DETECTION OF LATENT FINGERPRINTS WITH CYANOACRYLATES: NEW TECHNIQUES INVOLVING COLOURED AND PHOTOLUMINESCENT COMPOUNDS

A THESIS
SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY OF THE AUSTRALIAN NATIONAL UNIVERSITY
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May, 1986
The work described in this thesis is my own, except where specific reference is made to the contributions of other workers.

(S J YONG)
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ACKNOWLEDGEMENTS

It is with great pleasure that I express my sincere gratitude to Professor R.N. Warrener for his advice as my supervisor, and for the opportunity of doing my PhD in the Department of Chemistry.

I wish to thank my other supervisor, Dr. P.A. Margot, for his invaluable assistance, and Dr. H.J. Kobus and Mr. M. Stoilovic for their support and encouragement.

I am grateful to Dr. M. Rasmussen for his constructive comments on the early drafts of this thesis and to all members of staff in the Department for their assistance and co-operation.

I am, furthermore, grateful to the Australian National University for the financial assistance in the form of an A.N.U. Scholarship.

Finally, I must express my sincere appreciation to my wife for her tremendous support and understanding during the course of my studies at the A.N.U.
Various alkyl and aryl 2-cyanoacrylate polymers have been prepared and tested as fingerprint reagents. The methyl and ethyl ester polymers, when thermally depolymerised into their monomeric forms, showed selective repolymerisation which outlined the latent fingerprint ridges with a white layer of polymer. The phenyl ester showed selective deposition, but without the white colour and, therefore, the developed prints lacked contrast. The visibility of these prints has been enhanced by staining with fluorescent dyes.

A new apparatus is described which can be primed with either the 2-cyanoacrylate polymers or standard monomeric Superglues. This apparatus has a controlled heater which allows depolymerisation of the solid Superglue to form the cyanoacrylate monomer in situ and promotes rapid development of latent prints. It is termed the Rapid Vaporisation Technique (RVT) system and can be used to advantage with other solid compounds.

New formulations and fluorescent stains based on 4-chloro-7-nitrobenzofurazan are reported for improving the visualisation of cyanoacrylate-developed prints. The combination of RVT and fluorescent staining is especially effective and has found significant use in case work. However, on plastic-based and more porous surfaces, such as leather and glossy paper, an unacceptably high background was observed. A new technique called the Triple Treatment Technique (TTT) which is a combination of the RVT, metal deposition and fluorescent staining was developed and the improvement on the development of latent prints is remarkable.

A series of "one-stage" coloured and fluorescent solid compounds based on anthracene/2-cyanoacrylate and anthracene/2-cyanoacrylamide adducts were prepared and evaluated as fingerprint reagents. The coloured adducts lacked selectivity and
sensitivity and were found unsuitable. One of the fluorescent adducts, anthracene/(2-(7-nitrobenzofurazan-4-yl)aminoethyl) 2-cyanoacrylate adduct, showed reasonably good selectivity and sensitivity on a variety of substrate surfaces including polished leather and glossy paper.
CHAPTER ONE

INTRODUCTION
1.1. Types of Fingerprint Patterns

The friction skin ridges, present on the hands and feet at birth and persisting unchanged through life, have their own unique pattern and are capable of differentiating each individual from all others. They provide a practical means of infallible personal identification.

The science of fingerprint identification is based upon the ridge outlines of skin on the insides of the fingers and thumbs. The “friction skin” covering the palmar and plantar surfaces of the body is of equal value for the purposes of identification, but that of the fingers are more commonly used for classification and identification as they are most convenient for this purpose. The ridges on the skin of the first joints of fingers follow patterns of a definite design which are divided into four main types: Arches, Loops, Whorls and Composites (Figure 1.1). In the Arch type the ridges run from one side to the other, making no backward turn. The Loop pattern consists of one or more free recurving ridges and one point of delta (the point nearest to, and in front of, the divergence of ridges). In a Whorl some of the ridges make a turn through at least one circuit; there are two deltas. The Composite pattern is composed of two or more different patterns, separate and apart, exclusive of the arch.
1.2. Classification Systems

Fingerprint patterns are used for the classification of fingerprints which is simply the process of putting them into groupings. The purpose of a classification system is to facilitate the filing, searching and retrieval of recorded fingerprints. Based on the class characteristics of all of the ten fingers of individuals, the Henry System [Henry, 1900] yields a consistent unique descriptor which utilises both the letters of the alphabet and numerical figures. Its use is limited to determining the identity of an individual who is available to provide fingerprints. The Henry system, devised between 1894 and 1897, was first adopted in the various State Police Departments throughout Australia during the years 1903-1906. Since then, the system has been modified to handle large numbers of fingerprints.

As a means of identifying latent fingerprints from scenes of crimes five-finger and single-finger systems have been developed. No system has yet been developed to yield an unique descriptor of a single-fingerprint. The best that can be done is to classify similar fingerprints together by some systems for final comparison by the eye. In the Battley Single Fingerprint Classification System, the definitions for the fingerprint patterns conform to those used in the Henry system. However, Loops which appear to be Tented Arches and Whorls which appear to be Twinned Loops or Accidentals are filed according to the most obvious pattern rather than the one technically correct.

To identify a particular print as having been made by a particular person, the ridge characteristics or minutiae are considered with respect to their location, appearance and orientation when comparing two prints. Examples of ridge characteristics are: bifurcations (points where a ridge divides into two ridges), ridge endings, lakes (points where a ridge splits and then rejoins again forming an enclosure) and short ridges (Figure 1.2). Currently, there is no valid basis for requiring that a pre-determined minimum number of ridge characteristics must be present in two fingerprints in order to establish a positive identification. Minimum
Figure 1.2. Ridge Characteristics

- Short ridge
- Lake
- Bifurcation
- Ridge endings
quantitative standards for proof of identity range from 16 required by Scotland Yard and 17 in France to, reportedly, three in Bombay [Cowger, 1983].

Large single-fingerprint collections become too tedious to search manually. Computer systems costing many millions of dollars have been developed commercially (e.g. NEC, Printak and Logica). They do not use the pattern systems except for rough classification. Instead, the x, y coordinates and ridge direction of each characteristic of an inked print is determined automatically and stored in memory. The coordinates of the characteristics of an unknown latent are determined by a human operator. The computer then compares these sets of coordinates rapidly and produces a number of likely matches for final comparison by the human eye [Millard, 1974; Banner et al., 1974; Weigstein, 1974].

1.3. Detection of Latent Fingerprints
1.3.1. Nature of Latent Fingerprints

The detection of a latent or concealed fingerprint on a given surface involves the exploitation of the differences in the chemical composition and/or physical properties of the latent print material and the substrate. The primary components of a latent fingerprint are the excretions of the eccrine (sweat) and sebaceous (oil) glands and occasionally contaminated with that of the apocrine glands. The eccrine are the only glands in the ridged skin and they are distributed in excess of 400 cm\(^{-2}\). The sebaceous glands are most abundant on the face, and the apocrine glands in the armpits, the chest, abdominal and genital areas. Eccrine glands secret water, amino acids, urea, lactic acid, sugars, creatinine, choline, uric acid, chlorides, ammonia, metals (as salts), sulphates and phosphates. The sebaceous type secrets sebum which is composed of fatty acids, glycerides, wax esters, squalene, cholesterol and hydrocarbons (Table 1.1.). Proteins, carbohydrates, cholesterol and iron are secretions of the apocrine glands [Knowles, 1974].
The persistence of a latent print depends on the nature of the deposited material and that of the substrate. Smooth non-porous surfaces such as glass or chromed metal are excellent surfaces for the retention of greasy prints. Porous surfaces, such as paper and cardboard, absorb fingerprint deposits rendering fingerprints left on these surfaces completely invisible. Rough and coarsely striated surfaces do not allow the deposition of continuous ridges.

Table 1.1. Composition of Sebum [Knowles,74]

<table>
<thead>
<tr>
<th>Constituents</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free fatty acids</td>
<td>30</td>
</tr>
<tr>
<td>Triglycerides</td>
<td>27</td>
</tr>
<tr>
<td>Diglycerides</td>
<td>4</td>
</tr>
<tr>
<td>Monoglycerides</td>
<td>2</td>
</tr>
<tr>
<td>Wax esters</td>
<td>22</td>
</tr>
<tr>
<td>Squalene</td>
<td>10</td>
</tr>
<tr>
<td>Cholesterol</td>
<td>2</td>
</tr>
<tr>
<td>Cholesterol esters</td>
<td>2</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>1</td>
</tr>
</tbody>
</table>

1.3.2. Methods of Detection

The use of powders is, by far, the most common method of developing latent prints. Used primarily on non-porous surfaces, powder develops latent prints when it adheres to the moist or tacky substance composing the latent print. Many different types of powder have been developed for developing latent prints. Although the use of powders is a relatively simple process, the brushing action made with the brush can cause physical distortion to the latent prints. "Magnetic" powders, which are ferrous powders applied with a magnetic wand, has the advantage of being used without damaging latent prints. Photoluminescent powders which emit brightly under
ultraviolet illumination are used to develop latent prints on multi-coloured surfaces.

The current chemical reagents for developing latent fingerprints utilise the amino acids, fats, urea and chlorides present in the fingerprint deposits (Table 1.2.). Ninhydrin (2,2-dihydroxy-1,3-indanedione) is by far the best amino acid-sensitive reagent and has been applied to fingerprint science since 1954 [Oden, 1954; Morris et al., 1974]. It reacts with amino compounds (Scheme 1.1.) to produce a purple-coloured product (Ruhemann's Purple). Fingerprints so developed can be reprocessed with solutions of some metal salts, such as zinc chloride, and a colour

Table 1.2. Suitable reagents for some constituents of the fingerprint deposit

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorides</td>
<td>Silver nitrate</td>
</tr>
<tr>
<td>Amino acids</td>
<td>Ninhydrin</td>
</tr>
<tr>
<td>Urea</td>
<td>Dimethylaminocinnamaldehyde</td>
</tr>
<tr>
<td>Sebum</td>
<td>Powders</td>
</tr>
<tr>
<td></td>
<td>Physical developer</td>
</tr>
<tr>
<td></td>
<td>Small particle reagent</td>
</tr>
<tr>
<td></td>
<td>Iodine</td>
</tr>
<tr>
<td></td>
<td>Osmium tetroxide</td>
</tr>
<tr>
<td></td>
<td>Vacuum metal deposition</td>
</tr>
<tr>
<td></td>
<td>Radioactive gases ($^{35}$SO$_2$, $^{131}$I$_2$, $^{82}$Br$_2$)</td>
</tr>
<tr>
<td></td>
<td>Superglue (ethyl 2-cyanoacrylate)</td>
</tr>
</tbody>
</table>

Scheme 1.1.
change produced. Changing the colour of ninhydrin prints has not proved to be a great advantage. However, these reprocessed fingerprints show strong luminescence under argon ion laser light [Menzel, 1982], thereby visually enhancing the print. The enhancement of ninhydrin-developed fingerprints has been improved by using cadmium nitrate for complexation in place of zinc chloride. On difficult surfaces such as newsprint, manila and yellow papers, more reproducible and superior results were obtained [Stoilovic et al., 1986]. Analogues of ninhydrin (Figure 1.3) have also been developed [Almog et al., 1982].

![Image of chemical structures](image)

**Figure 1.3. Ninhydrin and some analogues [Almog, et al., 1982]**

I 2,2-dihydroxy-1,3-indanedione (ninhydrin; purple prints)
II 2,2-dihydroxybenz[e]indane-1,3-dione (benzo[e]ninhydrin; pink prints)
III 2,2-dihydroxybenz[f]inhane-1,3-dione (benzo[f]ninhydrin; blue-green)
IV 2,2-dihydroxy-5-chloro-6-methoxyindane-1,3-dione (purple prints)
They react with latent fingerprints to give different coloured prints—a useful feature particularly on coloured papers. Ninhydrin, and its analogues, are used for developing latent fingerprints on porous substrates such as paper and some forms of plastics. Unlike other methods, the ninhydrin method demands carefully controlled working conditions to achieve optimum results. Iodine [Almog et al., 1979] develops latent fingerprints "by being absorbed into the oily or fatty matter" to give a brownish coloration. Although effective on virtually any surface, iodine-developed prints are transient and have to be "fixed" with starch or 7,8-benzoflavone [Mashiko et al., 1977; Haque et al., 1983]. $p$-$N,N$-Dimethylaminocinnamaldehyde (DMAC) [Morris et al., 1973] reacts with urea (Scheme 1.2.) present in perspiration to form an intense red colour (Schiff’s base). This reagent is suitable for use on most types of paper, but is not as certain to develop latent prints as is ninhydrin. Due to its dependence on $p$H the development of latent fingerprints with DMAC is difficult to control. Furthermore, the high acidity of the solution may be destructive to some substrates. Silver nitrate, used for developing latent prints on porous substrates such as wood, paper and cloth, reacts with the sodium chloride present in latent prints to form the highly water-insoluble and light-sensitive silver chloride. Exposure of the
silver chloride to ultraviolet or sunlight causes decomposition to silver to produce a black image of the latent print [Taylor et al., 1984]. Since sodium chloride is water-soluble, this reagent is not suitable for processing objects which have been submerged in water.

More recently, physicochemical methods, such as Physical Developers (PD) and Small Particle Reagent (SPR) [Pounds et al., 1983] have been introduced. A Physical Developer is an unstable mixture of a reducing system and a reducible metal ion. In a typical solution based on silver and ferrous/ferric ions, the generalised reversible reaction taking place can be expressed by the equation:

\[
\text{Fe}^{2+} + \text{Ag}^+ \rightleftharpoons \text{Fe}^{3+} + \text{Ag}
\]

The negatively charged silver sols, which originate spontaneously as silver nuclei in the physical developer, form positively charged micelle in the presence of a cationic surfactant, e.g. dodecylamine acetate, and are inhibited from reducing other silver ions. Preferential deposition of the silver on the fingerprint ridges is believed to be triggered by highly water-insoluble components in the fingerprint deposit [Morris, 1975]. This reagent is suitable for processing paper which has been wetted or kept in a humid atmosphere and is no longer suitable for treatment with ninhydrin (amino acids are water-soluble). It can be used as a post-ninhydrin treatment whereby fingerprints having sufficient fatty material in the deposit can be developed by PD after the initial ninhydrin treatment has failed.

The SPR, which is a suspension of small particles in a detergent, e.g. silver or molybdenum disulphide in Manoxol OT (dioctyl sulphanesuccinate), works in a similar way to physical developer. It is not as good as ninhydrin or PD on paper, but is highly effective on other surfaces such as polythene, glass and painted surfaces. Its advantage over powders is that it can be used on wet surfaces.

The autoradiographic technique is particularly useful for the detection of latent
prints on porous surfaces such as fabrics and banknotes. It involves the exposure of the sample to an environment of radioactive gas, e.g. sulphur dioxide, iodine or bromine which reacts with the unsaturated lipids [Knowles, 1974]. An autoradiograph of the fingerprint is obtained by placing the radioactive-labelled fingerprint in contact with a sheet of X-ray film [Godsell, 1972].

Other techniques employed in the detection of latent prints include the use of lasers and vacuum metal deposition. Menzel and his co-workers [Dalrymple et al., 1977] reported in 1977 that inherent luminescence from latent fingerprints could be obtained on paper using an argon ion laser as the primary light source. However, Salares, Eves and Carey [Salares et al., 1979] were unable to reproduce these results. Chemically induced luminescence where latent fingerprints are treated with suitable reagents, such as 4-chloro-7-nitrobenzofurazan and ninhydrin/zinc chloride, can be excited with an argon ion laser or with a less powerful light source. An example of such a light source is the Unilite, a Xenon arc lamp, which has proved to be a valuable and cheaper alternative to the argon ion laser [Warrener et al., 1983; Kobus et al., 1983].

In the vacuum metal deposition technique [Theys et al., 1968; Thomas, 1974], gold is evaporated and deposited as a thin layer on the surface of the sample placed in an evacuated bell jar. Cadmium or zinc is subsequently evaporated which condenses around the fingerprint ridges revealing the fingerprint image. While effective for processing fabrics, this technique demands a high precision in the amount of gold to be initially deposited on the surface of the substrate. Moreover, the physical dimension of the chamber limits the range of evidential items which can be otherwise processed with this technique.

1.4. Cyanoacrylate esters as a Fingerprint Reagent

The first cyanoacrylate adhesives* appeared on the world's market in 1958 [Coover, 1976], but their potential as latent fingerprint developer was not realised
until much later. Superglue, the household name for cyanoacrylate adhesives, is essentially a pure sample of an alkyl 2-cyanoacrylate ester which contains a stabiliser to stop premature polymerisation. Commercial preparations usually employ the methyl or ethyl ester [Coover,1976]. Some commercial adhesives which can be used to develop latent fingerprints include Repco Super Glue 3™ (Loctite, Ireland), Cyanobond RP™ (Sumito Chemical Co., Japan) and Selleys Supa Glue™ (Australia). In each of these adhesives the major component is ethyl 2-cyanoacrylate (98-99%).

Norkus [Norkus,1982] reported that the Tokyo Metropolitan Police were conducting research into latent fingerprint development with glue fumes in 1978. The glue was claimed to work on tape, plastic and glass. In 1980, through Norkus, Kendall who worked at the Bureau of Alcohol, Tobacco and Firearms, Atlanta, USA, began his research on evaluating Superglue as a latent print developer on various articles, including aluminium foil, candy wrappers, cash boxes and plastic bags [Kendall,1982a]. At about the same time a chance observation by Edmunds and Wood of the Northamptonshire Police, England, that the vapour from Loctite Super Glue 3% developed latent fingerprints on a black plastic surface, led to the Home Office Central Research Establishment (HOCRE) investigating this fingerprint development method [Dabbs,1980]. Bourdon, a member of the North Bay Police in Canada, was also an early exponent of the cyanoacrylate technique. His research has since culminated in a marketed kit - Visuprint fuming chamber- for which he gained patents and is sold through Payton Scientific [Marshall,1983].

The use of Superglue (alkyl 2-cyanoacrylate esters) vapour to develop latent fingerprints has become a routine method in many fingerprint bureaux worldwide [Ball,1982]. Initial research conducted by Dr. H. Kobus in this laboratory in 1981 has shown this method to be simple and sensitive and particularly suited to polythene

* "Cyanoacrylate adhesives" and "Superglue" refer to alkyl 2-cyanoacrylate esters
and aluminium foil surfaces. Other qualities observed of the developed prints were the ease of visualisation and stability on the substrate surface. A vast potential was anticipated of this method and it forms the basis of research in this thesis.

1.4.1. Preparation and Properties of alkyl 2-cyanoacylates

One method of preparing alkyl 2-cyanoacylates involves the pyrolysis of an alkyl 3-acyloxy-2-cyanopropionate to give the desired alkyl 2-cyanoacylate and a carboxylic acid (Scheme 1.3.) [Adris, 1949]. In the second method, an alkyl cyanoacetate is condensed with formaldehyde to give a poly(alkyl 2-cyanoacylate) which is thermally depolymerised to yield a 2-cyanoacrylate ester (Scheme 1.4).

\[
\begin{align*}
\text{R'COO-CH}_2\text{CH-COOR} & \rightarrow \text{CH}_2=\text{C-COOH} + \text{R'COOH} \\
\text{CN} & \\
\text{R'COO-CH}_2\text{CH-COOR} & \rightarrow \text{CH}_2=\text{C-COOH} + \text{R'COOH} \\
\text{CN} &
\end{align*}
\]

Scheme 1.3.

\[
\begin{align*}
\text{NCCH}_2\text{CO}_2\text{R} + \text{HCHO} & \rightarrow \text{CH}_2=\text{C-CO}_2\text{R} \\
\text{CN} & \\
\text{CH}_2=\text{C-CO}_2\text{R} & \rightarrow \text{CH}_2=\text{C-CO}_2\text{R} \\
\text{CN} &
\end{align*}
\]

Scheme 1.4.
This condensation-depolymerisation process has been adopted by Eastman Kodak Company for the manufacture of industrial 2-cyanoacrylate adhesives. More recently, a new procedure was reported. It involves the synthesis of an anthracene/2-cyanoacrylate adduct as an intermediate [Ray et al., 1969].

