This is not surprising since earlier it was shown that this crystal structure produced anomalous energetic results.

DISCUSSION

The technique of atom-atom potentials applied to the conformational problem of AEA in CAEA has elucidated the nature of three of the four experimentally observed conformations of AEA. In addition, the calculations have corroborated the experimental findings which suggest the presence of domains of $P_c$ and $P_{21}$ space group symmetry. The domains have been shown to accommodate disordered molecules; however these must be isolated because of the experimental findings. Two important uses for the technique of lattice relaxation have emerged from this study, firstly, it offers a sensitive test of assumed crystallographic models, and secondly, in combination with the experimental technique of photocleavage provides a sensitive probe of the crystal microstructure.

The fourth site of AEA, which was not found in this work, could possibly be accounted for by a conformation of the disordered AEA molecule in the $P_c$ domain or an ordered AEA molecule in the $P_{21}$ domain which differs in a very subtle way from the eclipsed conformation that was found, and as such cannot be detected at this level of calculation. However the
experimental observations suggest that the $P_2$ site is associated with yet another type of lattice molecule. If this is so the site is most probably associated with a neighbour molecule of photocleaved disordered molecule in the $P_c$ lattice and/or a photocleaved molecule in the ordered $P2_1$ lattice. This conclusion is based on the fact that the $P_2$ site is a regular feature of the lattice and is therefore probably not associated with seemingly random molecules that may be found at dislocations, adjacent to vacancies or at domain boundaries. The progenitor molecule of the $P_2$ AEA conformation must have an orientation already displaced by the observed 7° or 8° since the experience gained in this work indicates that the photocleaved molecules change little in their orientation from that of their parent molecule. The calculations indicate that such a molecule is not present. It is tempting to associate the $P_2$ site with molecule 9 of the ordered $P2_1$ lattice which is adjacent to the origin-centred photocleaved molecule and/or molecule 10 which is adjacent to the origin-centred disordered photocleaved molecule of the $P_c$ lattice, see Tables 10, 14 and 15, and figure 6. The reason for this choice is not because of its orientational displacement, which is not particularly large, but instead because of its large centre of mass displacement. This would suggest that the $P_1$ and $P_2$ sites are intimately connected. One could imagine the $P_1$ conformation being formed and then displacing the proposed neighbour molecule. This molecule is then photocleaved and subsequently rotates as observed in experiment due to the resultant torques. Another possible source of the $P_2$ site has been considered in Appendix D. At this site the CAEA molecule is photocleaved adjacent to a disordered lattice molecule.

The conformations adopted by AEA can be correlated with their respective environments in each lattice. Consider a molecule of CAEA in an ordered $P_c$ lattice. Upon photocleavage the two anthracene moieties move
outwards, one encounters the ethane bridge of an adjacent molecule while the other opens into a certain region of "free volume" where there is no ethane bridge. As can be observed in figures 6, 13 and also 14 the adjacent ethane bridge constrains the anthracene moiety in a fixed position while the other anthracene moiety experiences limited freedom to adopt two conformations. In an ordered $P2_1$ lattice we note that there is still one anthracene moiety which opens onto an adjacent ethane bridge whereas the other anthracene moiety no longer opens into a region of "free volume" but instead into a region which is restrictive, figure 6. Thus it is understandable that in this conformation the anthracene moieties are held in an eclipsed conformation.

Earlier it was remarked that AEA at the sites A and A' tend to adopt a near eclipsed conformation following lattice relaxation. This is a puzzling finding since one would expect that the intramolecular forces would tend to increase the angle of rotation about the central bridging carbon-carbon bond. The calculated differences are however small and may be attributed to the errors in the simplistic model used.

