A computational study of the pyrrole···CO and pyridine···CO complexes

Terry J. Frankcombe

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Abstract

Pyrrole···CO and pyridine···CO van der Waals clusters in various configurations have been studied at the MP2/cc-pVQZ level in order to resolve ambiguity in previous microwave spectroscopy studies. For pyrrole···CO the previously proposed configuration – with the CO fragment bound to the pyrrole ring – was found to be the most stable. For pyridine···CO the “preferred” planar structure proposed by Bettens and Bauder [R.P.A. Bettens, A. Bauder, *J. Chem. Phys.* 102 (1995) 1501] was found to be significantly more stable than their competing structure, but two other structure of similar configuration to the pyrrole···CO cluster were found to be more stable. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Complexes of carbon dioxide and the aromatic molecules pyrrole (C_4NH_5) and pyridine (C_5NH_5) have previously been studied by high-resolution microwave spectroscopy [1,2]. While the pyrrole···CO complex was found to be structured with the CO molecule bound to the pyrrole ring with clear C_s symmetry, the pyridine···CO complex exhibited a planar structure with the CO molecule lying in the plane of the pyridine ring adjacent to the nitrogen atom. In neither case was the geometry of the ground state of the complex able to be assigned unambiguously. In both cases the experimental results suggested a particular ground state geometry, but were not able to rule out an alternate geometry with the CO molecule rotated to a distinctly different configuration. These possible geometries are shown in Fig. 1.

Kanakaraju and Kolandaivel [3] studied the pyrrole···CO complex using a number of quantum chemistry approaches. Their conclusion was that the most stable structure for the complex is with the CO fragment bound

spoke-like in the plane of pyrrole, orientated with nearly collinear C–O···H–N. Though not referring to that work, they found geometries similar to those suggested by Bettens, Huber and Bauder to be 3 kJ/mol less stable at the MP2/6-31G* level. The authors did not report on whether any symmetry was enforced on the geometries of the cluster.

Only a small number of other complexes of small aromatics and carbon dioxide have been studied theoretically, though microwave spectroscopic studies are more common. Apart from the work of Kanakaraju and Kolandaivel mentioned above, studies have been published for benzene···CO [4,5], phenol···CO [6] and aniline···CO [7]. These studies typically employ MP2 and hybrid DFT methodologies, which in general agree quite well. These three cases, representing three typical classes of bonding found in aromatic···CO complexes (hydrogen bonding to substituent groups, bonding to the π electrons in a parallel-like structure and bonding in the plane of the ring), give reasonable agreement with experimentally determined structures. Thus one can be reasonably confident that aromatic···CO clusters can be well described at the MP2 and hybrid DFT levels of theory, even when using the reasonably small basis sets of the above studies.

E-mail address: T.Frankcombe@chem.leidenuniv.nl

Fig. 1. Possible geometries identified by Bauder et al. for the (a) pyrrole...CO and (b) pyridine...CO complexes.

The aim of the work presented in this paper was to use quantum chemistry methods firstly to resolve the ambiguity in the observed structure of the pyrrole...CO and pyridine...CO complexes and secondly to explore other possible stable complex geometries.

2. Method

The Gaussian 03 program [8] was used for all calculations. The electronic energies of pyrrole...CO and pyridine...CO van der Waals complexes were calculated at the MP2 level of theory using Dunning's correlation consistent basis sets [9]. The MP2 level has previously been shown to give reasonable agreement with experiment for small aromatics complexed with CO [4–7]. Initial screening was performed at the MP2/AUG-cc-pVDZ level. During the initial screening full geometry relaxation of the cluster was performed starting from a range of potential cluster geometries of differing symmetries. For example, CO adsorption sites in the plane of the aromatic species in line with and between hydrogen atoms were considered, along with the CO molecule orientated in and out of the plane and with the CO molecule rotated to various positions. Cluster geometries in which the CO molecule bound to the face of the aromatic species (like those of Fig. 1a) were also considered. No constraints were placed on the geometry optimisations (that is, the cluster fragments were not held frozen). Clusters with point group symmetries above C_1 were tested for symmetry breaking by restarting the optimisation with the geometries perturbed slightly in order to break the symmetry.

The initial screening lead to the identification of a number of unique geometries that were local minima at the

Fig. 2. The interfragment parameters R , θ , ϕ , ρ , and η .