Polymerisation of alkyl 2-cyanoacrylate is initiated by bases and free radicals and the monomer must be stabilised by anionic inhibitors, such as metaphosphoric acid, phosphorus pentoxide, maleic acid and sulphur dioxide, and free-radical inhibitors including hydroquinone and catechol.

The electronic configuration of the alkyl 2-cyanoacrylates is responsible for their unique properties, such as the ability to polymerise rapidly at room temperature without the addition of a catalyst and the ability to form strong adhesive bonds. The fast forming adhesive bonds are the result of an anionic polymerisation initiated by weakly basic species. Polymerisation then propagates through the resultant carbanion (Scheme 1.5.) [Coover, 1976; Lee et al., 1984].

Scheme 1.5.
It is the combined resonance stabilising effects of both nitrile (-CN) and alkoxy carbonyl (-COOR) groups (Figure 1.4) which stabilises the anion and allowing the propagation to proceed to high molecular weight polymer. Attempts to replace the nitrile with nitro, chloro, \textit{p}-nitrophenyl and chlorosulphonyl groups have resulted in monomers which proved to be either unresponsive or too dynamic as adhesives [Ball, 1982].

1.4.2. Techniques for Accelerated Development of Latent Fingerprints

To date, the mechanism of latent fingerprint development using cyanoacrylate is largely unknown. Tuthill [Tuthill, 1982] postulated that "the latents are made visible as a result of the absorption of the glue vapours into the lipids and perspiration of the latent" and that "the vapours then polymerise in the print forming a hard white ridge deposit". While agreeing to the fact that components of the latent print deposit are capable of initiating the polymerisation of cyanoacrylate (Appendix 1), the need for cyanoacrylate vapours to be absorbed into the lipids before polymerisation takes place is both unlikely and unnecessary. Indeed reference to Figure 1.5 shows polymer chains grow out from the surface of the fingerprint deposit.
Attempts have been made to shorten the development time required to effect polymerisation of cyanoacrylate on the latent fingerprints. Kinetically, in a linear addition polymerisation the rate of propagation is proportional to the monomer concentration and the square-root of the initiator concentration [Hiemenz, 1984]. Therefore, by increasing the concentration of the cyanoacrylate vapour through accelerated vaporisation, development of latent fingerprints is speeded up.

Watkin [Watkin, 1983] of the National Research Council, Canada, carried out the development in an evacuated desiccator. The reduced pressure promotes vaporisation of the cyanoacrylate monomer placed in the bottom of the desiccator. The main disadvantage of this technique is the physical size of the desiccator which limits the range of articles that can be processed. The Visuprint, mentioned earlier, relies on a fan to effect vaporisation of the monomer in the chamber. Kendall and Rehn [Kendall et al., 1982] reported that cotton pads treated with sodium hydroxide promoted the release of cyanoacrylate fumes. They termed this technique the "Rapid Method of Superglue Fuming". In this technique, the accelerated vaporisation of
cyanoacrylate is caused by the heat generated from the exothermic polymerisation reaction of cyanoacrylate which is initiated by sodium hydroxide. It is an inefficient technique in that only some of the Superglue is effectively used (Appendix 2). Kendall [Kendall et al., 1982b] also used other chemicals such as triethylenediamine, \( N,N,N',N' \)-tetramethylethylenediamine and sodium bicarbonate. These chemicals released the fumes in a shorter time, but caused the cyanoacrylate to deposit indiscriminately on the substrate surface.

Dabbs and Jones [Dabbs et al., 1980] observed that the development of latent prints with cyanoacrylate adhesives at elevated temperatures was accelerated, but they stated that "heating the adhesive produces two undesirable effects, a) the reaction is less selective for fingerprints, because of the marked increase in fogging, b) the drops of adhesive polymerise too readily". Here in our laboratory, a carefully designed apparatus, the Rapid Vaporisation Technique (RVT) system (see Appendix 2), is used and no undesirable effects are observed. The RVT involves direct heating of the cyanoacrylate ester in an enclosed chamber in which the article to be processed is placed. Since the development of this apparatus, Olenik [Olenik, 1984] introduced the use of a light bulb as a heating device for the rapid vaporisation of Superglue. With this latter technique, the development of latent prints is difficult to control because the rate of heating cannot be controlled accurately.

1.4.3. Techniques of Enhancing Cyanoacrylate-developed Prints

Although strong cyanoacrylate-developed prints can be easily visualised and photographically recorded, weaker prints and those on light-coloured surfaces are often difficult to read because of insufficient contrast between the ridges and the surface of the substrate. Enhancing the visibility of such prints is therefore an advantage.

Photographically, cyanoacrylate-developed prints can be recorded by use of
oblique and axis lighting [Pfister, 1985], but only if the prints are reasonably strong. Dabbs and Jones [Dabbs et al., 1980] have reported the use of powders for improving the visibility of cyanoacrylate-developed prints. They found that Bristol Black was one of the more generally useful powders. This method is only good for smooth non-porous surfaces such as glass, perspex and chromed metal (Figure 1.6.).

Figure 1.6. Fresh fingerprint on perspex developed with Superglue and enhanced with Carbon Black.

Staining is an effective method of visually enhancing weak cyanoacrylate prints. Gentian Violet (Basic Violet 3) and coumarin 540, a fluorescent dye, were found to be particularly effective on clear polythene and reflective surfaces such as aluminium and chromed surfaces, respectively [Kobus et al., 1983]. Likewise, a relatively cheap fluorescent water-tracing dye was introduced by Olsen [Olsen, 1984] for use on metal and glass. Menzel and his co-workers [Menzel et al., 1983] were able to obtain favourable results from the use of Rhodamine 6G and the ninhydrin/zinc chloride
treatment for the enhancement of cyanoacrylate-developed prints in conjunction with the argon ion laser.

1.4.4. Advantages of the Cyanoacrylate Technique

Cyanoacrylate esters proved useful as a latent fingerprint developer. They comply with certain criteria desirable for latent fingerprint detection. These criteria include:

(1) high sensitivity to one or more major components of the fingerprint deposit (Appendix 1);
(2) ability to develop latent prints without physically destructing or distorting the ridges of the print as is the case with brushes used to dust latent prints;
(3) ability of the developed print to withstand harsh physical secondary treatment (e.g. enhancement by dusting) and to remain permanent under normal laboratory conditions;
(4) ability to develop latent fingerprints on a wide variety of surfaces [Jones, 1980];
(5) ability to develop aged latent fingerprints [Kendall, 1982a; Jones et al., 1980];
(6) ability to be used as a latent fingerprint developer without deployment of complicated and expensive supporting equipment requiring special operating skills, c.f. the laser and vacuum metal deposition unit.

The high selectivity and sensitivity of 2-cyanoacrylate ester as a latent fingerprint reagent is demonstrated by the clarity of the sweat pores present in the developed print (Figure 1.7.). The cyanoacrylate technique is therefore not only useful for the fingerprint examiner, but also to those working in the fields of edgeoscopy (the identification of persons by way of ridge edges) and poroscopy (the study of sweat pores on ridges) [Ashbaugh, 1982a, 1982b, 1983].
1.4.5. Disadvantages of the Cyanoacrylate Techniques

(1) In the liquid monomeric form, cyanoacrylate ester bonds skin and has to be handled with extreme care;

(2) Although the developed print is harmless, the developing vapour can be very irritating to the eyes and the respiratory tract;

(3) Cyanoacrylate ester, commercially available in tubes and in packets in the gel-form (Hard Evidence, Loctite) are relatively expensive;

(4) Development of latent prints on porous surfaces, such as newsprint paper, is not normally possible; and

(5) The currently used cyanoacrylate esters lack colour or photoluminescence which limits visualisation on some surfaces.

1.5. Aims of the Research

(1) Study the mechanism of interaction of cyanoacrylate ester with fingerprint deposits;
(2) Study and evaluate current techniques of developing latent fingerprints with cyanoacrylate and develop a more practical and efficient technique;

(3) Investigate methods of improving the visibility of cyanoacrylate-developed prints:
   (a) by preparing new fluorogenic stains to enhance the visibility of pre-formed cyanoacrylate print;
   (b) by chemically modifying deposited cyanoacrylate so that a fluorescent print can be obtained; and
   (c) by preparing coloured or photoluminescent "one stage" or "instant" fingerprint reagents.

This thesis entails, first, the synthesis and evaluation of new photoluminescent stains for the visual enhancement of cyanoacrylate-developed prints. Second, the development of the Triple Treatment Technique for detecting latent prints on semi-porous surfaces such as glossy paper and polished leather. Third, the preparation and evaluation of cyanoacrylate polymers and solid Superglues (adducts) as potential sources of cyanoacrylate monomers useful as fingerprint reagents. And finally, the synthesis and evaluation of new coloured and photoluminescent cyanoacrylates as "one-stage" fingerprint reagents.
CHAPTER TWO

VISUAL ENHANCEMENT OF CYANOACRYLATE-
DEVELOPED FINGERPRINTS
2. INTRODUCTION

Latent fingerprints on clear polythene, aluminium foil and chromed surfaces developed with ethyl 2-cyanoacrylate (Super Glue 3™, Loctite) are usually easy to visualise and consequently, to photograph, because of good contrast between the white ridges and the surface of the substrate. However, the visualisation of such prints on light-coloured or multi-coloured substrates, such as printed white polythene bags and ice cream or yoghurt containers, is often difficult. Useful prints can be missed during examination of an evidential item because of background interference with the faint white ridges produced by the cyanoacrylate.

Menzel and his co-workers [Menzel et al., 1983] stated that latent prints developed with Superglue were fluorescent. This fluorescence is not particularly intense and of little value unless the sample is illuminated using a powerful excitation light source such as an argon-ion laser. A more practical method of improving the visibility of cyanoacrylate-developed prints was reported by Kobus, Warrener and Stoilovic [Kobus et al., 1983]. They found that Gentian Violet, a visible dye, and Coumarin 540, a fluorescent dye, were particularly suited for staining weak cyanoacrylate-developed prints on clear polythene and reflective surfaces such as aluminium foil and chrome, respectively. However, when using these stains in general case work we observed some drawbacks. It was found that Gentian Violet was generally not sensitive enough and that there was an inconsistency in quality between stained prints. With Coumarin 540, an unacceptably high background fluorescence was obtained on white polythene and some plastic-based surfaces (Figure 2.1).

The background fluorescence could be due to the reaction between the substrate surface and the solvent(s) used in the stain formulations resulting in the penetration and retention of the stain in the surface. The Gentian Violet solution introduced by Kobus [Kobus et al., 1983] was prepared by dissolving the compound (5 g) and
phenol (10 g) in ethanol (50 ml) and diluted to 150 ml with water. The Coumarin 540 was prepared by dissolving the compound (0.01 g) in ethanol (150 ml). After several trials with other solvents including tetrahydrofuran, acetonitrile, 1,1,2-trichlorotrifluoroethane and butanol, it was found that new formulations based on acetonitrile and 1,1,2-trichlorotrifluoroethane (see Section 5.1.) gave more consistent results with Gentian Violet, but no improvement in sensitivity. Whereas with Coumarin 540, the background fluorescence was greatly reduced. However, on weak prints the results were still not satisfactory.

It was observed that the Stoke's shift (difference between excitation and emission maxima) of cyanoacrylate-developed prints stained with Coumarin 540 (see Figure 2.2.1.b.) was narrow (53 nm), which imposed limitations on the selection of filters. In order to avoid overlap of the excitation spectrum with transmittance, a compromise had to be reached at the expense of excitation and emission efficiencies [Kobus et al., 1983]. Stains with better spectroscopical characteristics and efficiency were developed to overcome these drawbacks.

Figure 2.1. Fingerprint on PVC sheet developed with Superglue and subsequently stained with Coumarin 540 [Kobus et al., 1983].
2.1. New Stains

In developing a new stain the following criteria were considered.

1. The stain had to be photoluminescent for high sensitivity;
2. It had to have high quantum yield [Guilbault, 1973]) so that the light source would not be a limiting factor and a relatively low-powered source could be used efficiently;
3. Its excitation wavelength should preferably be in the visible region so that it can be used on articles which fluoresce strongly under ultraviolet light;
4. Its excitation and emission maxima had to be as far apart as possible for easier selection of appropriate filters and better efficiency; and
5. Ability for different substituent groups to be attached thereby offering the potential for improved adsorption selectivities.

4-chloro-7-nitrobenzo-2-oxa-1,3-diazole (or 4-chloro-7-nitrobenzofurazan; NBD-Cl), introduced by Ghosh and Whitehouse [Ghosh et al., 1968a, 1968b; Imai et al., 1981] as a fluorogenic reagent for amines, has been used for the detection of latent fingerprints on paper [Salare et al., 1979; Kobus et al., 1983]. In view of the excitation maximum occurring outside the ultraviolet region and the high quantum yield of NBD-amino derivatives, the development of new stains was based on this reagent. NBD-Cl, a stable non-fluorescent compound undergoes nucleophilic substitution with an amine as shown in Scheme 2.1.

Seven amino derivatives of NBD-Cl were prepared using butylamine, diethylamine, ethanolamine, \( p \)-aminophenol, decylamine, octadecylamine and alanine (see Experimental Section 5.2.).

2.1.1. Results and Discussion

Of the seven NBD-amino derivatives prepared only NBD-\( p \)-aminophenol was non-fluorescent. It was therefore excluded from further evaluation.
Excitation and emission spectra of the remaining six fluorescent derivatives and Coumarin 540, in solution and solid (as stained prints) forms are shown in Figures 2.1.1 (a) and 2.1.1 (b). The fluorescence intensity of equimolar of each NBD-amino derivative in solution was recorded relative to that of Coumarin 540 which was set at 100%. All derivatives are 10-20% less fluorescent than Coumarin 540 except for NBD-diethylamine which is approximately 30 times less fluorescent. Here, it seems that a tertiary amino derivative of NBD is less fluorescent than a secondary one. This is attributed to steric interference which hinders the planarity (an essential feature of photoluminescent compounds) of the molecule [Wehry, 1973]. Likewise, the p-aminophenol derivative is not photoluminescent because the bulky phenyl group sterically hinders the planarity of the molecular structure and it also conjugates with the nitrogen lone-pair resulting in restricted conjugation with the benzozaadiazole nucleus [Ghosh et al., 1968].

The corrected excitation and emission spectra of all the cyanoacrylate-developed prints stained with the various solutions were recorded and shown with both the maximum excitation and emission peaks at full scale (100%). This is necessary because relative intensity can not be accurately measured from stained ridges. These
Figure 2.1.1.a. Corrected excitation and emission spectra of NBD-amino derivatives (in solution) with fluorescence intensity relative to that of Coumarin 540.
Figure 2.1.1.b. Corrected excitation and emission spectra of NBD-amino derivatives and Coumarin 540 (as stained cyanoacrylate prints) with spectral peaks at full scale (100%).
latter spectra provide accurate data for the selection of optimum filters for both the excitation and visualisation of prints stained with the new compounds. The quality of a stained print was assessed visually. Spectroscopic data of the various NBD-amino derivatives in solution and as stained cyanoacrylate prints are summarised in Table 2.1.1.a.

Table 2.1.1.a. Excitation and Emission Maxima of NBD-amino Derivatives in Solution and on Cyanoacrylate Deposit.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solution</th>
<th>Stained Prints</th>
<th>Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{ex}$</td>
<td>$\lambda_{em}$</td>
<td>$\Delta \lambda$</td>
</tr>
<tr>
<td>Coumarin 540</td>
<td>475</td>
<td>496</td>
<td>53</td>
</tr>
<tr>
<td>NBD-butylamine</td>
<td>447</td>
<td>523</td>
<td>90</td>
</tr>
<tr>
<td>NBD-diethylamine</td>
<td>446</td>
<td>533</td>
<td>90</td>
</tr>
<tr>
<td>NBD-ethanolamine</td>
<td>448</td>
<td>532</td>
<td>90</td>
</tr>
<tr>
<td>NBD-alanine</td>
<td>448</td>
<td>523</td>
<td>81</td>
</tr>
<tr>
<td>NBD-decylamine</td>
<td>447</td>
<td>524</td>
<td>82</td>
</tr>
<tr>
<td>NBD-octadecylamine</td>
<td>447</td>
<td>524</td>
<td>67</td>
</tr>
</tbody>
</table>

The spectra of the various compounds in the solution and solid (as stained prints) forms were compared and the following were observed:

(a) The excitation maxima of Coumarin 540 in the solid form has shifted to a lower wavelength (from 475 to 449 nm);

(b) The excitation maxima of the six NBD-amino derivatives shifted by 3-8 nm (to longer wavelengths) due to "solvent" effects of the solid cyanoacrylate polymer [Menzel et al., 1983];

(c) While the emission maximum for Coumarin 540 shifted by 6 nm (496-502 nm), that of the NBD-amino derivatives (except NBD- octadecylamine which shifted by 5 nm, from 524 to 519 nm) have shifted by 9 to 20 nm; and
(d) Except for NBD-octadecylamine, the Stoke's shifts of the stained prints were greater than that of the corresponding solutions.

As shown in Table 2.1.1.a., NBD-butylamine, NBD-ethanolamine and NBD-diethylamine, on stained cyanoacrylate-developed prints, have the greatest Stoke's shift ($\Delta \lambda_{\text{max}}$) of 90 nm while Coumarin 540 has the smallest shift of 53 nm. Based on these spectroscopical characteristics, the best stains would be NBD-butylamine, NBD-diethylamine and NBD-ethanolamine, and the worst, Coumarin 540. Consequently, the choice of optimum filters for the "best" stains is made easier without having to compromise for loss in excitation and emission efficiencies.

Detailed results from the assessment of the various NBD-amino derivatives, Coumarin 540 and Gentian Violet (as controls) on a variety of substrate surfaces (see Section 5.2.c.) are shown in Table 2.1.1.b.