In conclusion, the calculations have not led to a definitive conclusion on all aspects of the conformational problem but they do give clear trends on a number of its important features.
CHAPTER 6

DESCRIPTION OF THE COMPUTER PROGRAM
MAIN FLOW DIAGRAM

Main
Selects Program Segments

Coords
Data Input, Check and Preparation

Minim
Minimization Sequence Control

Axrot
Localized Mode Dynamics

Rcurve
Potential Curve Calculations

Trajec
Molecular Trajectory Calculations
**GENERAL MINIMIZATION**

- **MINIM**
- **ECAL**
  Calculates the total intermolecular potential energy of the molecules included in the minimization.
- **GLOB1**
  Directs minimization when the guest has internal degrees of freedom.
- **GLOB**
  Selects descent routines for rigid body potential energy minimization.
- **FUNMIN**
  Quasi-Newton descent method.
- **HESMIN**
  Modified-Newton descent method.
- **FUNVAL**
  Selects function to be minimized. Adds penalty terms if required. Holds component of centre of mass fixed if required.
FUNC

Directs the calculation of the potential energy, and derivatives of the potential, for each guest.

ENMOL

Directs the calculation of the potential energy, and derivatives of the potential, for each molecule included in the minimization that surrounds the guest(s).

ANGLE VARIABLE ROUTINES

JOULE

Calculates the potential energy of interaction of two molecules, plus contributions to the gradient $\nabla V_i$ and Hessian $\nabla^2 V_i$ (Chapter 3).

DERIV

Calculates the inner products required for the gradient $\nabla V_i$ and the Hessian $\nabla^2 V_i$ in the outer-most loop.
### ANGLE VARIABLE ROUTINES

<table>
<thead>
<tr>
<th>QUAT</th>
<th>QUABUL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid body rotations performed using quaternion form of the rotation matrix</td>
<td>Calculates $A_{\Omega}$ and $A_{\Omega\Omega}$ matrices. Chapter 3.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ROTAT/EULER</th>
<th>EROT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid body rotations performed using Euler angles.</td>
<td>Calculates the 1st and 2nd derivatives of the rotation matrix parametrized in terms of Euler angles.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ROTATO/ORTH</th>
<th>OROT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid body rotations performed about the laboratory $x$, $y$, and $z$ axes.</td>
<td>Calculates the 1st and 2nd derivatives of the rotation matrix parametrized in terms of the angles of rotation about the laboratory $x$, $y$, and $z$ axes.</td>
</tr>
</tbody>
</table>
COMPUTATION OF THE INTRAMOLECULAR POTENTIAL ENERGY

- **COORDS**
  - MINIM
    - **INTROT**
      - Calculates intramolecular potential curves.
    - **GLOB**
      - **HESMIN**
    - **GLOB1**
    - **FUNVAL**

- **INTERN**
  - Selects angle bending, ring bending, or bond rotation routines.
  - **BENANG**
    - Angle bending coordinate manipulation. Calculates the angle bending harmonic potential energy contribution, and all angle bending derivatives.
  - **BEND**
    - Rotation matrix and its derivatives required for angle bending
  - **BENBUT**
    - Ring bending coordinate manipulation, calculates the ring bending harmonic potential energy contribution, and all ring bending derivatives.

- **FUNC**
  - **ENMOL**
    - **INTGRD**
      - Calculates the intermolecular contribution to the internal gradients.
  - **INEN**
    - Calculates the non-bonded intramolecular potential energy.
  - **INPROD**
    - Calculates final intramolecular gradient inner products (see Eqn. 5.3 and associated text).
  - **INRNL**
    - Performs rotations about bridging bonds and calculates bond rotation derivatives. Normally calls INEN rather than the call through INTERN.

- **ROMAT**
  - Rotation matrix and its derivatives required for bond, or axis, rotations.
LOCALIZED MODE DYNAMICS

**FUNC**
- Calculates 1st and 2nd order perturbation corrections to the harmonic oscillator frequencies.

**PERT**
- Calculates 1st and 2nd order perturbation corrections to the harmonic oscillator frequencies.

**AXROT**
- Dynamics calculated using Method A of Appendix A.

**SDERIV**
- Dynamics calculated using Method B of Appendix A.

**SURF**
- Diagonalizes $\nabla^2 V_i$ in the principal molecular frame.

**DYNAM**
- Calculates and diagonalizes the dynamical self matrix.

**POTROT**
- Performs rotations of atomic position coordinates about principal molecular axes.

**BGPOL and associated routines**
- Performs the least squares fit of the polynomial (Appendix A) to the calculated potential curves.