MP2/AUG-cc-pVDZ level. Each of the identified cluster geometries were further optimised using a range of basis sets. No basis set superposition error (BSSE) correction was applied.

The cluster geometries are reported here with respect to the interfragment parameters indicated in Fig. 2. That is, the centre of mass separation and two polar angles (R , θ , ϕ) to give the position of the CO centre of mass with respect to the pyrrole/pyridine centre of mass and two polar angles (ρ , η) to indicate the orientation of the CO molecule with respect to the pyrrole/pyridine centre to nitrogen axis. The overall geometry can be characterised by θ and ϕ . If either angle is near zero or 180° then to the CO fragment lies roughly in the plane of the aromatic ring. If both angles are closer to 90° then to the CO fragment sits “above” the aromatic ring. In the former case $\rho \approx \theta$ and $\rho \approx \theta \pm 180^\circ$ with $\eta \approx 0$ correspond to “spoke” geometries where the CO axis lies along the interfragment axis.

3. Results

After screening at the MP2/AUG-cc-pVDZ level, 18 pyrrole...CO and 19 pyridine...CO stable cluster geometries were identified. Cluster configurations similar to those proposed by Bauder et al. [1,2] were found to be stable in both cases.

The geometries that were found to be stable at the MP2/AUG-cc-pVDZ level were then further optimised using successively larger basis sets. Basis sets up to quadruple zeta were used, with an without diffuse function augmentation. Fig. 3 shows the effect of altering the basis set for the pyrrole...CO geometries proposed by Bettens et al. [1]. The binding energies with respect to the infinitely separated fragments are shown in Fig. 3a, while Fig. 3b shows two of the geometric parameters defined in Fig. 2, namely the

Fig. 3. The effect of the basis set on the pyrrole...CO complex for the structures proposed by Bettens et al. [1]. Convergence of (a) the binding energy and (b) the centre of mass separation R and the angle η .

centre of mass separation R and the CO fragment to pyrrole plane angle η . The behaviour of the other three angles defined in Fig. 2 were found to be similar to that shown for η . The dotted line in Fig. 3a is the basis set limit [10] of the AUG-cc-pVXZ series. Fig. 3 indicates that the energetics and interfragment geometric parameters of the diffuse-augmented and unaugmented basis set series' are converging as the basis sets get larger, as expected. The agreement between the MP2/cc-pVQZ and MP2/AUG-cc-pVQZ cluster geometry is excellent and the convergence of the energetics is reasonable. MP2/cc-pVQZ was selected as an efficient but accurate level of theory.

A number of the cluster geometries that were found to be stable at the MP2/AUG-cc-pVDZ level were unstable when the optimisation was repeated with a larger basis set, with the geometry moving away from the MP2/AUG-cc-pVDZ configuration to one of the other stable configurations. At the MP2/cc-pVQZ level 16 of the initial 18 pyrrole...CO structures and 14 of the initial 19 pyridine...CO structures remained stable. The interfragment geometric parameters and cluster binding energies relative to the most probable structures proposed by Bauder et al. [1,2] are shown in Tables 1 and 2. The various unique pyrrole...CO structures are labelled F1–F16 with structures I and II of Bettens et al. [1] corresponding to F1 and F2, respectively. The pyridine...CO structures are similarly labelled S1–S14.

The relative energies and interfragment geometric parameters for the stable pyrrole...CO structures of

Table 1

Relative energy E (kJ/mol) and interfragment geometric parameters ($\text{\AA}$ and degrees) for stable pyrrole...CO clusters at the MP2/AUG-cc-pVQZ level

	E	R	θ	ϕ	ρ	η
F1	0.0	3.3233	90.84	89.82	0.00	18.64
F2	0.813	3.2204	86.07	88.96	180.00	−4.93
F3	1.018	5.1627	0.0	—	180.00	0.0
F4	5.979	4.9466	0.0	—	0.00	0.0
F5	5.737	4.6528	27.01	0.0	51.85	0.0
F6	5.732	4.6266	27.73	11.98	54.17	−12.69
F7	7.301	5.7245	69.57	0.0	−96.42	0.0
F8	8.527	5.3760	68.99	0.0	88.59	0.0
F9	6.318	4.7064	110.06	0.0	−0.24	0.0
F10	6.936	4.5471	104.09	0.0	−168.26	0.0
F11	7.757	4.8493	105.82	0.0	106.65	0.0
F12	8.783	5.5101	143.45	0.0	143.66	0.0
F13	6.814	4.6000	176.49	0.0	−86.41	0.0
F14	7.821	4.6309	179.91	89.98	0.07	−110.45
F15	8.260	5.3680	180.0	—	0.0	0.0
F16	7.861	4.8763	180.0	—	180.0	0.0