On clear polythene, all the test stains showed good to very good selectivity* and sensitivity* (see Table 2.1.1.b. and Figures 2.1.1.c. and 2.1.1.d.). Cyanoacrylate-developed prints stained with NBD-amino derivatives were highly fluorescent and the use of a Xenon arc lamp (Unilite) for illumination was more than adequate. The NBD-diethylamine derivative, although much less fluorescent in solution, is visually as good as other derivatives when used to stain cyanoacrylate-developed prints. Nevertheless, none of the stains was suitable for the enhancement of cyanoacrylate prints on painted (acrylic paint) aluminium. The background fluorescence was so high that the fingerprints were virtually invisible. On glass, plain aluminium, PVC and white polythene, fresh latent prints developed with Superglue and subsequently

---

* The selectivity of a fingerprint reagent is taken as the ability of the compound to be preferentially deposited on the fingerprint ridges. The sensitivity of the reagent is the visibility of the developed print.
Table 2.1.1.b. Quality Grading of cyanoacrylate-developed prints stained with the various compounds

<table>
<thead>
<tr>
<th>SURFACE</th>
<th>AGE</th>
<th>RIDGE FLUORESCENCE (Sensitivity)</th>
<th>BACKGROUND FLUORESCENCE (Selectivity)</th>
<th>OVERALL QUALITY*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>S1</td>
<td>S2</td>
<td>S3</td>
</tr>
<tr>
<td>Glass</td>
<td>Fresh</td>
<td>4</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>2-week</td>
<td>4</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Painted</td>
<td>Fresh</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Aluminium</td>
<td>2-week</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Fresh</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>(plain)</td>
<td>2-week</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>PVC</td>
<td>Fresh</td>
<td>4</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>2-week</td>
<td>1</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Clear</td>
<td>Fresh</td>
<td>4</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Polythene</td>
<td>17-month</td>
<td>4</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>White</td>
<td>Fresh</td>
<td>4</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Polythene</td>
<td>1-week</td>
<td>4</td>
<td>6</td>
<td>5</td>
</tr>
</tbody>
</table>

S1 = Coumarin 540; S2 = NBD-butylamine; S3 = NBD-diethylamine; S4 = NBD-ethanolamine; S5 = NBD-alanine; S6 = NBD-decylamine; S7 = NBD-octadecylamine; S8 = Gentian Violet

*Overall Quality = [(sensitivity + selectivity)/2]
Figure 2.1.1.c. Fingerprints on clear polythene developed with Superglue and subsequently stained with Coumarin 540 (A), NBD-butylamine (B), NBD-diethylamine (C) and NBD-ethanolamine (D).
Figure 2.1.1.d. Fingerprints on clear polythene developed with Superglue and subsequently stained with NBD-alanine (E), NBD-decylamine (F), NBD-octadecylamine (G) and Gentian Violet (H).
enhanced with NBD-amino derivatives (S2-S7) were of moderately good quality.

Aged (one week to 17 months) latent prints on these surfaces thus enhanced were generally not improved with any of the stains. However, NBD-ethanolamine, NBD-alanine and Gentian Violet did produce fairly good-contrast prints on white polythene.

Generally, all the fluorescent test stains (including Coumarin 540) had high affinity for the deposited cyanoacrylate polymer, as shown by the high fluorescence intensity of the stained ridges. The NBD-amino derivatives worked particularly well on clear polythene because they have virtually no affinity for the rather inert substrate surface. With Coumarin 540, the visible low background fluorescence could be due to interactions between the substrate surface and the compound itself. Gentian Violet works well on cyanoacrylate-developed prints which have a thicker deposit of cyanoacrylate over the ridges. The visibility of a developed fingerprint is dependent on the contrast between the ridges and the surface. With prints stained with Gentian Violet, this contrast depends on (a) the difference between the absorption maxima of the substrate surface and the stained ridges, and (b) the amount of dye present in the stained ridges. For the best contrast, both the difference in absorption maxima and the amount of dye in the ridges should be as large as possible. Thus, if a developed print has a relatively thin layer of cyanoacrylate deposit over the ridges, the amount of absorbed dye would be too small for sufficient incident light to be absorbed (i.e. transparent), resulting in poor contrast. With prints stained with fluorescent compounds, the contrast is determined by the emitted light from the stained ridges against a dark background through the use of appropriate filters. Usually, less of a fluorescent stain (and correspondingly less cyanoacrylate deposit) is required for the same degree of contrast than with a visible stain.

Despite the different substituents (alkyl, carboxylic and hydroxyl) attached to the various NBD-amino derivatives, the use of these new fluorescent stains on
plastic-based surfaces such as PVC, white polythene and painted surfaces was still not satisfactory in that the background fluorescence, although greatly reduced on some surfaces, was yet to be completely eliminated. This observation can be attributed to the solvent system of the staining solutions whereby one of the solvents used, acetonitrile, which make up only 10% of the total solvent volume, swells the plastic surface allowing the stain to penetrate and remain in the surface, in much the same way as the stain in the cyanoacrylate deposit is retained. Incidentally, it was found that cyanoacrylate polymer is soluble in neat acetonitrile and that increasing the proportion of acetonitrile in the stain formulation above 10% caused the cyanoacrylate-developed prints to deteriorate. As a means of minimising chemical attack on these surfaces, the proportion of acetonitrile could be reduced, but the amount of soluble compound is correspondingly reduced. Re-formulating the stains by using different solvent systems is a possible option but certainly not practical considering the number of different surfaces encountered.

2.1.2. Alternative Methods of Enhancing Cyanoacrylate-developed Prints

In an alternative approach to the enhancement of cyanoacrylate-developed prints, fluorogenic compounds were co-vapourised with Superglue in a chamber in which the articles were suspended. A series of fluorogenic compounds [Seitz, 1980; Ohki, 1976; Mayer et al., 1978; Lee et al., 1979] including fluorescamine, 4-chloro-7-nitrobenzofurazan, o-phthaldialdehyde, 4-dimethylaminocinnamaldehyde (DMAC), Rhodamine 6G, Coumarin 540, anthracene and NBD-butylamine were tested (see Experimental Section 5.3). Most of the developed prints were not fluorescent. Those developed with 4-dimethylaminocinnamaldehyde were fluorescent, but as shown in Figure 2.1.1.e., the fluorescence was unevenly distributed over the print. With anthracene,
the developed print was virtually invisible because of the high background fluorescence caused by the lack of selectivity of the compound.

Attempts were also made to chemically modify the deposited cyanoacrylate polymer so that chromophoric tags could be introduced and a fluorescent print obtained. Some of the attempts made included the reduction of the nitrile (-CN) group with lithium aluminium hydride (LiAlH₄) in dry ether to give (-CH₂NH₂) and reacting the latter with an amine-sensitive fluorogenic reagent, 4-chloro-7-nitrobenzofurazan. 8-aminoquinoline, which has the potential of forming photoluminescent metal complexes [Fanning et al., 1965; Casabo et al., 1976] was reacted with poly(ethyl 2-cyanoacrylate ester) according to DeFeo [DeFeo et al., 1963] (in tetrahydrofuran with sodium methoxide as catalyst) and Singh [Singh, 1971] (with sodium hydride in dimethylsulfoxide). Transesterification of the polymeric cyanoacrylate ester with 8-quinolinol, which also form photoluminescent metal complexes

Figure 2.1.1.e. Fingerprint on clear polythene developed by co-vaporisation of DMAC and Superglue as seen under white light (A), and Unilite (Xenon arc lamp) with 470 nm excitation and 550 nm barrier filters (B).
[White, 1960, 1964, 1966; Ohnesorge et al., 1962; Stepanora et al., 1978], in the presence of potassium fluoride [Polyakova et al., 1967] was tried, too. All these attempts were not successful.

2.2. The Development of the Triple Treatment Technique (TTT)

The nature of the substrate surface is often the source of the problem of visualising cyanoacrylate-developed prints subsequently stained with a fluorescent compound. By rendering it impermeable to stains, it is possible to overcome this problem. This led to the development of the Triple Treatment Technique.

In attempting to improve the Superglue/staining technique of latent print detection, two important features had to be preserved. They were:

(i) the high selectivity of Superglue as a latent fingerprint reagent; and
(ii) the high sensitivity of the fluorescent NBD-amino derivatives.

The one solution was to mask the entire substrate surface, except the fingerprint ridges, with a layer of non-porous material so that the surface is rendered inaccessible to the stain. Metal deposition [Kent et al., 1976] fulfils this requirement and was therefore applied as a secondary treatment to the Superglue fuming prior to staining. The results were remarkable.

A metal deposition unit consists of a glass bell jar which is evacuated by a diffusion pump that is backed by a rotary pump (Figure 2.2.). The article to be processed is placed at the top of the jar. After evacuation, a thin layer of gold (about 2 Å) is evaporated from an open boat. The thickness of gold is measured by using a quartz crystal monitor. Subsequently, cadmium or zinc is evaporated and condenses over the entire surface except the fingerprint ridges. According to Thomas [Thomas, 1974], in the development of latent fingerprints with metal deposition, "the gold sinks into the fatty layer on the fingerprint, out of the range of the incident
Figure 2.2. Vacuum metal deposition unit

cadmium". Gold deposited in between the ridges is within the range of the van der Waals force of attraction between the gold and cadmium and therefore causes condensation of the latter. In view of the rather porous nature of cyanoacrylate polymer, a similar mechanism may be involved in the development of cyanoacrylate-developed prints by metal deposition.

With the new "Triple Treatment Technique", the article to be processed undergoes three separate treatment processes - Superglue fuming, metal deposition and staining (preferably in that sequence).

The improvement achieved by this technique over the Superglue/staining technique was experimentally determined. Plastic-based surfaces, such as white polythene, PVC yoghurt containers and bank cards, and other more porous substrates including polished leather and glossy paper were some of the articles included in the evaluation (see Section 5.4.).
2.2.1. Results and Discussion

Results obtained from the evaluation of the Triple Treatment technique are shown in Table 2.2.1. On clear polythene (as control), no improvement was achieved because it was not a “problem” surface for the Superglue/staining technique. Prints on other substrates were improved to various extent, the most being on white polythene, polished leather, PVC yoghurt containers, sticky side of masking tape, the Australian

<table>
<thead>
<tr>
<th>Article</th>
<th>Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>White polythene</td>
<td>+++</td>
</tr>
<tr>
<td>Glossy paper</td>
<td>++</td>
</tr>
<tr>
<td>Leather (polished)</td>
<td>+++</td>
</tr>
<tr>
<td>Yoghurt container (PVC)</td>
<td>+++</td>
</tr>
<tr>
<td>Fabric (Dermicel surgical tape; non-sticky side)</td>
<td>+</td>
</tr>
<tr>
<td>Masking tape (sticky side)</td>
<td>+++</td>
</tr>
<tr>
<td>Bank note (A$5)</td>
<td>++</td>
</tr>
<tr>
<td>Green leaf (fresh)</td>
<td>+</td>
</tr>
<tr>
<td>Picture post card</td>
<td>++</td>
</tr>
<tr>
<td>Bank card (laminated PVC)</td>
<td>++</td>
</tr>
<tr>
<td>Passport laminate (glass beads)</td>
<td>+++</td>
</tr>
<tr>
<td>Painted aluminium</td>
<td>+++</td>
</tr>
<tr>
<td>Clear polythene (control)</td>
<td>±</td>
</tr>
</tbody>
</table>

Legend: ± no improvement
+ slight improvement
++ definite improvement
+++ very marked improvement

Table 2.2.1. Improvement achieved by using the TTT over the Superglue/staining technique
passport laminate and painted aluminium. These are articles whose surfaces are most vulnerable to the stains. With the yoghurt container, the PVC is softened by acetonitrile, and for leather and masking tapes, the polish and adhesive, respectively, are prone to chemical attack by this solvent. The passport laminate, which is made up of small glass beads glued together, and glossy paper are improved by this technique by having the porous surface rendered impermeable to stains. This technique was found to be effective in that aged prints on leather (up to 4 days old), white polythene, PVC sheets and biological samples such as leaves (fresh), can be processed (see Figure 2.2.1.a.). Although good quality prints on fabrics and bank notes are not producible with this technique, it is possible to visualise the general pattern of the print which can be useful for the purpose of "eliminating" suspects.

The combination of the Superglue fuming and metal deposition, or even metal deposition on its own, works well if the latent prints are fresh and the surface is light-coloured and of one colour. However, if the surface is multi-coloured, such as printed polythene and plastic containers, the use of fluorescent stains in combination with Superglue fuming and metal deposition is an advantage (see Figure 2.2.1.b.). Incidentally, the use of fluorescent stains for this technique is not limited to those of NBD-amino derivatives. Any stain with high relative quantum yield and spectroscopical characteristics similar to that of NBD-amino derivatives would work just as well.

One drawback of the triple treatment technique is the physical dimension of the developing chamber of the metal deposition unit which limits the range of articles that can be processed. Moreover, three separate stages of treatment is rather time consuming. The development of a "one-stage" fingerprint reagent would ideally overcome these drawbacks.
Figure 2.2.1a. Comparison of fingerprints developed with Superglue/NBD-butylamine and the Triple Treatment Technique (Superglue/metal deposition/NBD-butylamine):

(A) Painted aluminium (right half of print by TTT)
(B) White polythene (left half of print by TTT)
(C) Polished leather (left half of print by TTT)
(D) Fresh leaf (right half of print by TTT)
(E) Glossy paper (right half of print by TTT)
(F) A$5 note (right half of print by TTT)
Figure 2.2.1.b. Fingerprints on printed polythene developed with Superglue/metal deposition as seen under white light (A), and subsequently stained with NBD-butylamine and excited with a Xenon arc lamp; 450 nm excitation, 550 nm barrier filters (B).
3. INTRODUCTION

The commercially available ethyl 2-cyanoacrylate ester (Repco Super Glue 3™, Loctite) has been shown to impart good selectivity and sensitivity (particularly on dark-coloured surfaces) as a latent fingerprint reagent [Ball, 1982; Norkus, 1982; Kendall, 1982a]. However, because it is neither coloured nor highly photoluminescent, visualisation of developed prints can be limited due to poor contrast between the ridges and the substrate surface.

Coloured or photoluminescent compounds based on 2-cyanoacrylate esters could be synthesised and employed as "one-stage" fingerprint reagents which, as opposed to the Triple Treatment Technique, would develop latent prints without further treatment.

Before discussing our approach to the selection and synthesis of possible chromophoric cyanoacrylate reagents, some description of the basic features of colour absorption and photoluminescence is appropriate.

A more detailed and comprehensive theory of colour and photoluminescence in terms of molecular energy levels was made possible by the development of wave mechanics since 1926.

3.01. Colour

The colour of a substance depends upon the nature of the radiation leaving it and entering the eye of the observer. If the substance absorbs certain ranges of wavelengths from an illuminating radiation, the colour of this radiation will be different from that transmitted or reflected from the substance. A knowledge of the frequencies of radiation which are absorbed by a substance allows the colour of that substance to be determined (Table 3.a) [Coates, 1967].

All coloured compounds must contain at least one chromophoric group or chromophore, which is associated with the colour. Chromophores such as -NO₂,
-NO, -N=N-, )C=O, and )C=C(, introduce a potentiality for colour which is modified by the presence of groups termed auxochromes, e.g. -OH, -NH2, -NHR and -NR2.

The absorption of chromogens (molecules containing chromophores) can be shifted to longer wavelengths (bathochromic shift) or shorter wavelength (hypsochromic shift) by the introduction of auxochromes. Auxochromes can also increase the intensity of an absorption band (hyperchromic effect), or decrease it (hypochromic effect).

Electronic transitions that give rise to absorption in the visible and ultraviolet regions are based on the same principle. This is described under “Photoluminescence” below.

### 3.02. Photoluminescence

The absorption of radiant energies within the visible and ultraviolet regions is sufficient to cause electronic excitation accompanied by vibrational and rotational energy changes in a molecule. Only radiation of energies corresponding to the differences between permitted quantised energy levels for the molecules can be absorbed. When a molecule absorbs a photon, an electron in the ground electronic state is raised to an excited level, giving an excited singlet state (Figure 3.a). Excited molecules readily lose excess vibrational energy, e.g. via collisions with solvent molecules, and the lowest vibrational level \((v'=0)\) of the excited singlet is usually rapidly attained. If the excess energy is not further dissipated via photochemical reaction, photodissociation, or heat loss (radiationless decay), the electron returns to the ground electronic state with the emission of radiation of lower energy (longer...
wavelength) than that absorbed. This phenomenon is called *fluorescence*.

Phosphorescence, a delayed release of energy from an excited triplet state, involves an intersystem crossing from the excited singlet to the triplet state. A triplet state results when the spin of one of the electrons changes so that the spins are the same, or unpaired. The energy of the lowest vibrational level of the excited triplet state is lower than that of the excited singlet state and the emission of energy (phosphorescence), on returning to the electronic ground state, is always less than that of the related fluorescence. A specific property of phosphorescence, in contrast to fluorescence, is that it continues after the exciting source is removed, since spin-pairing must occur prior to emission. Fluorescence and phosphorescence are specific terms collectively referred to as *photoluminescence*.

Usually, absorption intensity increases with increase in conjugation in organic
systems. High intensity has been related to dipole-moment change during a transition; the larger the dipole moments, the higher the intensity. It is also affected by electron-configuration effects caused, for example, by auxochromes with an electron pair available, e.g. -OH and -NH₂.

In saturated hydrocarbons, the C-H and C-C orbitals are localised σ orbitals in the ground state. σ → σ* transitions occur at very high energies (ca. 130 nm) which can disrupt bonding in the molecule. Nonetheless, some saturated hydrocarbons do exhibit very weak fluorescence occurring in the 140-170 nm region [Hirayama et al., 1969]. Some highly conjugated non-aromatic compounds are fluorescent due to the occurrence of π → π* transitions which require less energy than the σ → σ* transition. Since the energy gap between successive occupied π orbitals in a conjugated carbon-chain system decreases with increase in the number of orbitals filled, the greater the conjugation, the longer the wavelength of absorption for π → π* transitions.

In molecules containing carbonyl groups (ketones, aldehydes, carboxylic acids) and heterocycles, the lone-pair electrons (non-bonding n electrons) are usually of higher energy than the π electrons. Consequently, n → π* transitions are of lower energy (corresponding to longer-wavelength absorption) than the π → π* transitions.

In general, the majority of intensely fluorescent organic compounds are aromatic. Like non-aromatic hydrocarbons, the intensity of fluorescence of unsubstituted aromatic compounds increases with increase in conjugation and a bathochromic shift is observed. In substituted aromatic compounds, electron-releasing substituents, such as -OH, -NH₂ and OCH₃, often enhance fluorescence and electron-withdrawing groups repress it. Electron-withdrawing substituents, such as -NO₂ and C=O groups, possess low-lying (n, π*) singlets which increases the extent of singlet → triplet intersystem crossing; such compounds exhibit very weak to intense phosphorescence. It should be noted that electron-releasing groups have a strong
tendency to hydrogen-bond with the solvent or with other solutes, increasing the efficiency of internal conversion (e.g. from the excited singlet to a vibrational level in the electronic ground state) and decreasing the fluorescence intensity.

Environmental factors can influence the fluorescence of molecules. The polarity of the solvent can either shift the absorption and emission spectra to longer wavelength (bathochromic shift), or to shorter wavelength (hypsochromic shift), depending on the nature of the solute. Thus $\lambda_{\text{max}}$ for nitrobenzene shifts towards the red with increasing polarity of the solvent because the excited (more polar) state is more highly stabilised than the ground state owing to solvation. A bathochromic shift caused by the polarity of the solvent can be explained as follows. When a molecule is excited to the metastable "Frank-Condon" excited state, solvent reorientation occurs producing a lower energy-level "equilibrium" excited state, in which the solvent configuration is optimal for the geometry and electronic distribution of the excited molecule. Emission occurs from the equilibrium excited state, forming a Frank-Condon ground state. The equilibrium ground state is then formed following relaxation of the solvent.