**OROT**
- Performs rotations of atomic position coordinates about principal molecular axes.

**JOULE**
POTENTIAL CURVE CALCULATIONS

RCURVE
Calculates potential curves as a function of the angle of rotation about each principal inertial axis.

POTROT | FUNC

MOLECULAR TRAJECTORY CALCULATIONS

TRAJEC
Controls the trajectory calculation.

RK
4th order Runge-Kutta integration scheme.

FTORQ
Calculates forces and torques.
APPENDIX A

DYNAMICS

At the completion of each minimization localized external mode frequencies of oscillation of some molecules constituting the defect are calculated to help confirm the 'physical reality' of the computed equilibrium structure. Usually this only includes, for instance, a guest molecule oscillating in its potential well in its environment of neighbours which are held fixed at their computed equilibrium positions. Two simple procedures are used in the calculation of the frequencies. The first is based on the calculation of potential curves about and along chosen axes, and the second, on the diagonalization of the dynamical self-matrix.

Method A

In this method it is assumed that the librational motion occurs about the principal molecular inertial axes and the translational motion along the laboratory cartesian axes. Separate potential curves are calculated about the equilibrium position as a function of each of these rotation or translation variables (usually five points on either side of the equilibrium position up to $2^\circ - 3^\circ$ and 0.01nm are required for the method to work). A separate least squares fit of the polynomial

$$V(x) = V_0 + V_1 x + V_2 x^2 + V_3 x^3 + V_4 x^4$$

is made to each of the curves, where $x$ is the particular displacement variable. Then the transition energy for each mode is calculated by treating the motion as a one-dimensional harmonic oscillator using the appropriate harmonic potential constant $V_2$. Anharmonic effects, which
were always found to be small, are treated to second order in the perturbation $V_j x^j + V_n x^n$ in the basis of the Hermite polynomials.

**Method B**

Phonon frequencies for a pure, perfect lattice of molecules are calculated in the harmonic approximation by solving the following $6n$ eigenvalue equations [126,127,177] where $n$ is the number of molecules in the unit cell

$$
\sum_{j,j'} \left\{ c_{ss'}^{jj'}(q) - \omega^2 \delta_{ss'} \delta_{jj'} \right\} t_{s',q}^{j'} = 0
$$

where

- $\delta_{ss'}$ is the Kronecker delta
- $q$ is the wave vector
- $s$ labels the molecules of a unit cell
- $j$ labels the components of the displacement vector of molecule $s$
- $\omega$ is the angular frequency
- $t_{s',q}^{j'}$ is the $j'$th mass-reduced component of the displacement vector of the $s'$th molecule. It is related to the components of the normal displacement vector by $t_{s',q}^{j'} = \sqrt{M_j / M_j'} t_{s',q}^{j'}$, where $M_j$ in the principal inertial cartesian frame corresponds to the molecular mass for translational displacements and to the appropriate inertial moment for the rotational displacements about the principal inertial axes.
is the matrix whose elements \((s_j, s_j')\) are given by

\[
\frac{1}{\sqrt{M_j M_{j'}}} \sum_l \frac{\partial^2 V}{\partial \mu_j^l, \partial \mu_{j'}^l} \cdot e^{i\mathbf{q} \cdot \mathbf{r}}
\]

where the subscript \(\mathbf{q}\), which labels the unit cells, has
been added to the components of the displacement vectors of
molecules \(s\) and \(s'\), with \(\mathbf{q} = 0\) an arbitrarily chosen
origin unit cell, and \(V\) is the total intermolecular
potential energy (see Eqn. (3.1)).