Table 2

Relative energy E (kJ/mol) and interfragment geometric parameters ($\text{\AA}$ and degrees) for stable pyridine...CO clusters at the MP2/AUG-cc-pVQZ level

	E	R	θ	ϕ	ρ	η
S1	0.0	4.6471	14.06	0.0	133.24	0.0
S2	1.847	4.6206	9.26	0.0	85.79	0.0
S3	4.792	5.1272	88.77	0.0	87.98	0.0
S4	3.802	5.5328	87.79	0.0	−101.77	0.0
S5	5.653	5.6431	117.97	0.0	112.49	0.0
S6	4.422	5.9781	116.28	0.22	−67.51	0.39
S7	4.698	5.1481	149.31	0.0	148.75	0.0
S8	3.613	5.5578	149.57	0.0	−30.95	0.0
S9	5.782	5.6876	179.98	0.66	179.97	0.0
S10	4.326	6.0080	179.98	0.34	0.03	0.0
S11	0.618	3.3218	85.84	90.00	0.02	−8.95
S12	−0.047	3.2989	86.77	90.00	179.98	−2.75
S13	−1.072	3.2425	85.47	89.60	89.60	−3.00
S14	2.053	3.5778	87.74	89.94	156.02	−90.73

Table 1 confirm that F1 (structure I of [1]) was found to be the most stable, and thus the most likely observed structure. F2 (structure II of [1]) was the next most stable structure, less than 1 kJ/mol higher in energy. These two structures are related primarily by a $\sim 180^\circ$ rotation around the interfragment axis (which is nearly perpendicular to the pyrrole plane). A third structure, F3, lay just over 1 kJ/mol higher in energy than F1. In this structure the CO fragment lies exactly on the C_2 axis of the pyrrole molecule, adjacent to the latter's N atom, with the C atom of the CO fragment towards the ring. No other structure lay less than 5.7 kJ/mol above the energy of the F1 structure, a significant amount of energy when compared to the binding energy of the F1 complex of 10.6 kJ/mol.

For pyridine...CO the situation was considerably less clear cut. The structures proposed by Bettens and Bauder [2] were again found to be low energy, stable structures with S1 around 1.8 kJ/mol lower in energy than S2, in

accordance with the proposal of [2]. However, unlike the pyrrole...CO case described above, these were not the structures calculated to be the most energetically favourable. Structures S12 and S13 were found to be 0.05 and 1 kJ/mol, respectively, lower in energy than the S1 structure that best fit Bettens and Bauder's microwave data. Both S12 and S13 are structures in which the CO fragment lies above the pyridine ring, similar to the low energy configurations of pyrrole...CO. S12 has the CO fragment almost aligned with the symmetry axis of the pyridine fragment giving the cluster C_s symmetry. The O atom of the CO fragment lies toward the N atom of the pyridine fragment, dipped toward the pyridine plane slightly. The S13 structure has the CO fragment rotated nearly 90° to its position in S12, around an axis perpendicular to the plane of the pyridine fragment. A third structure S11, similar to S12 but with the fragments rotated relative to one another by 180° , was found to lie 0.6 kJ/mol higher in energy than S1 making it significantly lower in energy than S2. The energies of the various stable pyridine...CO structures were spread more than the pyrrole...CO case (where two structures were clearly separated from the rest). The binding energy of the pyridine...CO cluster was also slightly lower than that of pyrrole...CO, being 8.9 kJ/mol for the most tightly bound S13 structure.