Temperature can affect fluorescence intensity in liquid solution. As the temperature is lowered, the viscosity of the medium is increased and collisional quenching of fluorescence is decreased, causing an increase in fluorescence intensity. However, if the solute has two or more excited states, increasing the temperature can increase fluorescence intensity. At high temperatures, thermal excitation of the triplet back to the excited singlet state causes "delayed fluorescence" which is spectrally identical to the "normal" fluorescence. Other environmental effects worth noting are: pH, metal ions, heavy atoms and presence of other solutes.
3.3. EFFECT OF R' SUBSTITUENTS ON SELECTIVITY OF CYANOACRYLATE ESTERS

3.3.1 Introduction

The chromophoric or fluorescing "tag" can be introduced into the ester through the "R" group, as shown in Scheme 3.1.1:

\[ \text{CN} \quad \text{CN} \]
\[ \text{CO}_2\text{Tag} \quad \text{CO}_2\text{Tag} \]

CHAPTER THREE

SYNTHESIS AND EVALUATION OF "ONE STAGE" COLOURED AND PHOTOLUMINESCENT FINGERPRINT REAGENTS

The possibility of producing these "one-stage" cyanacrylate compounds to be employed successfully as latent fingerprint reagents is determined initially by preparing and evaluating (with respect to selectivity) cyanacrylate esters with different simple "R" moieties.

The general method employed in the synthesis of these esters involved the condensation of the respective estermonomers with formaldehyde and subsequently depolymerising (at elevated temperatures and reduced pressure) the product formed (Scheme 1.4).

A series of cyanacrylate esters with different alkyl moieties of varying number of carbon including an aromatic ester were prepared. These moieties include methyl, ethyl, isobutyl, propyl, butyl, isopropyl and phenyl (see Sections 3.3.1 and 3.3.2). The prepared esters were evaluated as latent fingerprint reagents (see Section 3.3.1).
3.1. EFFECT OF "R" SUBSTITUENTS ON SELECTIVITY OF CYANOACRYLATE ESTERS

3.1.1. Introduction

The chromophoric or fluorogenic "tag" can be introduced into the ester through the "R" group, as shown in Scheme 3.1.1.a.

\[
\begin{array}{c}
\text{CH}_2\text{-C} & \text{CN} \\
\text{CO}_2\text{Tag} & \rightarrow [\text{CH}_2\text{-C} & \text{CN} \\
\text{CO}_2\text{Tag}]_n \\
\text{Coloured/fluorescent} & \text{fluorescent polymer} \\
2\text{-cyanoacrylate} & \text{deposited on ridges}
\end{array}
\]

Scheme 3.1.1.a.

The possibility of producing these "one-stage" cyanoacrylate compounds to be employed successfully as latent fingerprint reagents is determined initially by preparing and evaluating (with respect to selectivity) cyanoacrylate esters with different simple "R" moieties.

The proposed method employed in the synthesis of these esters involved the condensation of the respective cyanoacetates with formaldehyde and subsequently depolymerising (at elevated temperatures and reduced pressure) the product formed (Scheme 1.4).

A series of cyanoacrylate esters with different alkyl moieties of varying number of carbons including an aromatic ester were prepared. These moieties include methyl, n- butyl, t- butyl, benzyl and phenyl (see Sections 5.5.1. and 5.5.2.). The prepared esters were evaluated as latent fingerprint reagents (see Section 5.5.3.).
3.1.2. Results and Discussion

Methyl 2-cyanoacrylate and \(n\)-butyl 2-cyanoacrylate were obtained in the liquid monomeric form. The other esters (\(t\)-butyl, benzyl and phenyl) repolymerised readily on distillation and were obtained as solid polymers. A comparison between the use of liquid (monomeric) and solid (polymeric) ethyl 2-cyanoacrylate as fingerprint reagents has shown that prints developed with the latter were of equally good quality (see Appendix 3). It was therefore decided that all the prepared cyanoacrylate esters (including ethyl 2-cyanoacrylate, as control) should be evaluated in one form, that is, as solid polymers (see Section 5.5.2.).

All six cyanoacrylate polymers showed varying degrees of selectivity and sensitivity. Methyl 2-cyanoacrylate and ethyl 2-cyanoacrylate showed good sensitivity as depicted by the white ridges of the developed prints. The other polymers produced grey-coloured prints which were difficult to visualise due to poor contrast between the ridges and the clear polythene surface (i.e., poor sensitivity). This poor visibility was not improved by prolonged exposure of the latent prints to the cyanoacrylate vapour. It is not known with great certainty as to why prints developed with some of the polymers produced such low opacity, but it could be attributed to the following observations:

1. Highly amorphous polymers, such as methyl, ethyl and \(n\)-butyl 2-cyanoacrylates which were allowed to polymerise spontaneously into solid blocks, were transparent; and
2. Polymers made up of short polymer chains, such as ethyl 2-cyanoacrylate polymerised in water, were highly opaque.

It is therefore probable that the varying degree of crystallinity between the different polymers is responsible for the varied opacity [Cowie, 1973].

In order to improve the visibility of these "grey" or "transparent" prints, they were stained separately with Gentian Violet, a dark-violet visible dye, and NBD-butylamine, a fluorescent compound (see Chapter 2). Gentian Violet failed
to improve the visibility of these prints because it was not sensitive enough as a stain (see Chapter 2). NBD-butylamine, on the other hand, was more sensitive. With the latter, good contrast and ridge details (i.e., good selectivity) were shown by methyl, ethyl, and phenyl 2-cyanoacrylates. High background fluorescence, indicating poor selectivity, were shown by n-butyl, t-butyl, and benzyl 2-cyanoacrylates. The use of NBD-butylamine therefore serves to provide a means of determining the selectivity of those polymers with poor sensitivity. Because staining with fluorescent compounds, such as NBD-butylamine, can be employed effectively as an enhancement technique, the sensitivity of a cyanoacrylate ester (as depicted by the visibility of developed prints) is not a critical factor so far as the quality of the enhanced print is concerned. This is shown in the case of phenyl 2-cyanoacrylate whereby the originally developed print appeared grey and difficult to visualise, but showed good contrast after staining with NBD-butylamine.

A summary of the observations made of the various polymers as latent fingerprint reagents is shown in Table 3.1.2. Photographs of the stained prints are shown in Figure 3.1.2.

Based on the above observations, the following conclusions are drawn:

1. The sensitivity and selectivity of alkyl 2-cyanoacrylate esters decreases with increase in carbon chain (or carbon number);

2. The sensitivity of phenyl 2-cyanoacrylate (an aromatic ester) is lower than that of methyl 2-cyanoacrylate and ethyl 2-cyanoacrylate, but its selectivity is on par with them;

3. Provided that a cyanoacrylate ester imparts good selectivity, the visibility of the developed prints can be improved by staining with a suitable fluorescent compound.

Nonetheless, the most important finding derived from this evaluation is that phenyl 2-cyanoacrylate (an aromatic analogue) could impart good selectivity as a latent fingerprint reagent. This indicates the possibility of preparing and putting into use a
coloured or photoluminescent cyanoacrylate-based fingerprint reagent.

Table 3.1.2. *Evaluation of Prints Developed with Cyanoacrylate Polymers*

![Chemical structure of cyanoacrylate polymers]

<table>
<thead>
<tr>
<th>R</th>
<th>Developed Print</th>
<th>Stained (G.Violet)</th>
<th>Stained (NBD-butyl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>Good contrast, white ridges.</td>
<td>Good contrast and ridge details</td>
<td>Good contrast and ridge details</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>Good contrast, white ridges</td>
<td>Good contrast and ridge details</td>
<td>Good contrast and ridge details</td>
</tr>
<tr>
<td>(CH₂)₃CH₃</td>
<td>very weak print, grey ridges</td>
<td>very faint ridges</td>
<td>very high background fluorescence</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>very weak print, grey ridges</td>
<td>very faint ridges</td>
<td>High background fluorescence</td>
</tr>
<tr>
<td>CH₂C₆H₅</td>
<td>weak print, grey ridges</td>
<td>Faint ridges</td>
<td>High background fluorescence</td>
</tr>
<tr>
<td>Ph</td>
<td>weak print, grey ridges</td>
<td>Faint ridges</td>
<td>Good contrast and ridge details</td>
</tr>
</tbody>
</table>
Figure 3.1.2. Latent fingerprints on clear polythene developed with the various esters of 2-cyanoacrylate and stained with NBD-butylamine (using 450 nm source and 550 nm barrier filters) and Gentian Violet (under white light).
3.2. DIELS-ALDER ADDUCTS AS PRIMERS FOR CYANOACRYLATE-BASED FINGERPRINT REAGENTS

3.2.1. INTRODUCTION

In the preceding section of this chapter (Section 3.1), it was mentioned that in the synthesis of some of the 2-cyanoacrylate esters, namely, the n-butyl, t-butyl, benzyl and phenyl esters, they repolymerised readily during the distillation process and had to be obtained as solid polymers. Although solid polymers as primers for the generation of cyanoacrylate vapour were as effective as the corresponding monomers (Appendix 3), they were technically more difficult to prepare. First, the build-up of solid polymer in the cooling condenser causes clogging. Next, there is the problem with collecting the product from the condenser. These problems lead to an ultimately poor yield. With the liquid monomer, there are problems with handling (Superglue bonds skin) and storage (the monomer has to be chemically stabilised and stored in sealed containers at low temperatures to avoid spontaneous polymerisation). This prompted the search for an alternative method of preparing 2-cyanoacrylate esters and the Diels-Alder reaction was employed.

3.2.1.1. The Diels-Alder Reaction ([4 + 2]π Cycloaddition)

The Diels-Alder reaction, named after its discoverers, is one of the most versatile synthetic organic reactions. It is also the most important example of cycloaddition whereby a conjugated diene (4 π-electron system) reacts with a compound with a double bond (a 2 π-electron system) or dienophile to form a cyclic compound (adduct). The two new sigma (σ) bonds are formed at the expense of two π bonds of the diene and dienophile (see Scheme 3.2.a.).

The mechanism of the Diels-Alder reaction was first studied in 1928 with the elucidation of the structure of the cyclopentadiene/p-benzoquinone adduct [Diels et al., 1929]. In the transition state of cycloaddition, stabilisation derives from the
overlap between the highest occupied molecular orbital (containing two electrons) of one reactant and the lowest unoccupied molecular orbital (empty orbital) of the other. In the case of a [4 + 2] cycloaddition, such as 1,3-butadiene and ethylene, overlap of the highest occupied diene level ($\psi_2$) with the lowest unoccupied dienophile level ($\pi^*$) [or of the lowest unoccupied diene level ($\psi_3$) with the highest occupied dienophile level ($\pi$)] brings together orbital lobes of the same phase and bonding occurs (see figure 3.2.b). It is generally agreed that most, if not all, Diels-Alder reactions are concerted, but whether they are synchronous remains a subject of controversy [Dewar et al., 1984].

The Diels-Alder reaction takes place readily with a wide variety of reactants. It
is favoured by the presence of electron-withdrawing groups in the dienophile and electron-releasing groups in the diene. There are several aspects to the stereochemistry of this reaction. First, the diene must be in the \textit{s-cis} conformation so that the ends of the conjugated system can \textit{reach} the double bond of the dienophile. Second, with respect to the dienophile, the reaction is highly stereospecific (\textit{syn} addition); the configuration of the dienophile being retained in the products. Finally, in the addition of cyclic dienophiles to cyclic dienes, the reaction occurs primarily in the \textit{endo} rather than an \textit{exo} fashion; that is, the tendency of any other unsaturated groups in the dienophile to lie \textit{near} the developing double bond in the diene moiety.

\textbf{3.2.1.2. The Retro-Diels-Alder (Retrodiene) Reaction}

The reverse Diels-Alder, or retro-Diels-Alder, reaction is particularly useful for the synthesis of inaccessible olefinic compounds [Kwart \textit{et al.}, 1968]. Diels and Alder reported in 1929 that the decomposition of furan/maleic anhydride adduct by heating to the melting point (125\textdegree C) regenerated the starting materials [Diels, 1929\textsuperscript{b}].

In general, a synthesis of this type involves the thermal fragmentation of a suitable bicyclic olefin system to yield the unsaturated product and a cyclic diene fragment (see Scheme 3.2.c.).
The most widely used cyclic dienes for synthetic applications include cyclopentadiene [Martin et al., 1982], furan [Takano et al., 1974; Alder, 1937], tetraphenylcyclopentadienone [Allen et al., 1962], 6,6-diphenylfulvene [Ichihara et al., 1974], anthracene [Ripoll et al., 1974], dimethyl phthalate [McCay, 1971] and pyrrole [Wirth et al., 1982] and their derivatives.

In the synthesis of acetylenedicarbonylchloride (1), the direct treatment of acetylene dicarboxylic acid with phosphorus pentachloride gave only chloro fumarylchloride. However, treatment of the anthracene/acetylenedicarboxylic acid adduct (2) with phosphorus pentachloride produced normal acid chloride (3). Heating this compound with maleic anhydride (MA) at 190°C yielded anthracene/maleic anhydride adduct (4) and acetylenedicarboxylchloride [Diels et al., 1938].

The retro-Diels-Alder reaction has also been used to generate unstable intermediates, such as diimide in situ [Corey et al., 1962] and ethylenetetracarboxylic-dianhydride in solution [Sauer et al., 1967], using anthracene as the cyclic diene. There is a seemingly endless number of olefinic compounds which have been synthesised using this reaction [Kwart et al., 1968; Ripoll et al., 1978; Sauer et al., 1980].
3.2.1.3. Synthesis of 2-cyanoacrylate Monomers via Anthracene Adducts

There are several reports in the literature on the synthesis of monofunctional 2-cyanoacrylate and bis(2-cyanoacrylate) monomers based on Diels-Alder and retro-Diels-Alder reactions.

Ray and Doran [Ray et al., 1969] have effected the Knoevenagel condensation of formaldehyde and an alkyl cyanoacetate in the presence of anthracene, wherein the 2-cyanoacrylate monomer liberated was trapped as the stable anthracene adduct (5) rather than polymerising to the homopolymer. Heating the anthracene adduct in the presence of maleic anhydride yielded the monofunctional alkyl 2-cyanoacrylates and the anthracene/maleic anhydride adduct (see Scheme 3.2.d.).
In the synthesis of bis(2-cyanoacrylate) monomers, which are used as dental adhesives, the anthracene/ethyl 2-cyanoacrylate adduct (5) was hydrolysed to the anthracene/2-cyanoacrylic acid adduct (6). Conversion of the latter to the acid chloride (7) or alkali metal salt followed by esterification with an organic dihalide or glycol gave the bis-anthracene adducts (8), precursors to bis(2-cyanoacrylate) monomers (9). Retrodiene scission was effected by heating the bis-adducts with maleic anhydride in refluxing xylene to yield bis(2-cyanoacrylate) monomers (see Scheme 3.2.e.) [Buck, 1978].
Scheme 3.2. e. Synthesis of bis(2-cyanoacrylate) monomers via anthracene adducts

[Buck, 1978]
3.2.2 Ethyl 2-cyanoacrylate Adducts as Primers: Choosing a suitable Cyclic Diene

We decided to investigate this retro Diels-Alder process as a potential converter and source of the cyanoacrylate monomers in vapour form.

Ethyl 2-cyanoacrylate (EtCA) which has two electronegative groups (nitrile and ester carbonyl), is a strong dienophile. It readily undergoes Diels-Alder reaction with a conjugated diene, such as anthracene [Buck, 1978], to form an adduct. This compound can be heated in the RVT process to effect retrodiene scission with the subsequent formation of the 2-cyanoacrylate ester monomers in situ which promotes rapid development of latent fingerprints (see Scheme 3.2.2.a.).

Scheme 3.2.2.a. Anthracene/ethyl 2-cyanoacrylate adduct as a primer for latent fingerprint development
In order to synthesise and be able to use the ultimate coloured or photoluminescent adduct as a primer for latent fingerprint development, it is necessary to determine experimentally the most suitable cyclic diene(s). This involved the synthesis of a series of ethyl 2-cyanoacrylate adducts and making an evaluation of their suitability as latent fingerprint reagents (see Section 5.6).

Six cyclic dienes were included in the synthesis of the adducts. They were: cyclopentadiene (10), anthracene (12), 1,3-diphenylisobenzofuran (14), diphenylfulvene (16), 1,3-cyclohexadiene (18) and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (20) (see Table 3.2.2.b. and Section 5.6.).
Table 3.2.2.b. *Proposed ethyl 2-cyanoacrylate adducts*

<table>
<thead>
<tr>
<th>Cyclodiene</th>
<th>Expected adduct</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="10" alt="Cyclohexene" /></td>
<td><img src="11" alt="Adduct" /></td>
</tr>
<tr>
<td><img src="12" alt="Cyclooctadiene" /></td>
<td><img src="13" alt="Adduct" /></td>
</tr>
<tr>
<td><img src="14" alt="Benzodioxole" /></td>
<td><img src="15" alt="Adduct" /></td>
</tr>
<tr>
<td><img src="16" alt="Cyclopentene" /></td>
<td><img src="17" alt="Adduct" /></td>
</tr>
<tr>
<td><img src="18" alt="Chlorocyclopentane" /></td>
<td><img src="19" alt="Adduct" /></td>
</tr>
<tr>
<td><img src="20" alt="Chlorocyclopentene with methoxy" /></td>
<td><img src="21" alt="Adduct" /></td>
</tr>
</tbody>
</table>
3.2.3. RESULTS AND DISCUSSION

Of the six cyclic dienes treated with ethyl 2-cyanoacrylate, four showed positive reaction. They were: cyclopentadiene, anthracene, 1,3-diphenylisobenzofuran and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene. Cyclopentadiene and 1,3-diphenylisobenzofuran reacted readily with ethyl 2-cyanoacrylate at room temperature. Anthracene and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene formed the corresponding adducts at 90°C and 120°C, respectively. Cyclopentadiene/ethyl 2-cyanoacrylate (11) and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene/ethyl 2-cyanoacrylate (21) adducts were obtained as oils and the other two adducts, (13) and (15) as solids (see Table 3.2.3.a.).

Results obtained from the evaluation of the various adducts as latent fingerprint reagents are shown in Table 3.2.3.b.

Latent prints developed with cyclopentadiene/ethyl 2-cyanoacrylate (11) and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene/ethyl 2-cyanoacrylate (21) adducts lacked contrast, with the ridges being faint. Prints developed with the other two adducts, anthracene/ethyl 2-cyanoacrylate (13) and 1,3-diphenylisobenzofuran/ethyl 2-cyanoacrylate (15), were of equally good quality as those developed with liquid ethyl 2-cyanoacrylate (Superglue), showing good selectivity and sensitivity.