The localized mode description corresponds to setting \(\mathbf{q} = 0\) and
\(s = s' = 0\) i.e. the origin molecule. Thus we must find the eigenvalues
\(\omega^2\) of the matrix \(G\). For simplicity we consider \(G\) to be a real
symmetric \(6 \times 6\) matrix since the rotational displacements do not commute.
Translational periodicity has been introduced, in part, to illustrate the
results for naphthalene.

Ito et al \cite{91} in an examination of the Raman active zone-centre
rotational modes of naphthalene (Appendix B) attribute the three pairs of
in-phase and out-of-phase modes to displacements which may be considered to
be about the principal inertial \(L\), \(M\), and \(N\) axes. These correspond
to the highest, middle range, and lowest frequency pairs respectively.
Pawley has shown \cite{126} that the rotational modes do not occur about the
principal inertial axes but instead about axes displaced from them. For
the purpose of the comparisons made here Ito's description will suffice.
The rotational frequencies we calculate can be thought of as the average
of the zone-centre symmetrical and anti-symmetrical pairs. The translational
frequencies can be thought of as corresponding to zone-boundary modes. By
assuming sinusoidal dispersion we can draw the simple conclusion that our
calculated frequencies should be lower than the corresponding zone-centre frequencies.

The results obtained for the room temperature naphthalene crystal structure are listed in the table. The results for the two methods are in agreement. The rotational frequencies are in good agreement with the experimental results except for the highest frequency mode. This is probably due to the neglect of correlated motion. The translational frequencies exhibit the correct behaviour. From this illustration we may conclude that the localized mode description is a useful method for checking the physical reality of computed equilibrium defect structures.
Comparison of Localized Mode Frequencies with Experimental Results

Librational Force Constants (kJ mol\(^{-1}\) rad\(^{-2}\))

<table>
<thead>
<tr>
<th>Axis</th>
<th>Method A</th>
<th>Method B</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>424</td>
<td>423</td>
</tr>
<tr>
<td>M</td>
<td>684</td>
<td>693</td>
</tr>
<tr>
<td>N</td>
<td>334</td>
<td>333</td>
</tr>
</tbody>
</table>

Librational Frequencies (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Axis</th>
<th>Method A</th>
<th>Method B</th>
<th>Expt. Av.</th>
<th>D.M.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>87</td>
<td>88</td>
<td>117</td>
<td>100</td>
</tr>
<tr>
<td>M</td>
<td>70</td>
<td>68</td>
<td>73</td>
<td>72</td>
</tr>
<tr>
<td>N</td>
<td>41</td>
<td>41</td>
<td>49</td>
<td>44</td>
</tr>
</tbody>
</table>

Translational Frequencies (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Axis</th>
<th>Symmetry</th>
<th>Method A</th>
<th>Method B</th>
<th>Expt.</th>
<th>D.M.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>a,N</td>
<td>A</td>
<td>62</td>
<td>68</td>
<td>99</td>
<td>88</td>
</tr>
<tr>
<td>b,M</td>
<td>B</td>
<td>48</td>
<td>47</td>
<td>66</td>
<td>59</td>
</tr>
<tr>
<td>c',L</td>
<td>A</td>
<td>47</td>
<td>38</td>
<td>?</td>
<td>45</td>
</tr>
</tbody>
</table>

* Calculated from the complete dynamical matrix at \( q = 0 \).
APPENDIX B

THE SYMMETRY OF THE ZONE-CENTRE EXTERNAL PHONONS OF NAPHTHALENE

In order to determine which of the irreducible representations of the P2_1/a space group of naphthalene govern the transformations of the zone-centre external phonons, it is necessary to consider how a suitable set of translationally symmetrized basis functions transform under the operations of the underlying point group of the space group. At \( q = 0 \) the star of the wave-vector contains only the zero wave-vector, and the group of the wave-vector is identical to the factor group. Therefore the transformation of the basis functions under the operations of the factor group need to be found.