4. Discussion

The intention of this work was to distinguish between the structures proposed by Bauder et al. [1,2] that were not sufficiently resolvable from the experimental data available. In the case of pyrrole...CO, the calculations presented here support the "preferred" structure of Bettens et al. [1] of an approximately C_s cluster with the CO fragment bound to the pyrrole ring, oriented so that the carbon atom of CO points toward the nitrogen of the pyrrole ring. There remain, however, several discrepancies between the potential minimum structure F1 of this work and structure I of [1], whether one considers the latter's rigid-monomer least squares fit or their vibrationally averaged model potential fit. Structure F1 exhibited a smaller angle between the CO bond axis and the pyrrole C_2 axis. The angle between the pyrrole plane and the line between the centres of mass was slightly closer to a right angle in F1, but this could be due to the ambiguity involved in defining the pyrrole plane when the pyrrole fragment is allowed to relax. While the analysis of the experimental data lead to a cluster of C_s symmetry, the full relaxation in the present work allowed the CO fragment to move off the symmetry plane slightly, but the small displacement (corresponding to a CO fragment centre of mass displacement of 0.01 Å) means one should not lend too much weight to the symmetry breaking. The centre of mass separation between the fragments of F1 was found to be slightly smaller, by 0.18 Å when compared to the equilibrium position fit and by 0.07 Å when compared to the model potential results.

A more serious discrepancy between structure I of [1] and the present F1 is the binding energy. While the fully

relaxed F1 was 10.6 kJ/mol lower in energy than the infinitely separated fragments, the model intermolecular potential fit by Bettens, Huber and Bauder indicated an intermolecular potential well of less than half that depth (4.5 kJ/mol). It is worth noting, however, that the potential well depth determined by Bettens, Huber and Bauder was quite sensitive to the form of the model potential used to fit their experimental data. In that work a model potential based on a three parameter Morse potential rather than a two parameter Lennard-Jones potential lead to high correlation between the potential well depth and the other potential parameters, indicating that the experimental data that was available for the fit was not highly sensitive to the potential well depth. Thus the potential minimum binding energy was somewhat ill-defined in their fit. The presence of intrafragment vibrations, particularly in pyrrole, may also lead to a reduced effective interfragment potential well compared to the fully relaxed structure obtained in this work, however any such effect is likely to be small.

It is unclear why Kanakaraju and Kolandaivel [3] found a structure similar to the present F4 structure to be the most stable. One possibility is that the 6-31G* basis set used by them is not sufficiently large. Fig. 3 shows that double zeta basis sets (larger than the 6-31G-series basis sets used previously) can lead to significant errors in the calculated binding energy, though presumably some of the error shown in Fig. 3 was due to BSSE which can be approximately corrected for by applying the usual counterpoise procedure.

For the pyridine...CO complex the confirmation of the preferred structure of Bettens and Bauder [2] was not as straight-forward. In this work S1 (similar to structure I of [2]) was clearly more stable than S2 (similar to structure II of [2]). However the fact that two structures with the CO fragment bound to the pyridine ring were found to be more stable considerably weakens the support for the structure proposed by Bettens and Bauder. The S1 structure of this work is otherwise in good agreement with that previously proposed, exhibiting a fragment centre of mass separation greater than 4.6 Å and very similar interfragment orientation. The binding energy calculated in this work for S1 (7.9 kJ/mol) once more overestimates the model potential fit of Bettens and Bauder (5.8 kJ/mol), but to less a degree than in the pyrrole...CO case described above. The binding energy thus seems not to be a good discriminant between the structures that may have otherwise supported either S1 or the bound to ring structures.

A number of features of the present calculations could be used to account for the disagreement between the experimental pyridine...CO geometry and the results presented above. Though the MP2 formulation has been used successfully in the past for similar complexes [7,4–6], a higher level of theory may be required. No correction for BSSE has been applied in this work, though the results presented in Fig. 3 suggest that the cc-pVQZ basis set used gives results close to the basis set limit. Zero-point energy (ZPE) corrections have not been applied. While ZPEs calculated for similar complexes are not particularly large

(1.4–3.9 kJ/mol [7,4]), Ikeshoji and Nakanaga [7] showed that different configurations of the aniline···CO complex could vary in ZPE by up to 1 kJ/mol. Such a variation in the considered pyridine···CO clusters could potentially render S1 or S2 the most stable.

5. Conclusion

In this work, the energetics of various configurations of pyrrole···CO and pyridine···CO have been investigated. The principle aim was to determine which of the structures determined by Bauder et al. [1,2] were the most stable structures. In both cases the “preferred” structures (F1 and S1) were found to be significantly more stable than the competing structures previously proposed (F2 and S2). However, in the case of pyridine···CO this picture was complicated by finding two structures of a completely different geometry, with the CO fragment bound to the face of the pyridine ring, that were more stable. Bettens and Bauder [2] reported finding no evidence for such a structure despite looking specifically for it. No explanation for this discrepancy has been definitively identified.

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