The poor sensitivity and selectivity obtained with the first two adducts, (11) and (21), can be attributed to the interference from the fragmented cyclic dienes, cyclopentadiene (b.p. 40°C) and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (b.p. 108-110°C/11 mmHg), which are released as vapours when the respective adducts were heated in the RVT system. Presumably, a great proportion of cyclic diene and ethyl 2-cyanoacrylate vapours in the developing chamber reacts with each other to re-form Diels-Alder adducts which settle on the surface of the sample resulting in poor selectivity and the grey colour. On the contrary, anthracene (m.p. 216°C) and 1,3-diphenylisobenzofuran (m.p. 128°C), both being solids at ambient temperatures and less volatile than ethyl 2-cyanoacrylate monomers, do not interfere with the actual
<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Reaction Temp. (°C)</th>
<th>m.p. (°C)</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td><img src="image" alt="Structure I" /></td>
<td>20</td>
<td>oil</td>
<td>Cyclopentadiene/ethyl 2-cyanoacrylate adduct or Ethyl bicyclo[2.2.1]hepta-5-ene-2-cyano2-carboxylate</td>
</tr>
<tr>
<td>II</td>
<td><img src="image" alt="Structure II" /></td>
<td>90</td>
<td>127</td>
<td>Anthracene/ethyl 2-cyanoacrylate adduct or Ethyl 9,10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxylate</td>
</tr>
<tr>
<td>III</td>
<td><img src="image" alt="Structure III" /></td>
<td>20</td>
<td>132-134</td>
<td>1,3-diphenylisobenzofuran/ethyl 2-cyanoacrylate adduct or Ethyl 1,3-diphenyl-1,3-ethanoisobenzofuran-8-cyano-8-carboxylate</td>
</tr>
<tr>
<td>IV</td>
<td><img src="image" alt="Structure IV" /></td>
<td>120</td>
<td>oil</td>
<td>5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene/ethyl 2-cyanoacrylate adduct or Ethyl bicyclo[2.2.1]hepta-5-ene-7,7-dimethoxy-1,4,5,6-tetrachloro-2-cyano-2-carboxylate</td>
</tr>
</tbody>
</table>
development of the latent prints. Thus, the good quality of the developed prints.

Table 3.2.3.b. *Prints Developed with the Various ethyl 2-cyanoacrylate Adducts*

<table>
<thead>
<tr>
<th>Adduct</th>
<th>Developed Print</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I) Cyclopentadiene/EtCA</td>
<td>Faint ridges</td>
</tr>
<tr>
<td>(II) Anthracene/EtCA</td>
<td>Good selectivity and sensitivity</td>
</tr>
<tr>
<td>(III) 1,3-diphenylisobenzofuran/EtCA</td>
<td>Good selectivity and sensitivity</td>
</tr>
<tr>
<td>(IV) 5,5-dimethoxy-1,2,3,4-tetra-chlorocyclopentadiene/EtCA</td>
<td>Faint ridges</td>
</tr>
</tbody>
</table>

Syntheses of coloured and photoluminescent 2-cyanoacrylate adducts, to be described later, were based on anthracene because it is relatively cheap and easily available.
3.3. PHOTOLUMINESCENT ANTHRACENE/2-CYANOACRYLATE ADDUCTS

3.3.1. INTRODUCTION

As described in Section 3.1., it was found that phenyl 2-cyanoacrylate (Table 3.1.2.) showed good selectivity but poor sensitivity (i.e. grey-coloured prints) as a latent fingerprint reagent.

It is envisaged that by replacing the phenyl group with a fluorogenic tag, the new reagent would impart better sensitivity.

In Chapter 2, NBD-amino derivatives were synthesised and found to be highly fluorescent. Such derivatives could be suitable as fluorogenic tags to be introduced in the anthracene/2-cyanoacrylate adducts. This would involve the hydrolysis of anthracene/ethyl 2-cyanoacrylate adduct (13) and the subsequent esterification of the anthracene/2-cyanoacrylic acid adduct (6) with an amino-alcohol derivative of NBD-Cl, such as NBD-ethanolamine (22), to yield an anthracene/NBD 2-cyanoacrylate adduct (23) (see Scheme 3.3.1.a.).

Heating the photoluminescent adduct (23) would effect retrodiene scission with the generation of anthracene as the eliminated cyclic 'diene' and an active photoluminescent 2-cyanoacrylate monomer (24). Latent fingerprint development could be promoted by exposing the latent prints to the vapour of this monomer (see Scheme 3.3.1.b.).

The synthesis and evaluation of two such fluorescent adducts, viz. anthracene/2-(7-nitrobenzofurazan-4-yl)aminoethyl 2-cyanoacrylate and anthracene/2-(N-(7-nitrobenzofurazan-4-yl)-N-methylamino)ethyl 2-cyanoacrylate are described in Section 5.7.
Scheme 3.3.1.b. Proposed Route of Synthesis of Photoluminescent Adduct
Scheme 3.3.1.b. Proposed development of Latent Fingerprints with Photoluminescent Adduct

3.3.2. RESULTS AND DISCUSSION

The anthracene/2-(7-nitrobenzofurazan-4yl)aminoethyl 2-cyanoacrylate adduct (23) (m.p. 203-205°C) obtained as an orange-coloured solid (see Section 5.7.1., Figure 3.4.2 and Tables 5.7.1.a. and 5.7.1.b.), decomposed readily when heated in the RVT system. The cyanoacrylate ester generated and deposited on the walls of the RVT as a light yellow film, exhibits a high fluorescence when illuminated with blue
light (using a 450 nm interference filter) and viewed through a 550 nm interference filter.

Results obtained from the evaluation of this compound as a fingerprint reagent (Experimental Section 5.7.2.) are shown in Table 3.3.2.a. The developed fingerprints appeared "transparent" under white light.

Table 3.3.2.a. *Prints on Various Substrates Developed with anthracene/2-(7-nitrobenzofurazan-4-yl)aminoethyl 2-cyanoacrylate Adduct*

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Developed Print</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium foil</td>
<td>Good selectivity; moderate fluorescence intensity</td>
</tr>
<tr>
<td>Painted aluminium</td>
<td>Good selectivity; moderate fluorescence intensity</td>
</tr>
<tr>
<td>Clear polythene</td>
<td>Good selectivity; low fluorescence intensity</td>
</tr>
<tr>
<td>White polythene</td>
<td>Moderate fluorescence intensity; unevenly distributed</td>
</tr>
<tr>
<td>Glossy paper</td>
<td>Good selectivity; low fluorescence intensity</td>
</tr>
<tr>
<td>PVC</td>
<td>Good selectivity; moderate fluorescence intensity</td>
</tr>
<tr>
<td>Polished leather</td>
<td>Low fluorescence intensity; fragmented ridges</td>
</tr>
</tbody>
</table>

Illuminated with a Xenon arc lamp using the appropriate filters (see Section 5.7.2.), fingerprints developed with this photoluminescent adduct produced low to moderately high fluorescence intensity. On aluminium foil, painted aluminium and PVC sheets, the developed prints were of good contrast and ridge details. On glossy paper and clear polythene, although the developed prints were much less fluorescent as on aluminium foil, the ridge detail was good (see Figure 3.3.2.a). On polished leather, the ridges were fragmented because of the grainy nature of the substrate surface. An uneven distribution of fluorescence intensity was observed with
developed prints on white polythene.

When illuminated with short-wave ultraviolet light the developed prints on painted aluminium and aluminium foil produced a higher level of fluorescence intensity, showing good ridge details and contrast between the ridges and the surface. This blue emission which is similar to that of anthracene in colour and intensity shows that anthracene, too, has an affinity for the fingerprint deposit. This was verified by the exposure of latent fingerprints on aluminium foil to anthracene vapour whereby highly photoluminescent prints, showing good selectivity, were obtained. However, on surfaces which fluoresce strongly under ultraviolet light, such as white polythene, anthracene is not suitable because of poor contrast between the ridges and the surface.

In order to improve the sensitivity of the photoluminescent primer, another adduct with a lower melting point was synthesised. Anthracene/2-(N-(7-nitrobenzofurazan-4-yl)-N-methylamino)ethyl 2-cyanoacrylate adduct (m.p. 125-128°C) (see Figure 3.4.2) decomposed more readily than the earlier adduct (23), but the developed prints on aluminium foil showed far lower fluorescence intensity. This may be attributed to the lower fluorescence intensity of the fluorogenic moiety which is a tertiary amine (see Chapter 2). Because of the lower fluorescence intensity no further evaluation of this adduct was made.

Visual assessment of the prints developed with these two fluorescent adducts showed that much less of the fluorescent polymer was deposited on the fingerprint ridges than with methyl or ethyl 2-cyanoacrylate esters. A quantitative comparison has not been made because the weights of cyanoacrylate deposited bear no direct relationship to that of the corresponding fingerprint deposits. This was verified by weighing sets of latent prints on aluminium foil and weighing the corresponding amount of ethyl 2-cyanoacrylate deposited after 30 minutes of development time (see Table 3.3.2.b.). A quantitative assessment of the weight of cyanoacrylate deposited is, therefore, both irrelevant and unnecessary.

Attempts were made to improve the development technique by increasing the
Table 3.3.2.b. Weights of latent prints and corresponding ethyl 2-cyanoacrylate deposited (Vacuum Technique [Watkin, 1983])

<table>
<thead>
<tr>
<th>Set</th>
<th>Weight of latent prints (mg)</th>
<th>Weight of Superglue (mg)</th>
<th>R*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.14</td>
<td>0.77</td>
<td>5.50</td>
</tr>
<tr>
<td>2</td>
<td>0.30</td>
<td>0.57</td>
<td>1.90</td>
</tr>
<tr>
<td>3</td>
<td>0.09</td>
<td>0.52</td>
<td>5.78</td>
</tr>
<tr>
<td>4</td>
<td>0.16</td>
<td>0.60</td>
<td>3.75</td>
</tr>
<tr>
<td>5</td>
<td>0.05</td>
<td>0.37</td>
<td>7.40</td>
</tr>
<tr>
<td>6</td>
<td>0.42</td>
<td>0.10</td>
<td>0.24</td>
</tr>
<tr>
<td>7</td>
<td>0.86</td>
<td>0.43</td>
<td>0.50</td>
</tr>
<tr>
<td>8</td>
<td>1.33</td>
<td>0.25</td>
<td>0.19</td>
</tr>
<tr>
<td>9</td>
<td>0.59</td>
<td>0.27</td>
<td>0.46</td>
</tr>
<tr>
<td>10</td>
<td>0.02</td>
<td>0.07</td>
<td>3.50</td>
</tr>
<tr>
<td>11</td>
<td>0.04</td>
<td>0.64</td>
<td>16.00</td>
</tr>
<tr>
<td>12</td>
<td>0.06</td>
<td>0.66</td>
<td>11.00</td>
</tr>
<tr>
<td>13</td>
<td>0.09</td>
<td>1.79</td>
<td>19.89</td>
</tr>
<tr>
<td>14</td>
<td>0.37</td>
<td>0.70</td>
<td>1.89</td>
</tr>
<tr>
<td>15</td>
<td>0.11</td>
<td>0.92</td>
<td>8.36</td>
</tr>
</tbody>
</table>

* R is the ratio of the weight of Superglue to that of the corresponding latent prints.

Vapour concentration in the developing chamber. For this, a modified air-tight RVT system was used and the chamber was evacuated (0.5 mmHg) with a rotary oil pump. This technique did not improve the visibility of the developed prints.

The relatively poor selectivity of these adducts could be attributed to the volatility of the generated cyanoacrylate monomers. Indeed, with such bulky fluorogenic groups attached to the cyanoacrylate ester it is highly probable that anthracene might be more volatile than the monomer and, therefore, interfere with the fingerprint development.

Although these two photoluminescent adducts have not shown particularly outstanding results, there is enough "evidence" to show that the use of Diels-Alder adducts as primers for the generation of photoluminescent 2-cyanoacrylate monomers is a potential research avenue.
Figure 3.3.2.a. Latent fingerprints on various surfaces developed with anthracene/2-(7-nitrobenzofurazan-4-yl)aminoethyl 2-cyanoacylate adduct (illuminated with Unilite using the 450 nm and 550 nm interference filters for excitation and barrier, respectively): Aluminium foil (A); Painted aluminium (B); Glossy paper (C); PVC (D); and Leather (E).
3.4. COLOURED ANTHRACENE/2-CYANOACRYLATE ADDUCTS

3.4.1. INTRODUCTION

In order to visualise fingerprints developed with photoluminescent reagents, such as the photoluminescent adducts described in Section 3.3., it is necessary to illuminate the prints with a primary light source of the appropriate wavelength (for excitation) and view them through an appropriate barrier filter. This procedure normally requires the article to be examined in a dark room where the light source and the photographic equipment are set up. By using a visible or coloured reagent, the developed prints can be visualised and photographed under normal white light (e.g. sunlight or tungsten light). This is an advantage particularly if the article to be examined cannot be physically removed and brought into the laboratory.

The proposed synthetic route for the preparation of coloured anthracene/2-cyanoacrylate adducts is identical to that used in the synthesis of photoluminescent adducts (Scheme 3.3.1.a.) except that a chromophoric tag is introduced instead of fluorogenic ones. It involves the esterification of anthracene/2-cyanoacrylic acid adduct (6) with a chromophoric tag in the form of a coloured alcohol or amine to yield a coloured ester (25) or amide (26) adduct, respectively (see Scheme 3.4.1.a.).

By using various coloured alcohols and amines as chromophoric "tags", the corresponding coloured adducts were obtained (Section 5.7.1). 4'-nitrophenyl-4-azophenol, a red-coloured azo compound, was used to obtain a red-coloured adduct. In general, azo compounds can offer a range of colours depending on the auxochromes introduced. Likewise, 2-(1-azulyl)ethanol (dark blue) and 1-aminoanthraquinone (red), which are examples of the azulyl and anthraquinone chromophores, respectively, were used to prepare the corresponding coloured adducts. In the synthesis of white-coloured adducts, the following alcohols were used: phenol, 2-naphthol, benzyl alcohol and phenethyl alcohol. This set of alcohols was used so as to determine the selectivity of 2-cyanoacrylate esters with bulky
Coloured amide adduct Coloured ester adduct

Scheme 3.4.1.a. Proposed route for the synthesis of coloured adducts

aromatic "R" groups. Compounds which fluoresce under ultraviolet light, such as 7-hydroxycoumarin and 7-hydroxy-4-methylcoumarin were used to prepare adducts which could be used to produce ultraviolet-photoluminescent prints. 8-aminoquinoline* and 8-quinolol, which form photoluminescent metal complexes [Fanning et al., 1965; Ohnesorge et al., 1962] were also included. Adducts obtained from these two compounds could be used to develop latent prints in the usual manner (using the RVT) and subsequently treating the developed prints with metal salts to produce the ultraviolet-photoluminescent prints (see Scheme 3.4.1.b.)

*8-aminoquinoline/zinc complex has been prepared and used as a photoluminescent dusting powder in our laboratory. Illuminated with long-wavelength ultraviolet light, a bright green emission is obtained [Stoilovic, 1983].
3.4.2. RESULTS AND DISCUSSION

All the selected alcohols and amines reacted with anthracene/2-cyanoacrylic acid adduct forming the corresponding adducts with yields ranging from 27.6% for 2-(1-azulyl)ethanol to 99.7% for 8-aminoquinoline (see Tables 3.4.2.a. and 5.7.1.b.).

4'-nitrophenyl-4-azophenyl and 2-(1-azulyl)ethanol formed the corresponding red and blue-coloured adducts. However, 1-aminoanthraquinone, a red-coloured compound, formed a yellow-coloured adduct. This is because the electron-withdrawing carbonyl group in the carboxamide moiety restricts the availability of
<table>
<thead>
<tr>
<th>Structure</th>
<th>R</th>
<th>Abbreviation</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>CN C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>A/ECA</td>
<td>Anthracene/ethyl 2-cyanoacrylate adduct or Ethyl 9, 10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxylate</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>A/PCA</td>
<td>Anthracene/phenyl 2-cyanoacrylate adduct or Phenyl 9, 10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxylate</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>A/QCA</td>
<td>Anthracene/8-quinolinyl 2-cyanoacrylate adduct or (8-quinolinyl) 9,10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxylate</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>A/NCA</td>
<td>Anthracene/2-naphthyl 2-cyanoacrylate adduct or (2-naphthyl) 9,10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxylate</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>A/PECA</td>
<td>Anthracene/phenethyl 2-cyanoacrylate adduct or Phenethyl 9,10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxylate</td>
</tr>
<tr>
<td>Structure</td>
<td>R</td>
<td>Abbreviation</td>
<td>Name</td>
</tr>
<tr>
<td>-----------</td>
<td>---</td>
<td>--------------</td>
<td>------</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>CH₂C₆H₅</td>
<td>A/BCA</td>
<td>Anthracene/benzyl 2-cyanoacrylate adduct or Benzyl 9,10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxylate</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>CH₂CH₂NH</td>
<td>A/NBAECA</td>
<td>Anthracene/(2-(7-nitrobenzofurazan-4-yl) aminoethyl) 2-cyanoacrylate adduct or (7'-nitrobenzofurazanyl-4-aminoethano) 9,10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxylate</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>Me</td>
<td>A/MCCA</td>
<td>Anthracene/4-methylcoumarin-7-yl 2-cyanoacrylate adduct or 7(4-methylcoumarin) 9,10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxylate</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td></td>
<td>A/CCA</td>
<td>Anthracene/coumarin-7-yl 2-cyanoacrylate adduct or (7-coumarin) 9,10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxylate</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>CH₂CH₂</td>
<td>A/AECA</td>
<td>Anthracene/2(1-azulylethyl) 2-cyanoacrylate adduct or 2(1-azulylethyl) 9,10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxylate</td>
</tr>
<tr>
<td>Structure</td>
<td>R</td>
<td>Abbreviation</td>
<td>Name</td>
</tr>
<tr>
<td>-----------</td>
<td>---</td>
<td>--------------</td>
<td>------</td>
</tr>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>CH₂CH₂-N-Me</td>
<td>A/NBMAECA</td>
<td>Anthracene/2-(N-(7-nitrobenzofurazan-4-yl)-N-methyl-amino)ethyl 2-cyanoacrylate adduct or (7-nitrobenzo-furazanyl-4-N-methylaminoethano) 9,10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxylate</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>CN-CONHR</td>
<td>A/QCAm</td>
<td>Anthracene/8-quinolinyl 2-cyanoacrylamide adduct or (8-quinolinyl) 9,10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxamide</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td></td>
<td>A/AQCAm</td>
<td>Anthracene/(9,10-anthraquinonyl) 2-cyanoacrylamide adduct or (9,10-anthraquinonyl) 9,10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxamide</td>
</tr>
</tbody>
</table>
Figure 3.4.2.

*Anthracene/ethyl 2-cyanoacrylate adduct (A/ECA)*

*Anthracene/(4'-nitrophenyl-4-azophenyl) 2-cyanoacrylate adduct (A/NPAPCA)*
Anthracene/(2-(7-nitrobenzofurazan-4-yl)aminoethyl 2-cyanoacrylate adduct (A/NBAECA)

Anthracene/(N-(7-nitrobenzofurazan-4-yl)-N-methylamino)ethyl 2-cyanoacrylate adduct (A/NBMAECA)

Figure 3.4.2.
Anthracene/(1-azulylethyl) 2-cyanoacrylate adduct (A/AECA)

Anthracene/(9,10-anthraquinonyl) 2-cyanoacrylate adduct (A/AQCAm)

Figure 3.4.2.
electrons from the nitrogen for conjugation with the anthraquinone moiety causing the absorption maximum to shift to a lower wavelength; thus the colour change. The various coloured adducts are shown in Figure 3.4.2. The anthracene/coumarin-7-yl 2-cyanoacrylate adduct was photoluminescent (blue emission) under long-wavelength ultraviolet light. Adducts of phenol, 8-quinolinol, 2-naphthol, phenethyl alcohol, benzyl alcohol, 7-hydroxy-4-methylcoumarin and 8-aminoquinoline were white-coloured and non-photoluminescent.

Results obtained from the assessment of prints developed with the various coloured adducts are shown in Table 3.4.2.b.