A suitable set of functions for constructing the reducible representations spanned by the librations and translations separately at \( q = 0 \) are:

\[
u_j(k) = N^{-\frac{1}{2}} \sum_i u_j(1k)\]

where \( u_j(1k) \) is the \( j \)-th component of the molecular displacement at the \( k \)-th site in the 1-th unit cell, and \( N \) is the number of unit cells. Operations of the group of the wave-vector transform the \( u_j(k) \) into linear combinations of displacement coordinates:

\[
\langle a | i_{\alpha} | u_j(k) \rangle = \sum_j C_{jj'}u_j'(k')
\]

where \( \alpha \) is the rotation operator and \( i_{\alpha} \) the non-primitive translational operator associated with \( \alpha \) in the factor group.

The character table for the irreducible representations of the factor group, \( C_{2h} \), of naphthalene is:
where the identity element $E$ and the inversion element $i$ leave the molecules unchanged while the two-fold rotation about the $b$ monoclinic axis $C^b_\text{C}$ and the reflection in the plane perpendicular to the $b$ axis $\sigma^b$ interchange the molecules in the unit cell.

Remembering that translations transform as polar vectors, and rotations as axial vectors it is a straightforward procedure to examine how the $u_j(k)$ for naphthalene transform under the factor group operations. Clearly the matrix representations of $C^b_2$ and $\sigma^b$ must have zero trace for both translations and rotations; the matrix representations for $E$ must have a trace of 6 for both translations and rotations, whilst the matrix representation of the inversion operator $i$ must have a trace of -6 for translations and 6 for rotations. Therefore the character table for the reducible representations must have the following form:

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$C^b_2$</th>
<th>$i$</th>
<th>$\sigma^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A^u_g$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A^u_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B^g_g$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B^u_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

These may be decomposed in the usual manner to give:

$$\Gamma^\text{TRANS} = 3A^u_u + 3B^u_u$$
$$\Gamma^\text{ROT} = 3A^g_g + 3B^g_g$$
The three zero frequency phonon modes correspond to translations along the 'b' monoclinic axis \((A_u)\), and 'a' and 'c' axes \((B_u)\), therefore

\[
\Gamma_{\text{TRANS.OBSERVED}} = 2A_u + B_u
\]

It is obvious that there can be no mixing of the translational and rotational motions at \(q = 0\). Also the rotational modes must be Raman active and the translational modes infra-red active with one mode producing an electric dipole variation parallel to the 'a-c' plane and two modes producing an electric dipole variation parallel to the 'b' monoclinic axis.

Ito et al [91] have assigned the symmetry to the six rotational modes and determined an approximate description of them. Bokhenkov et al [10] have determined the symmetry assignment of the translational frequencies. A treatment of the symmetry of phonons is given by Schnepp and Jacobi [142].
APPENDIX C

MOLECULAR DYNAMICS

The method of molecular dynamics is too time consuming to be applied to the problem of lattice relaxation, however, it could prove to be useful in developing an understanding of phenomena occurring in small assemblies of molecules, for instance, a study of crystal nucleation may be possible. As a first step toward such objectives molecular dynamics routines were implemented for the study of the temporal evolution of a rigid body interacting with a stationary set of molecules. In the following we report the sequence of steps required to solve the Euler and Newton equations of motion. These equations are [51]

$$\frac{d\omega_p}{dt} = (N_p - \omega \times \omega \cdot (I_p - I_p)) / I_p$$

$$\frac{d\gamma}{dt} = \frac{1}{2} s^T \gamma_p$$

$$\frac{d^2 r}{dt^2} = \frac{dv}{dt} = \frac{F}{m}$$

where the subscript $p_\alpha$ denotes the $\alpha$th principal molecular inertial axis and the other terms have their usual meaning:

$\omega$ angular velocity

$N$ the torque, which is first computed in the laboratory frame by $N_1 = \mathbf{r} \times \mathbf{F}$ and is then transformed to the principal molecular frame by $N_p = A \cdot N_1$ where $A$ is given in Eqn. (3.8).

$I$ moment of inertia
\( \mathbf{r} \)  
centre of mass position vector

\( \mathbf{v} \)  
linear velocity vector

\( \mathbf{F} \)  
force vector

\( m \)  
molecular mass

The second equation gives the time rate of change of the angle variables which is given in Eqn. (3.16).