Anthracene/2-cyanoacrylate adducts of phenol, 2-naphthol, phenethyl alcohol and benzyl alcohol impart good selectivity (grey print) but poor sensitivity as shown by the faint ridges of the developed prints. Prints developed with anthracene/8-quinolyl 2-cyanoacrylamide and subsequently treated with zinc chloride exhibit a weak green-coloured fluorescence under short-wavelength ultraviolet illumination, but not evenly distributed over the print. This can be attributed to the physical weakness of the developed prints which were partly removed during the zinc chloride treatment. With anthracene/8-quinolinyl 2-cyanoacrylate, the developed prints did not show any photoluminescence under ultraviolet light and they appeared faint under white light.

The other adducts, including the red-coloured anthracene/(4'-nitrophenyl-4-azophenyl) 2-cyanoacrylate, the blue-coloured anthracene/2(1-azulylethyl) 2-cyanoacrylate, and the yellow-coloured anthracene/(9,10-anthraquinonyl) 2-cyanoacrylamide adducts showed poor selectivity and sensitivity with the developed prints, appearing "transparent" under white light. This lack of sensitivity (or colour) is attributed to the small amount of compound being deposited on the fingerprint ridges coupled with the generally poor sensitivity of visible-coloured reagents (see Chapter 2).

Attempts were made to improve the development technique by increasing the vapour concentration in the developing chamber, as described in Section 3.3.2. No
Table 3.4.2.b. Assessment of Prints Developed with the various adducts

<table>
<thead>
<tr>
<th>Adduct</th>
<th>Colour of Adduct</th>
<th>Developed Prints</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/NPAPCA</td>
<td>Red</td>
<td>Poor selectivity and sensitivity; very weak print</td>
</tr>
<tr>
<td>A/PC</td>
<td>White</td>
<td>Good selectivity, poor sensitivity; weak print</td>
</tr>
<tr>
<td>A/QCA</td>
<td>White</td>
<td>Poor selectivity and sensitivity</td>
</tr>
<tr>
<td>A/NCA</td>
<td>White</td>
<td>Good selectivity, poor sensitivity</td>
</tr>
<tr>
<td>A/PECA</td>
<td>White</td>
<td>Fairly good selectivity, poor sensitivity</td>
</tr>
<tr>
<td>A/BCA</td>
<td>White</td>
<td>Good selectivity, poor sensitivity</td>
</tr>
<tr>
<td>A/MCCA</td>
<td>White</td>
<td>Poor selectivity and sensitivity</td>
</tr>
<tr>
<td>A/CCA</td>
<td>White</td>
<td>Poor selectivity</td>
</tr>
<tr>
<td>A/AECA</td>
<td>Dark blue</td>
<td>Poor selectivity and sensitivity</td>
</tr>
<tr>
<td>A/QCAm</td>
<td>White</td>
<td>Weak photoluminescence (unevenly distributed)</td>
</tr>
<tr>
<td>A/AQCAm</td>
<td>Yellow</td>
<td>Poor selectivity and sensitivity</td>
</tr>
</tbody>
</table>

improvement was observed.

As explained in Section 3.3.2., the poor selectivity of the generated 2-cyanoacrylate monomers could be attributed to low volatility as a result of the bulky chromophores being introduced.
CHAPTER FOUR

CONCLUSION
Arising from the study of the mechanism of interaction of cyanoacrylate ester with fingerprint deposits, it was found that the deposition of ethyl 2-cyanoacrylate (Superglue) on latent fingerprints was triggered by the presence of basic salts, e.g. sodium lactate and weak bases, such as water and alcohols. Being highly sensitive to bases present in the fingerprint deposit, alkyl 2-cyanoacrylate is able to develop weak latent prints. Rapid chemical methods such as the cotton pad/NaOH method accelerate the vaporisation of cyanoacrylate monomers by generating heat from the polymerisation reaction between the cyanoacrylate monomer and the highly basic chemicals, e.g. sodium hydroxide. The development of the Rapid Vaporisation Technique (RVT) provides a more efficient alternative. This apparatus has a controlled heater which allows for the rapid vaporisation of monomeric liquid Superglues as well as the depolymerisation of solid cyanoacrylate polymers to form the cyanoacrylate monomer \textit{in situ} and promotes rapid development of latent prints.

Various cyanoacrylate polymers have been prepared and evaluated as fingerprint reagents. The methyl and ethyl esters showed selective polymerisation and outlined the latent fingerprint ridges with a layer of white polymer. The phenyl ester, although just as selective, did not produce the white colour and therefore, the developed prints lacked sensitivity and contrast. The visualisation of such "transparent" prints, and those on light-coloured substrate surfaces, has been improved by the development of new formulations for staining reagents and the preparation of fluorescent derivatives of 4-chloro-7-nitrobenzofurazan as fluorescent stains.

The combination of the RVT and fluorescent staining is effective on clear polythene, aluminium foil and chromed surfaces. On plastic-based and more porous surfaces, such as leather, high background fluorescence was observed. It was found that the solvent system of the stain was responsible for this occurrence. One component of the solvent system, acetonitrile, softens the plastic surface enabling the stain to penetrate and remain on the surface. The Triple Treatment Technique
(TIT) which is a combination of the RVT, metal deposition and fluorescent staining, overcomes this problem by rendering the entire substrate surface, except the fingerprint ridges, impermeable to stains with a thin coating of metal. This technique provides remarkable improvement to the quality of prints on a wide variety of surfaces so developed.

Enhancement of cyanoacrylate-developed prints by chemical modification, such as reduction of the nitrile group to an amine and subsequent reaction with 4-chloro-7-nitrobenzofurazan, and transesterification and aminolysis with chromophoric alcohols and amines, respectively, was not successful.

A series of "one-stage" coloured and fluorescent compounds based on anthracene/2-cyanoacrylate and anthracene/2-cyanoacrylamide adducts were prepared and evaluated as latent fingerprint reagents. The coloured adducts were not suitable because they showed poor sensitivity and selectivity. One of the fluorescent adducts, anthracene/(2-(7-nitrobenzofurazan-4-yl)aminoethyl) 2-cyanoacrylate, showed reasonably good selectivity and sensitivity on a variety of surfaces including aluminium foil, clear polythene, PVC, polished leather and glossy paper.

Considering all the avenues related to the detection of latent prints with cyanoacrylate that have been explored, the "one-stage" fluorescent reagent has the greatest potential. Future work in this area should involve the synthesis of adducts with the cyclodiene moiety having a higher boiling point than the corresponding 2-cyanoacrylate moiety. Thus, by retaining the eliminated cyclodiene in the heating element, interference from the latter can be minimised. Examples of cyclodiienes which could be suitable for this purpose include 9-nitroanthracene (b.p. 275°C), 1-hydroanthracene (b.p. 234°C), 9,10-diphenylanthracene (m.p. 245°C) and other derivatives of anthracene. The use of adducts with more volatile cyclodiene moieties than the corresponding 2-cyanoacrylate esters is, technically, not a feasible alternative because the eliminated cyclodiene can not be removed discriminately from the cyclodiene/2-cyanoacrylate ester vapour mixture (e.g. using a pump) formed in the
RVT developing chamber.

For fluorescent cyanoacrylate latent fingerprint reagents to impart good selectivity, the fluorogenic "tags" attached to them should not be bulky. Therefore, the use of fluorogenic chromophores should not be limited to those based on 7-nitrobenzofurazan, but should be extensively explored.
MATERIALS AND EQUIPMENT

MATERIALS

The chemicals used were of analytical grade and obtained from various sources as listed below:

- Acetic acid
- Acetone
- 1-aminobenzotriazole
- p-anisic acid
- 8-aminopyrimidine
- Anisole
- Benzyl alcohol
- n-Butanol
- n-Hexanol
- Benzylamine
- Chloroacetic acid
- Cotton and 54
c-Flours
- 4-chloro-7-nitroquinolinone
- n-Butanol
- Dodecylamine
- 4-Dimethylaminomethylbenzaldehyde
- Dinaphthol
- Dodecylamine
- Chloroform
- Dichloromethane
- 1,3-diphenyl-2-propanone
- 1,5-dithiophene-1,2,3,4-tetra-
  chloroethane
- 1,3-cyclohexadione
- Diphenylketone
- Diethyloxalate
- Anthracene
- Butylamine

CHAPTER FIVE

EXPERIMENTAL SECTION
MATERIALS AND EQUIPMENT

MATERIALS

The chemicals used were of analytical grade and obtained from various sources as listed below.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>Alanine</td>
<td>BDH</td>
</tr>
<tr>
<td>1-aminoanthraquinone</td>
<td>Aldrich</td>
</tr>
<tr>
<td>p-aminophenol</td>
<td>Ega Chemie</td>
</tr>
<tr>
<td>8-aminoquinoline</td>
<td>Fluka</td>
</tr>
<tr>
<td>Azulene</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>May and Baker</td>
</tr>
<tr>
<td>n-butanol</td>
<td>May and Baker</td>
</tr>
<tr>
<td>t-butyl alcohol</td>
<td>May and Baker</td>
</tr>
<tr>
<td>Butylamine</td>
<td>Fluka</td>
</tr>
<tr>
<td>Cyanoacetic acid</td>
<td>BDH</td>
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<tr>
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Ethyl cyanoacetate
Fluorescamine
Furan
Gentian Violet
Glycerol
Hydrochloric acid
8-hydroxyquinoline
7-hydroxycoumarin
Linolenic acid
Lithium aluminium hydride
Methyl cyanoacetate
4-methyl-7-hydroxycoumarin
Methyl methacrylate
Methyl linolenate
Methyl stearate
1-octadecene
Octadecylamine
Oleyl alcohol
Paraformaldehyde
Paraffin
Phenol
Phenethyl alcohol
\(\alpha\)-phthalaldehyde
Phosphorus pentachloride
Phosphorus pentoxide
Potassium fluoride
Rhodamine 6G
Stearic acid
Silica, No. 7734
Sodium carbonate
Sodium hydroxide
Sodium lactate
Sodium methoxide
Sodium propionate
Squalene
Styrene
Super Glue 3

May and Baker
Fluka
Merck
BDH
May and Baker
May and Baker
Fluka
Aldrich
Ega Chemie
Fluka
Koch Light, UK
Aldrich
BDH
Sigma
Sigma
Aldrich
Ega Chemie
Ega Chemie
May and Baker
BP
May and Baker
May and Baker
Fluka
Hopkin-Williamson, UK
May and Baker
BDH
BDH
Ega Chemie
Merck
May and Baker
May and Baker
Ajax, Australia
Fluka
BDH
Aldrich
Ajax, Australia
Repco, Loctite
EQUIPMENT

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<tr>
<td>1,1,2-trichlorotrifluoroethane</td>
<td>ICI, Australia</td>
</tr>
<tr>
<td>Tristearin</td>
<td>BDH</td>
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<tr>
<td>Unilite (150w Xenon arc lamp)</td>
<td>Forensic Science Research Unit, A.N.U.</td>
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<tr>
<td>Vacuum metal deposition unit,</td>
<td>W. Edwards, England</td>
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<td>W.F. O’Brien, Canberra</td>
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SPECTRAL ANALYSIS

All n.m.r. spectra were obtained on the Varian EM-360A (60 mHz) and infrared spectra, on the Perkin Elmer 283 Infrared Spectrophotometer. The excitation and emission spectra were obtained on the Perkin Elmer MPF-44B Fluorescence Spectrophotometer with a DCSU-2 Differential Corrected Spectra Unit attached. Samples were submitted to the Research School of Chemistry, A.N.U. for Mass spectral and microanalysis.
5.1. Improved Formulations for Stains

(a) Solutions

Coumarin 540 (1.4 mg) was dissolved in acetonitrile (10 ml) and diluted to 100 ml. with 1,1,2-trichlorotrifluoroethane. For Gentian Violet, the compound (0.1 g) was dissolved in acetonitrile (10 ml.), absolute ethanol (10 ml.) and diluted to 100 ml. with 1,1,2-trichlorotrifluoroethane.

(b) Application and Visualisation of Stains

Fresh and one-year-old latent prints on clear polythene and aluminium foil developed with Super Glue 3%, Loctite, were stained either by dipping the article in the staining solution for 2-3 seconds or by applying the latter directly to the article with a Pasteur pipette. The excess was immediately washed off with water. For larger items, the stains can be applied by using a spray technique. An air-powered refillable spray pack (Mistlon, Australian Life Products Ltd.) was used and the results obtained were comparable to that of the Pasteur pipette or dipping techniques.

Prints stained with Gentian Violet were visualised under white light. Those treated with Coumarin 540 were visualised using the Unilite Xenon arc lamp with the 450 nm and 550 nm interference filters for excitation and viewing, respectively.

5.2. Synthesis and Evaluation of NBD-amino derivatives

(a) Synthesis

The butylamine and decylamine derivatives, described below, have been prepared on a very small scale (not isolated) for analytical purposes and reported [Mellbin et al., 1984; Ahnoff et al., 1981; Latham et al., 1976; Lancet et al., 1977; MacPhee et al., 1977].
The following procedure is representative of the method employed for the reaction of 4-chloro-7-nitrobenzofurazan (NBD-Cl) with nucleophilic amines by substituting chloride to form the corresponding 4-amino-7-nitrobenzofurazan (NBD-amino) derivatives.

A solution of n-butylamine (1.1 g, 15 mmole) in ether (5 ml.) was added dropwise to a mixture of NBD-Cl (3 g, 15 mmole) and sodium carbonate (1.6 g) in anhydrous ether (50 ml.) The mixture was refluxed at 40°C for two hours. On cooling, the sodium carbonate was removed by filtration through a small column of silica (Merck 7734). The solvents were removed with a rotary evaporator and the solids dissolved in minimum ethyl acetate. The product was separated by column chromatography (80 g silica; chloroform as eluant) and obtained in 62% (2.2 g) yield. Recrystallisation from ethyl acetate/n-hexane formed bright orange-coloured crystals (m.p. 90°C).

Analysis- Calcd.: C,50.84; H,5.12; N,23.72
Found: C,50.84; H,5.10; N,23.50

(II) NBD-diethylamine

Recrystallisation from ethyl acetate/n-hexane formed red-coloured crystals (m.p. 134-135°C) and obtained in 82% yield.

Analysis- Calcd.: C,50.84; H,5.12; N,23.72
Found: C,50.82; H,5.15; N,23.49

(III) NBD-ethanolamine

A mixture of chloroform-ethanol (19:1) was used as eluant for column chromatography. Recrystallisation from dichloromethane/petroleum ether formed red-orange coloured crystals (m.p. 150°C) and obtained in 71% yield.
Analysis- Calcd.: C,42.86; H,3.60; N,24.99
Found: C,42.73; H,3.53; N,24.45

(IV) NBD-p-aminophenol

Recrystallisation from ethyl acetate/petroleum ether formed red-coloured crystals (m.p. 218°C) and obtained in 96% yield.

Analysis- Calcd.: C,52.95; H,2.96; N,20.58
Found: C,53.15; H,2.99; N,20.05

(V) NBD-decylamine

Recrystallisation from n-hexane formed red-coloured crystals (m.p. 105°C) and obtained in 69% yield.

Analysis- Calcd.: C,59.98; H,7.55; N,17.49
Found: C,60.53; H,7.72; N,17.36

(VI) NBD-octadecylamine

The product was obtained in 92% yield. Recrystallisation from n-hexane formed red-coloured crystals (m.p. 107-108°C).

Analysis- Calcd.: C,66.63; N,9.32; N,12.95
Found: C,66.39; N,9.50; N,12.88

(VII) NBD-alanine

This compound was prepared according to Jurrs [Jurrs et al., 1983]. 7-chloro-4-nitrobenzofurazan (0.4 g, 2 mmole) was dissolved in absolute methanol (60 ml.) and saturated β-alanine in 1M sodium bicarbonate (3 ml.) was added. The mixture was stirred at room temperature for 12 hours, acidified with 20% hydrochloric acid and the solvents removed with a rotary evaporator. The brown solids were
washed with water and a little chloroform. Recrystallisation from ethyl acetate/petroleum ether gave a light brown-coloured compound (m.p. 202°C) and obtained in 50% yield.

Analysis: Calcd.: C, 42.89; H, 3.20; N, 22.22

Found: C, 42.90; H, 3.09; N, 21.92

(b) **Excitation and Emission Spectra**

(i) **Solution**

A 5.5 x 10^{-5} M solution of each of the NBD-amino derivatives (except NBD-p-aminophenol) and Coumarin 540 was prepared by dissolving the compound in acetonitrile (10 ml.) and diluting to 100 ml. with 1,1,2-trichlorotrifluoroethane. The measurements were made with a stoppered 1 cm-pathlength quartz cell on the Perkin-Elmer MPF-44B Fluorescence Spectrophotometer.

(ii) **Solid**

Cyanoacrylate-developed prints on clear polythene were stained separately with a 0.002% (w/v) solution of each of the NBD-amino derivatives (except NBD-p-aminophenol) and Coumarin 540. The solutions were prepared as described above. The stained print was cut into size (1.5 x 3 cm) and placed in a specially made holder and its excitation and emission spectra recorded.

(c) **Evaluation of Stains**

(i) **Preparation of Prints and Solutions**

Fresh (less than 12 hours old) and aged (1 week to 17 months) latent prints impressed on sheets of glass, plain and painted aluminium, PVC, and white and clear polythene were developed with Super Glue 3 (Loctite) using the RVT. The respective
staining solutions of NBD-amino derivatives and Coumarin 540 were prepared by dissolving ca. 20 mg of each compound in acetonitrile (10 ml.) and diluted to 100 ml. with 1,1,2-trichlorotrifluoroethane. The staining solution of Gentian Violet was prepared by dissolving 0.1g in 10 ml. of acetonitrile and 10 ml. of ethanol and diluted to 100 ml. with 1,1,2-trichlorotrifluoroethane.

(ii) Staining and Assessment

Staining was carried out by applying the staining solution with a Pasteur pipette directly to the cyanoacrylate-developed print followed immediately by washing with tap water and drying between tissues.

The fluorescent prints were visualised using a Xenon arc lamp (Unilite) with the 450 nm and 550 nm interference filters for excitation and viewing, respectively. The Gentian Violet-stained prints were visualised under white light. Assessment of each print was based on two criteria:

(a) sensitivity- graded according to the colour/fluorescence intensity of the fingerprint ridges; and 

(b) selectivity- graded according to the colour/fluorescence intensity of the surface background.

The overall quality of a print was represented by the numerical average of these two graded criteria, which in essence, is effectively the contrast between the ridges and the surface. Grading was made as follows:

<table>
<thead>
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<th>Colour/fluorescence Intensity</th>
<th>Sensitivity (ridge intensity)</th>
<th>Selectivity (surface intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None to low</td>
<td>1-2</td>
<td>5-6</td>
</tr>
<tr>
<td>medium</td>
<td>3-4</td>
<td>3-4</td>
</tr>
<tr>
<td>high</td>
<td>5-6</td>
<td>1-2</td>
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</tbody>
</table>
Thus, an excellent fluorescent print would be graded 6 for its high ridge fluorescence intensity (i.e. high sensitivity) and 6 for its low surface background fluorescence intensity (i.e. high selectivity) giving an Overall Quality grading of \[(6+6)/2\] = 6.