With the initial conditions at \( t = 0 \), \( \mathbf{r} = \mathbf{r}_0 \), \( \mathbf{v} = \mathbf{v}_0 \), \( \mathbf{g} = \mathbf{g}_0 \), \( \omega_p = \omega_{p0} \) which define the 13-vector

\[ \mathbf{x}_0 = (\mathbf{r}_0, \mathbf{v}_0, \mathbf{g}_0, \omega_{p0}) \]

we can define the time rate of change of the \( \mathbf{x} \) vector

\[
\frac{d\mathbf{x}}{dt} = \mathbf{F}(\mathbf{x})
\]

Then using time increments \( \Delta t \) of the order \( 10^{-14} - 10^{-15} \) sec we can employ a 4th order Runge-Kutta scheme to integrate the equations of motion:

\[
\begin{align*}
K_1 &= \mathbf{F}(\mathbf{x}_n) \cdot \Delta t \\
K_2 &= \mathbf{F}\left(\mathbf{x}_n + \frac{K_1}{2}\right) \cdot \Delta t \\
K_3 &= \mathbf{F}\left(\mathbf{x}_n + \frac{K_2}{2}\right) \cdot \Delta t \\
K_4 &= \mathbf{F}\left(\mathbf{x}_n + K_3\right) \cdot \Delta t \\
\mathbf{x}_{n+1} &= \mathbf{x}_n + \frac{1}{6} (K_1 + 2K_2 + 2K_3 + K_4)
\end{align*}
\]

The cycle then repeats.
APPENDIX D

FURTHER CALCULATIONS ON THE ECLIPSED CONFORMATIONS OF AEA

Two possible lattice structures which might at first seem able to account for the $P_2$ conformation of AEA are briefly examined. A consideration of figure 6 of Chapter 5 suggests that the case in which there is an ethane bridge directed toward each anthracene moiety of AEA should be investigated. This corresponds to a molecule of CAEA in the $P2_1$ and $Pc$ lattices being disordered at the lattice sites $0 - \frac{1}{2} \frac{1}{2}$ and $0 \frac{1}{2} - \frac{1}{2}$ respectively. Where the disordered lattice molecule has its ethane bridge directed oppositely to that in the ordered lattice. We would anticipate that the ethane bridges constrain AEA in an eclipsed conformation. In addition, the presence of the second ethane bridge might be expected to impart a large torque to, and thus produce a rotation of, the molecule of AEA so as to account for the non-fluorescent site $P_2$.

The calculations were performed in the same way as those reported in Chapter 5 except that the minimization was started from the perfectly eclipsed conformation. This is entirely reasonable in view of our earlier findings. It was found, as might be expected, that the conformation adopted by AEA was essentially identical in both the $P2_1$ and $Pc$ lattices. This conformation was perfectly eclipsed with an orientation that was again essentially the same as that of the parent CAEA molecule. The characteristics of this site are listed in the accompanying Table. An examination of these results will lead to the conclusion that this site would probably be spectroscopically indistinguishable from the eclipsed sites that have already been found. The figure illustrates the conformation adopted by AEA in a...
rigid lattice. This conformation is given since the earlier calculations on this system using the experimental data indicated that lattice relaxation was not particularly informative. Certainly lattice relaxation would not alter the orientation of the molecule greatly.

We conclude that this disordering is not responsible for the second fluorescent site. Further disorder in the neighbourhood of the photocleaved molecule can be expected to produce only minor orientational changes. This is evident from the previous calculations on similar conformations in both the $P_{2_1}$ and $P_c$ lattices.
OPTIMUM INTRAMOLECULAR VARIABLES
(Units: degrees)

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<th>( \theta_3 )</th>
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POTENTIAL ENERGY
(Units: kJ mol\(^{-1}\))

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AEA adjacent to a disordered molecule in $P_c$ CAEA.
REFERENCES


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