5.3. Co-vaporisation of ethyl 2-cyanoacrylate with Fluorogenic Compounds

The RVT with two heating elements was used. Two drops of Super Glue 3 were deposited on one of the heating spoons with a heat setting of 60-70°C. 0.1-0.2 g of the fluorescent compound was deposited on the other spoon with a heating setting of 10-20°C above the melting point of the test compound. Latent prints impressed on clear polythene sheets suspended in the developing chamber were developed by the vapours evolved. This procedure was repeated for each of the following compounds (melting point in brackets [°C]): fluorescamine (154-156); 4-chloro-7-nitrobenzofurazan (97); o-phthaldialdehyde (54-56); 4-dimethylaminocinnamaldehyde (136-138); Rhodamine 6G (255-260); Coumarin 540 (206); anthracene (216) and NBD-butylamine (90). The developed prints were visualised using the Unilite with the 450 nm and 550 nm filters for excitation and viewing, respectively (anthracene-developed prints were illuminated with short-wave ultraviolet light).

5.4. Evaluation of the Triple Treatment Technique

Fresh fingerprints were impressed on the various test samples and developed with Super Glue 3 using the RVT. Half of the developed print was covered longitudinally with a masking tape. The entire surface was exposed to metal deposition (gold followed by zinc). The masking tape was removed and the whole print (half with cyanoacrylate and the other half with the additional coating of zinc)
was stained with a 0.02% (w/v) solution of NBD-butylamine in acetonitrile (10% v/v) and 1,1,2-trichlorotrifluoroethane (90% v/v). The two halves of the print were compared visually using the Unilite for illumination. A 450 nm interference filter with a half-bandwidth of 50 nm was used as the source (excitation) filter and a 550 nm interference filter with the same half-bandwidth as the viewing (barrier) filter.

Each print was assessed according to the degree of improvement achieved by the new technique. The degree of improvement was categorised into one of four grades: no improvement (±); slight improvement (+); definite improvement (++); and very marked improvement (++++).

5.5. EFFECT OF "R" SUBSTITUENTS ON SELECTIVITY OF CYANOACRYLATE ESTERS

5.5.1. Synthesis of 2-cyanoacrylate esters

Cyanoacrylate esters with methyl, n-butyl, t-butyl, benzyl and phenyl groups were prepared as described below. Of the five cyanoacetate esters required for the preparation of the corresponding cyanoacrylate esters, methyl cyanoacetate was obtained commercially.

(1) n-butyl cyanoacetate

\[
\text{NCCH}_2\text{CO}_2\text{Et} + \text{C}_4\text{H}_9\text{OH} \xrightarrow{\text{KF}} \text{NCCH}_2\text{CO}_2\text{C}_4\text{H}_9 + \text{EtOH}
\]

The transesterification of ethyl cyanoacetate with n-butanol in the presence of potassium fluoride was carried out according to Polyakova [Polyakova et al., 1967]. The product was collected at 48-50°C/0.2 mmHg in 66% yield.

N.m.r. spectrum- \(\delta_H\) (CDCl\(_3\)): 4.25(t, J=12Hz, 2H, -CH\(_2\)-C\(_3\)H\(_7\)); 3.50(s,2H, NCCH\(_2\)); 1.85-0.75(m,7H,-C\(_3\)H\(_7\)).
(II) t-butyl cyanoacetate

\[ \text{NCCH}_2\text{CO}_2\text{H} + \text{PCl}_5 \rightarrow \text{NCCH}_2\text{COCl} + \text{POCl}_3 + \text{HCl} \]
\[ \text{NCCH}_2\text{COCl} + (\text{CH}_3)_2\text{COH} + \text{C}_6\text{H}_5\text{N}((\text{CH}_3)_2 \rightarrow \text{NCCH}_2\text{CO}_2\text{C}((\text{CH}_3)_2 + \text{C}_6\text{H}_5\text{N}((\text{CH}_3)_2\cdot\text{HCl} \]

The synthesis of t-butyl cyanoacetate followed Ireland [Ireland et al., 1973]. The product was collected at 36°C/0.008 mmHg in 47.5% yield.

N.m.r. spectrum- \( \delta_\text{H}(\text{CDCl}_3) \): 3.40(s,2H,NCCH\(_2\)); 1.55(s,9H,-C(CH\(_3\))\(_3\). 

(III) Benzyl cyanoacetate

\[ \text{NCCH}_2\text{CO}_2\text{Et} + \text{C}_6\text{H}_5\text{CH}_2\text{OH} \rightarrow \text{NCCH}_2\text{CO}_2\text{CH}_2\text{C}_6\text{H}_5 + \text{EtOH} \]

Benzyl acetate was prepared by transesterification of ethyl cyanoacetate with benzyl alcohol according to Dahn [Dahn et al., 1959]. The product was collected at 100°C/0.09 mmHg in 53% yield.

N.m.r. spectrum- \( \delta_\text{H}(\text{CDCl}_3) \): 7.40(s,5H,C\(_6\text{H}_5\)); 5.25(s,2H,-OCH\(_2\)); 3.45(s,2H,NCCH\(_2\). 

(IV) Phenyl cyanoacetate

\[ 2\text{NCCH}_2\text{CO}_2\text{H} + 2\text{PhOH} + \text{POCl}_3 \rightarrow 2\text{NCCH}_2\text{CO}_2\text{Ph} + \text{HPO}_3 + 3\text{HCl} \]

Phenyl cyanoacetate was prepared by reacting cyanoacetic acid with freshly distilled phenol in the presence of phosphorus oxychloride according to Ziegler [Ziegler et al., 1957]. The product was purified by vacuum distillation (110-114°C/0.03 mmHg) and obtained in 44% yield. Crystallisation from dichloromethane yielded white crystals (m.p. 41.5°C; Lit. 41°C [Zeigler et al., 1957]).

N.m.r. spectrum- \( \delta_\text{H}(\text{CDCl}_3) \): 7.68-7.08(m,5H,C\(_6\text{H}_5\)); 3.70(s,2H,NCCH\(_2\).
(V) Methyl 2-cyanoacrylate

The following procedure is representative of the method employed in the condensation of a cyanoacetate ester with formaldehyde to form the corresponding 2-cyanoacrylate ester [Coover et al., 1968].

A mixture of methyl cyanoacetate (49.5 g, 0.5 mole), powdered paraformaldehyde (12 g, 0.4 mole), benzene (20 ml), piperidine (0.05 g) and 10% aqueous sodium hydroxide (10 drops from Pasteur pipette) contained in a 100 ml. two-neck round-bottom-flask fitted with a Dean-Stark device was heated at 100°C. When no more water-benzene azeotrope was collected (or after 2.5 hr.), 3-sulfolene (0.5 g), hydroquinone (1.0 g) and phosphorus pentoxide (1.05 g) were added and the benzene distilled off. The viscous residue was distilled in vacuo to give 39.4 g (88.7% yield) of methyl 2-cyanoacrylate; b.p. 92°C/0.15 mmHg.

N.m.r. spectrum- δ_H(DCl_3): 7.15(s,1H,CH=); 6.72(s,1H,CH=); 3.93(s,3H,-OCH_3).

(VI) n-butyl 2-cyanoacrylate

This compound, in the monomeric form, was collected at 63-65°C/0.14 mmHg in 44% yield.

N.m.r. spectrum- δ_H(DCl_3): 7.13(s,1H,CH=); 6.70(s,1H,CH=); 4.35 (t, J=12Hz,2H, -CH_2C_3H_7); 2.00-0.70(m,7H,-C_3H_7).

(VII) t-butyl 2-cyanoacrylate

This ester was collected as white rubbery flakes of polymer deposited in the condenser.

I.r. spectrum- ν_max(film) cm⁻¹: 2990, 2940, 2250(nitrile); 1740(ester).

Mass spectrum- 153(M⁺,0.03%); 80(CH₂=C(CN)CO⁺,100%); 57(Me₃C⁺,97%).
5.5.2. Preparation of poly(2-cyanoacrylates)

Methyl 2-cyanoacrylate and n-butyl 2-cyanoacrylate, obtained in the liquid monomeric form, were stored at 4°C for two weeks after which the products became hard, transparent polymers. The ethyl 2-cyanoacrylate polymer was prepared by dissolving Repco Super Glue 3™ (1 g) in acetone (20 ml) at 0°C in an ice bath and stirred with water (20 ml). The resultant precipitate was dried with a rotary evaporator. t-butyl, benzyl and phenyl 2-cyanoacrylate esters were obtained in the polymeric form, as mentioned earlier. All six polymers were ground into powders.

5.5.3. Evaluation of cyanoacrylate polymers

(a) Development of latent prints

The use of polymeric cyanoacrylate esters for the development of latent prints
requires the depolymerisation of the solids at high temperatures. An apparatus, called the Rapid Vaporisation Technique (RVT) system, was designed for this purpose (Appendix 2). Using the RVT, latent prints impressed on clear polythene sheets were developed with the various polymers. The samples were removed from the developing chamber when sufficient ridge details were observed. Where no prints were visible, the development was terminated after 30 minutes.

(b) Staining

Some of the developed prints appeared white while others were grey. In order to make a visual assessment of the various developed prints, they were enhanced by staining. Two stains were used: Gentian Violet, which is a visible stain, and NBD-butylamine (see Methods for preparation), photoluminescent stain. The composition and technique of application of these stains are described in Section 5.2.(c).

(c) Visualisation

Prints stained with Gentian Violet were visualised under normal white light and those with NBD-butylamine, using a Xenon arc lamp with a 450 nm and a 550 nm interference filter for excitation and barrier, respectively.

5.6. Synthesis of ethyl 2-cyanoacrylate Adducts

The reaction between ethyl 2-cyanoacrylate and the diene was initially carried out on a small scale. Super Glue (1 drop) was added to a solution of the diene (approximately 10 mg) in CDCl$_3$ (0.5 ml) contained in an n.m.r. tube. The tube was sealed and after 30 minutes at room temperature, the n.m.r. spectrum was run. This spectrum was compared with those of ethyl 2-cyanoacrylate and the diene in CDCl$_3$. If the reaction did not proceed, the tube was heated for a further 30 minutes at 50°C
(in oil bath) and the n.m.r. spectrum re-checked. Where necessary, the procedure was repeated at 80, 100 and 130°C.

Of the six dienes treated with ethyl 2-cyanoacrylate, four showed positive reaction. They were: cyclopentadiene and 1,3-diphenylisobenzofuran (at room temperature), anthracene (at 80°C) and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (at 120°C). The scaled-up procedures are described below.

(I) Cyclopentadiene/ethyl 2-cyanoacrylate adduct

(Ethyl bicyclo[2.2.1]hepta-5-ene-2-cyano-2-carboxylate)

A solution of freshly distilled cyclopentadiene (4 g, 0.06 mole) in dry dichloromethane (5 ml) was added dropwise to Super Glue™ (5 g, 0.04 mole) in dry dichloromethane (5 ml) in an ice bath. The mixture was stirred for 12 hours at room temperature. The dichloromethane and excess cyclopentadiene were removed with a rotary evaporator in vacuo and the product purified on a chromatography column (silica, 160 g; mixture of 1:19 ethanol-chloroform as eluant). The product was obtained as an oil in 99.5% (7.6 g) yield.

N.m.r. spectrum- $\delta_H$(CDCl$_3$): 6.42(q,J=9Hz,1H,cyclo H); 5.95(q,J=9Hz,1H, cyclo H); 4.27(q,J=22Hz,2H,-OCH$_2$-); 3.60-1.60(m,6H,cyclo H); 1.30(t,J=15Hz,3H,-CH$_3$).

Mass spectrum: 191(M$^+$,1.65%); 80(H$_2$C=C(CN)CO$^+$,14.79%); 66(cyclopentadiene, 100%).

(II) Anthracene/ethyl 2-cyanoacrylate Adduct

(Ethyl 9,10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxylate)

A mixture of anthracene (7 g), Super Glue™ (5 g), hydroquinone (0.1 g) and dry benzene (70 ml) was refluxed at 90°C for 12 hours. On cooling, the benzene was
removed by distillation under reduced pressure (20 mmHg, 50°C) and the solids dissolved in chloroform (200 ml). Unreacted cyanoacrylate was removed as a polymer precipitate by washing with water (3 x 20 ml). The organic layer was dried over anhydrous sodium sulphate and the chloroform removed under reduced pressure with a rotary evaporator. The product was purified by recrystallisation from ethanol and was obtained in 84% (10 g) yield; m.p. 127°C (Lit. 124.5-126.5°C [Buck, 1978]).

N.m.r. spectrum- $\delta_H$(CDCl$_3$): 7.60-7.10(m,8H,C1-8 aromatic H); 4.90(s,1H, C9-H); 4.45(t,J=5Hz,1H,C10-H); 4.15(q,J=24Hz,2H,-OCH$_2$-); 2.80(dd,J=13,3Hz,1H,C12-H); 2.10(dd,J=13,3Hz,1H,C12-H); 1.20(t,J=14Hz,3H,-CH$_3$).

(III) 1,3-diphenylisobenzofuran/ethyl 2-cyanoacrylate Adduct

(Ethyl 1,3-diphenyl-1,3-ethanoisobenzofuran-8-cyano-8-carboxylate)

1,3-diphenylisobenzofuran (1 g, 3.7 mmole) and hydroquinone (0.01g) were dissolved in dry dichloromethane (10 ml) in an ice bath. A solution of Super Glue$^\text{TM}$ (0.48 g, 3.8 mmole) in dichloromethane (5 ml) was added dropwise. The mixture was stirred for 16 hours at room temperature. The dichloromethane was removed with a rotary evaporator and the oily residue crystallised from ethanol. 1.12 g (76.6% yield) of the crystal leaflets (m.p. 132-134°C) was obtained.

N.m.r. spectrum- $\delta_H$(CDCl$_3$): 8.14-7.08(m,14H,aromatic H); 3.87(q,J=21Hz, 2H,-OCH$_2$-); 3.42(d,J=12Hz,1H,C9-H); 2.70(d,J=12Hz,1H, C9-H); 0.81(t,J=14Hz,3H,-CH$_3$).

Analysis- Calcd.: C,78.97; H,5.35; N,3.54
Found: C,78.64; H,5.40; N,3.39
**IV** 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene/ethyl 2-cyanoacrylate Adduct

(Ethyl bicyclo[2.2.1]hepta-5-ene-7,7-dimethoxy-1,4,5,6-tetrachloro-2-cyano-2-carboxylate)

A mixture of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (1 g, 3.8 mmole), Super Glue™ (0.5 g, 4 mmole) and hydroquinone (0.01 g) in dry toluene (15 ml) was refluxed at 120°C for 20 hours. The toluene was removed at reduced pressure. The product was purified on a chromatograph column (silica, 50 g; a mixture of 1:4 petroleum ether-dichloromethane as eluant). 1.42 g (96% yield) of the oily product was obtained.

**N.m.r. spectrum**- δH(d6-benzene): 3.85(q,J=21Hz,2H,-OCH2); 3.45(s,3H, OCH3); 3.15(s,3H, OCH3); 2.90(dd,J=16,12Hz,1H,C3-H); 2.64(dd,J=16,12Hz,1H,C3-H); 0.87(t,J=14Hz,3H,-CH2CH3).

**Analysis**- Calcd.: C,40.13; H,3.37; Cl,36.45.

Found: C,40.15; H,3.35; Cl,36.44.

5.6.1. Evaluation of ethyl 2-cyanoacrylate Adducts

Latent fingerprints were impressed on clear polythene and developed with each of compounds I - IV (see Section 5.6.) using the RVT (see Appendix 2 for procedure). The developed prints were compared with that of a Super Glue™-developed print under normal white light.

5.7. Photoluminescent and Coloured Adducts

5.7.1. Synthesis

(I) Anthracene/2-cyanoacrylic acid Adduct

To a solution of anthracene/ethyl 2-cyanoacrylate adduct (10 g, 0.033 mole) in tetrahydrofuran (100 ml) was added a solution of sodium hydroxide (20% w/v; 50 ml)
and this resulting mixture stirred at room temperature for 15 hours. The solvents were distilled off at reduced pressure (20 mmHg, 40°C). Excess water (a total of 800 ml) was added to dissolve the white solids. The unchanged ester was extracted with dichloromethane (2 x 50 ml). The aqueous solution was acidified with concentrated hydrochloric acid to pH 2 and the solids were filtered off, washed with water and dried over phosphorus pentoxide in vacuo (20 mmHg) for 24 hours. 9.05 g (99.7% yield) of the product was obtained; m.p. 206-209°C (Lit., 208-209°C [Buck, 1978]).

N.m.r. spectrum - δ_H(CD3OD): 7.62-7.08(m,8H,Cl-8 aromatic H); 4.95(s,1H, C9-H); 4.85(s,1H,OH); 4.45(t,J = 5Hz,1H,C10-H); 2.75(dd, J=13,3Hz,1H,C12-H); 2.05(dd,J=13,3Hz,1H,C12-H).

(II) NBD-ethanolamine

(see Section 5.2. for preparation)

(III) NBD-N'-methylethanolamine (see Scheme 2.1.)

To a mixture of 7-chloro-4-nitrobenzofurazan (2 g) and sodium carbonate (1.1 g) in absolute methanol (50 ml) was added N'-methylethanolamine (0.75 g) and stirred at room temperature for 2 hours. The orange-coloured solids were filtered off and washed with methanol. Recrystallisation from a mixture of 1:1 chloroform-ethanol gave 1.78 (74.8% yield) of bright orange-coloured needles (m.p. 177°C).

N.m.r. spectrum - δ_H(d6-DMSO): 8.60(d,J=9Hz,1H,C5-H); 6.50(d,J=9Hz,1H, C6-H); *5.00(t,J=11Hz,1H,-OH); 4.23(t,11Hz,2H,CH2CH2); 3.86(t,J=11Hz, 2H,CH2CH2); 3.60(s,3H,N-CH3). [* this triplet removed from spectrum by addition of D2O].

Analysis: Calcd.: C,45.38; H,4.23; N,23.52.

Found: C,45.10; H,4.21; N,23.35.
This alcohol was prepared according to Meldola [Meldola, 1885] (see Scheme 5.7.1.a). *p*-nitroaniline (10 g, 0.072 mole) was dissolved in concentrated hydrochloric acid (20 ml, 0.23 mole) and placed in an ice bath. Ice (5 g) was added followed by a solution of sodium nitrite (5 g, 0.072 mole) in water (5 ml), dropwise. The mixture was stirred for 0.5 hour at 0°C. A solution of phenol (6.80 g, 0.072 mole) in ethanol (5 ml) was added dropwise and stirred at room temperature for 2 hours. The solids were filtered off and recrystallised from toluene to give 8.7 g (49.7% yield) of brick-red-coloured prisms (m.p. 218-219°C; Lit., 219-219.5°C [Heilbron, 1965]).

N.m.r. spectrum- \( \delta_H (CD_3OD): 8.50(d, J=9Hz, 2H, aromatic H); 8.15-7.90(m, 4H, aromatic H); 7.00(d, J=9Hz, 2H, aromatic H); 4.85(s, 1H, OH). \)

(V) 2-(1-azulyl)ethanol

\[ \text{Scheme 5.7.1.b.} \]
This compound was prepared according to McDonald [McDonald et al., 1972] (Scheme 5.7.1.b.). To a solution of azulene (0.5 g, 3.9 mmole) in dry dichloromethane (120 ml) in an ice bath was added anhydrous aluminium chloride (1.07 g, 8.0 mmole) with stirring. After 20 minutes, a solution of ethylene oxide (0.4 ml) in dichloromethane (40 ml) was added dropwise and the solution stirred for a further 10 minutes. The blue-coloured solution was poured into iced hydrochloric acid (10% w/v; 1 litre) and the organic layer was separated with a separating funnel. This dichloromethane layer was washed with 10% hydrochloric acid (2 x 50 ml) and water (5 x 100 ml), and dried over anhydrous sodium sulphate. The solvent was evaporated and the blue-coloured residue was chromatographed on alumina (Active basic, 150 g). A mixture of 19:1 petroleum ether-dichloromethane eluted 0.23 g of azulene and chloroform eluted a second blue band of 2-(1-azulyl)ethanol (0.23 g, 34% yield). Recrystallisation from carbon tetrachloride formed blue-coloured needles.

(VI) Anthracene/(4'-nitrophenyl-4-azophenyl) 2-cyanoacrylate Adduct

[(4'-nitrophenyl-4-azophenyl) 9,10-dihydro-9,10-ethanoanthracene-11-cyano-11-carboxylate]

The following procedure is representative of the method employed in the esterification and aminolysis of the anthracene/2-cyanoacrylic acid adduct with fluorogenic and chromophoric alcohols and amines, respectively.

To a mixture of 4'-nitrophenyl-4-azophenol (0.97 g, 4 mmole) and anthracene/2-cyanoacrylic acid adduct (1.10 g, 4 mmole) in dry pyridine (20 ml) was added freshly distilled phosphorus oxychloride (0.2 ml, 2 mmole) and stirred at 50°C for 12 hours. On cooling, the solvents were removed with a rotary evaporator at reduced pressure. The red-coloured solids were dissolved in chloroform (200 ml) and
washed with 2M hydrochloric acid (2 x 50 ml) and water (2 x 50 ml). The organic layer was dried over anhydrous sodium sulphate, the chloroform evaporated, and the residue was chromatographed on silica (Merck 7734, 100 g). A mixture of 19:1 dichloromethane-ethanol was used as eluant. 1.8 g (90% yield) of orange-coloured solids were obtained. Recrystallisation from chloroform/ petroleum ether formed red-coloured crystals (m.p. 199-201°C).

N.m.r. spectrum- 8H(CDCl₃): 8.48(d, J=9Hz, 2H, azophenyl H); 8.08(d, J=9Hz, 4H, azophenyl H); 7.70-7.15(m, 10H, azophenyl H & C1-8 H); 5.15(s, 1H, C9-H); 4.53(t, J=5Hz, 1H, C10-H); 2.95(dd, J=14, 3Hz, 1H, C12-H); 2.30(dd, J=14, 3Hz, 1H, C12-H).

Analysis- Calcd.: C, 71.99; H, 4.03; N, 11.19
Found: C, 71.92; H, 4.08; N, 11.16

A summary of all the 13 synthesised adducts detailing method of purification, yield, n.m.r. spectrum, analysis and melting point are shown in Table 5.7.1.a. and Table 5.7.1.b.
Table 5.7.1.a(1)  
**N.M.R. of anthracene adducts (in CDCl₃)**

![Chemical Structure Image]

<table>
<thead>
<tr>
<th>Adduct</th>
<th>R</th>
<th>$H_{a,b}$</th>
<th>$H_c$</th>
<th>$H_d$</th>
<th>C1-C8 (m)</th>
<th>Other (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/ECA</td>
<td>$C_2H_5$</td>
<td>2.80(dd)</td>
<td>4.45(t)</td>
<td>4.90(s)</td>
<td>7.60-7.10</td>
<td>4.15(q,J=24Hz,2H,-OCH₂); 1.20(t,J=14Hz,3H,-CH₃)</td>
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<tr>
<td>A/NPAPCA</td>
<td>$\mathcal{O}-N=N-\mathcal{O}-NO_2$</td>
<td>2.90(dd)</td>
<td>4.53(t)</td>
<td>5.15(s)</td>
<td>(superimposed)</td>
<td>8.48(d,J=9Hz,2H,aromatic H); 8.08(d,J=9Hz,4H,aromatic H); 7.70-7.15(m,2H,aromatic H).</td>
</tr>
<tr>
<td>A/PCA</td>
<td>$C_6H_5$</td>
<td>2.93(dd)</td>
<td>4.47(t)</td>
<td>5.12(s)</td>
<td>7.75-6.93</td>
<td>(superimposed) 7.75-6.93(m,5H,aromatic H)</td>
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<tr>
<td>A/QCA</td>
<td></td>
<td>3.00(dd)</td>
<td>4.50(t)</td>
<td>5.36(s)</td>
<td>(superimposed)</td>
<td>8.97(dd,J=4,2Hz,1H,arom.H); 8.20(dd,J=9,2Hz,1H,arom.H); 7.87-7.10(m,4H,arom.H).</td>
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<tr>
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<td>2.97(dd)</td>
<td>4.50(t)</td>
<td>5.18(s)</td>
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<td>(superimposed) 7.98-7.02(m,7H,arom.H)</td>
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<tr>
<td>A/PECA</td>
<td>$CH_2CH_2C_6H_5$</td>
<td>2.75(dd)</td>
<td>4.40(t)</td>
<td>4.75(s)</td>
<td>7.60-6.73</td>
<td>(superimposed) 7.60-6.73(m,5H,arom.H); 4.28(t,J=14Hz,2H,-OCH₂); 2.93(t,J=13Hz,2H,-CH₂-Ph).</td>
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Table 5.7.1.a.(2) (continued)

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<th>Adduct</th>
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<th>$H_{a,b}$ (J=13, 3Hz)</th>
<th>$H_c$ (J=5Hz)</th>
<th>$H_d$</th>
<th>Cl-C8 (m)</th>
<th>Other (R)</th>
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<td>A/BCA</td>
<td>CH$_2$C$_6$H$_5$</td>
<td>2.80(dd)</td>
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<td>4.83(s)</td>
<td>7.65-6.82</td>
<td>7.65-6.82(m,5H,arom.H); 5.12(d,J=2Hz,2H,-OCH$_2$).</td>
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<td>2.15(dd)</td>
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<td>A/MCCA</td>
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<td>5.14(s)</td>
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<td>7.77-6.95(m,3H,arom.H); 6.35-6.28(m,1H,C3-H); 2.40(s,3H,-CH$_3$).</td>
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<td>4.53(s)</td>
<td>8.67-6.37</td>
<td>8.67-6.37(m,7H,arom.H); 4.43-4.30(m,2H,CH$_2$CH$_2$); 3.48(t,J=14Hz,2H,CH$_2$CH$_2$).</td>
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<td>2.12(dd)</td>
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<td>4.58(t)</td>
<td>5.00(s)</td>
<td>7.62-6.83</td>
<td>9.65(broad S,1H,=NH); 8.70(d,J=9Hz,1H,benzo H); 6.60(d,J=9Hz,1H,benzo H); 4.45-4.17(m,2H,CH$_2$CH$_2$); 4.00-3.73(m,2H,CH$_2$CH$_2$).</td>
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### Table 5.7.1.a.(3) (continued)

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<th>$H_d$</th>
<th>C1-C8 (m)</th>
<th>Other (R)</th>
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<td>CH$_2$CH$_2$-N-Me</td>
<td>2.70(dd)</td>
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<td>7.70-7.10</td>
<td>8.55(d, $J=9$Hz, 1H, benzo H); 6.20(d, $J=9$Hz, 1H, benzo H); 4.68-4.22(m, 4H, CH$_2$CH$_2$); 3.46(s, 3H, -CH$_3$).</td>
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<td>4.98(s)</td>
<td>7.75-7.02</td>
<td>10.82(broad s, 1H, -NH); 9.04(q, $J=6$ Hz, 1H, arom.H); 8.57(q, $J=9$Hz, 1H, arom.H); 8.27(dd, $J=9$, 2Hz, 1H, arom. H); 7.75-7.02(m, 3H, arom.H).</td>
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### Table 5.7.1.b.(2) (continued)

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<th>Adduct</th>
<th>m.p. (°C)</th>
<th>Purification</th>
<th>Yield(%)</th>
<th>Analysis</th>
<th>Calculated</th>
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<td>C: CHCl₃/EtOH</td>
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</table>

C.C: = column chromatography, silica (Merck,7734); C: = crystallisation; PE = petroleum ether (b.p. 60-80°C);
* microanalysis constantly incorrect, mass spectrum: 495(M⁺,0.46%); 317(2-cyanoacrylate ester,17.60%); 178(anthracene,100%).
5.7.2. Evaluation

(a) Development of Latent Prints

Fresh latent prints were impressed on aluminium foil and developed with the various adducts using the RVT (see Appendix 2). With anthracene/ (2-(7-nitrobenzofurazan-4-yl)aminoethyl) 2-cyanoacrylate and anthracene/2-(N-(7-nitrobenzofurazan-4yl)-N-methylamino)ethyl 2-cyanoacrylate adducts, where initial results with aluminium foil were favourable, other substrates such as leather, glossy paper, PVC sheets, clear polythene and white polythene were included in the evaluation.

(b) Metal Complexation

Prints developed with anthracene/8-quinolinyl 2-cyanoacrylate and anthracene/8-quinolinyl 2-cyanoacrylamide adducts were dipped briefly in a solution of saturated zinc chloride in ethanol. The samples were dried in between tissues and the prints assessed.

(c) Visualisation

Prints developed with the visible-coloured adducts were assessed under normal white light and those with anthracene/coumarin 2-cyanoacrylate were visualised under long-wavelength ultraviolet light. Prints developed with anthracene/(2-(7-nitrobenzofurazan-4-yl)aminoethyl 2-cyanoacrylate and anthracene/2-(N-(7-nitrobenzofurazan-4-yl)-N-methylamino)ethyl 2-cyanoacrylate adducts were illuminated with a Xenon arc lamp using a 450 nm and 550 nm interference filters for excitation and viewing, respectively. With anthracene/(8-quinolinyl) 2-cyanoacrylate and anthracene/8-quinolinyl 2-cyanoacrylamide adducts, the developed prints, which were subsequently treated with zinc chloride, were visualised under short-wavelength ultraviolet light.
Effect of Functional Groups on Cyanoacrylate Deposition

Hypothetically, the deposition of cyanoacrylate on latent fingerprints is the result of polymerisation of the monomer on the ridges which is triggered by secretory products containing anionic functional groups. To verify this supposition, an experiment was designed which involved making prints with pure chemicals showing separately a range of functional groups present in fingerprint deposits.

METHOD

The effect of sixteen compounds which are chemically related to components of the fingerprint deposit on cyanoacrylate deposition was assessed. The following functional groups were selected: hydroxyl (-OH), hydroxide (OH⁻), unsaturated C=C bonds, esters (-COOR), carboxylate salts (-COO⁻) and carboxylic acids (-COOH). These functional groups were found in oleyl alcohol, glycerol, 1-octadecene, stearic acid, linolenic acid, squalene, methyl stearate, methyl linolenate, tristearin, octadecane, 1-octadecanol, n-decanol, sodium lactate (syrup), 70% aqueous sodium propionate, 2M sodium hydroxide and distilled water. A list of the various test compounds and the corresponding functional groups found in them are shown in Table A.1.

A control latent fingerprint and a simulated print were impressed side by side on a sheet of aluminium foil (4x6 cm). The simulated print was made by applying the test compound directly to a clean rubber fingerprint stamp with a stiff brush and stamped on the foil. The prints were developed with ethyl 2-cyanoacrylate using the RVT (Appendix 2). This procedure was repeated for each test compound. Liquid or paste-like test compounds were used undiluted and solid ones were dissolved in minimum amount of chloroform prior to application onto the stamp. The brush and stamp were cleaned with chloroform and a detergent (teepol) between tests.
Table A.1. Functional Groups of Test Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Functional Groups</th>
<th>Found on</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleyl alcohol</td>
<td>Unsat. C=C; hydroxyl</td>
<td>unsat.alcohols</td>
</tr>
<tr>
<td>Glycerol</td>
<td>hydroxyl</td>
<td>alcohols</td>
</tr>
<tr>
<td>n-decanol</td>
<td>hydroxyl</td>
<td>alcohols</td>
</tr>
<tr>
<td>1-octadecene</td>
<td>unsat.C=C</td>
<td>unsat.hydrocarbon</td>
</tr>
<tr>
<td>stearic acid</td>
<td>carboxylic (-COOH)</td>
<td>fatty acids</td>
</tr>
<tr>
<td>linolenic acid</td>
<td>unsat.C=C; -COOH</td>
<td>unsat.fatty acids</td>
</tr>
<tr>
<td>squalene</td>
<td>unsat.C=C</td>
<td>squalene</td>
</tr>
<tr>
<td>methyl stearate</td>
<td>ester (COOR)</td>
<td>glycerides</td>
</tr>
<tr>
<td>methyl linolenate</td>
<td>unsat.C=C; ester</td>
<td>unsat.glyceride</td>
</tr>
<tr>
<td>tristearin</td>
<td>ester (COOR)</td>
<td>glyceride</td>
</tr>
<tr>
<td>octadecane</td>
<td>sat.hydrocarbon</td>
<td>hydrocarbons</td>
</tr>
<tr>
<td>1-octadecanol</td>
<td>hydroxyl (-OH)</td>
<td>alcohols</td>
</tr>
<tr>
<td>*sodium lactate</td>
<td>Na⁺; carboxylate (COO⁻); hydroxyl.</td>
<td>inorganic salts</td>
</tr>
<tr>
<td>sodium propionate</td>
<td>Na⁺; -COO⁻</td>
<td>inorganic salts</td>
</tr>
<tr>
<td>sodium hydroxide</td>
<td>Na⁺; OH⁻</td>
<td>salts</td>
</tr>
<tr>
<td>water</td>
<td>H⁺; OH⁻</td>
<td>water</td>
</tr>
</tbody>
</table>

*Prepared by reacting equimolar of lactic acid and aqueous sodium hydroxide and subsequently dried with a rotary evaporator in vacuo.

In assessing the developed prints, each simulated print was compared with the control in terms of "whiteness". The "whiteness" of a print indicates the amount of cyanoacrylate deposited on it: a white print having a thicker deposition of polymer than a "clear" one. A simulated print as white as the control was graded '+'; a
not-so-white, '±', and a clear one,'-'.

RESULTS

The sensitivity of the various test compounds to cyanoacrylate ester is shown in Table A.1.1. Sodium hydroxide, sodium lactate and sodium propionate prints showed equally positive response to cyanoacrylate as the control print. Water and glycerol showed a less positive response. The rest of the test compounds did not show any cyanoacrylate deposited on them.

DISCUSSION

With regard to the supposition that basic species in the fingerprint deposit is responsible for the initiation of cyanoacrylate polymerisation and subsequent development of the latent print, the following general conclusions are drawn:

(a) Salts, particularly those that are basic in aqueous solutions (e.g. 1% aqueous sodium lactate has a pH of 11.4) strongly promote polymerisation of cyanoacrylate;

(b) Water and glycerol (a triol), containing hydroxide ions and hydroxyl groups, respectively, to a lesser extent, do promote polymerisation; and

(c) Fatty acids, monoalcohols, hydrocarbons and esters, both saturated and unsaturated, do not promote polymerisation.

These findings provide us with a general idea of the various components which are capable of causing the deposition of cyanoacrylate polymer on the fingerprint ridges, but do not explain why latent prints submerged in water over a period of time can still be developed with cyanoacrylate ester. It could be an unknown compound or a phenomenon whereby atmospheric moisture is absorbed by the fingerprint deposit that enables the development.
Table A.1.1. *Response of Test Compounds to ethyl 2-cyanoacrylate*

<table>
<thead>
<tr>
<th>Test Compound</th>
<th>Response*</th>
</tr>
</thead>
<tbody>
<tr>
<td>oleyl alcohol</td>
<td>-</td>
</tr>
<tr>
<td>glycerol</td>
<td>±</td>
</tr>
<tr>
<td>1-octadecene</td>
<td>-</td>
</tr>
<tr>
<td>stearic acid</td>
<td>-</td>
</tr>
<tr>
<td>linolenic acid</td>
<td>-</td>
</tr>
<tr>
<td>squalene</td>
<td>-</td>
</tr>
<tr>
<td>methyl stearate</td>
<td>-</td>
</tr>
<tr>
<td>methyl linolenate</td>
<td>-</td>
</tr>
<tr>
<td>tristearin</td>
<td>-</td>
</tr>
<tr>
<td>octadecane</td>
<td>-</td>
</tr>
<tr>
<td>1-octadecanol</td>
<td>-</td>
</tr>
<tr>
<td>n-decanol</td>
<td>-</td>
</tr>
<tr>
<td>sodium lactate</td>
<td>+</td>
</tr>
<tr>
<td>sodium propionate</td>
<td>+</td>
</tr>
<tr>
<td>sodium hydroxide</td>
<td>+</td>
</tr>
<tr>
<td>distilled water</td>
<td>±</td>
</tr>
<tr>
<td>latent print (control)</td>
<td>+</td>
</tr>
</tbody>
</table>

* As compared to the control print: (+) as white; (±) not as white; (-) clear.
APPENDIX 2

The Rapid Vaporisation Technique (RVT)

The Rapid Vaporisation Technique (RVT) has been designed to accelerate the vaporisation of cyanoacrylate esters and consequently to promote rapid development of latent fingerprints. Development of the RVT was based on an investigation made of Kendall and Rehn's "Rapid Superglue Fuming" technique which involves the use of cotton pads treated with sodium hydroxide [Kendall et al., 1982]. It was found that the polymerisation of Superglue (ethyl 2-cyanoacrylate) initiated by sodium hydroxide coated over the cellulose fibres was highly exothermic; a significant rise in temperature occurred in the pads (130°C was recorded using a thermocouple). The use of raw glass wool, which is a source of anionic hydroxyl groups, produced similar results (Figure A2.1.). Since the pads and wool are merely providing heat it would be

Figure A.2.1. Latent fingerprint on clear polythene developed with Superglue/cotton pad (left half of print) and Superglue/glass wool (right half)
expected that conventional heating would provide more efficient vaporisation.

The RVT involves direct heating of the cyanoacrylate ester to accelerate its vaporisation. It can be applied to developing chambers of practically all sizes and shapes (see Figure A2.2.). Essentially, the RVT consists of a glass chamber (modified glass beakers and fish tank were used), a 25 watt soldering iron with a copper spoon attached to the tip and a calibrated controlling unit for controlling the rate of heating. The evidential article is suspended on a wire frame placed in the chamber. Development of latent prints commences when the spoon is charged with 1-2 drops of cyanoacrylate monomer and the controlling unit turned on. The article is inspected regularly and removed when sufficient fingerprint detail is revealed. Since the rate of heating is controlled by the controlling unit, solid reagents, such as cyanoacrylate polymers, can be used as primers. Heat settings of 60-70°C and 150-160°C were applied for the vaporisation of liquid (monomeric) and solid (polymeric) ethyl 2-cyanoacrylates, respectively (see Appendix 3).

Figure A2.2. Various systems of the Rapid Vaporisation Technique (RVT)
APPENDIX 3

Use of Solid 2-cyanoacrylate Polymers as Latent Fingerprint Reagent

Solid cyanoacrylate polymers can be depolymerised at high temperatures and the monomers so formed used to develop latent fingerprints. The RVT (Appendix 2) has been designed for this purpose. The quality of latent prints developed with liquid and solid ethyl 2-cyanoacrylate is comparable (Figure A3).

Figure A3. Latent Fingerprints on clear polythene developed with ethyl 2-cyanoacrylate using the Rapid Vaporisation Technique: (A) Solid Polymer and (B) Liquid Monomer.
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