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PHOTOCHEMISTRY OF AROMATIC COMPOUNDS
INVOLVING CHARGE TRANSFER

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By

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A Thesis
Submitted to the Faculty of Graduate Studies
In Partial Fulfilment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University
November, 1973

Doctor of Philosophy (1973) McMaster University,
(Chemistry) Hamilton, Ontario.

TITLE : Photochemistry of Aromatic Compounds Involving Charge Transfer

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NUMBER OF PAGES : (vii)-127

SCOPE AND CONTENTS:

Photoreaction of naphthalene with pyrrole in various solvents has been studied. The major products are 2-(1,4-dihydro-1-naphthyl)-pyrrole and 2-(1,2-dihydro-2-naphthyl)-pyrrole which together comprise 85% of the products mixture. Solvent dependence of both products ratio and quenching of naphthalene fluorescence have also been investigated. The evidence suggests that the reaction is initiated by charge transfer from pyrrole to the lowest excited singlet naphthalene followed by a proton shift from the N-position of pyrrole to a negative charge center in the naphthalene ring. Using N-deuteriopyrrole in the reaction, it was found that deuterium is incorporated at the naphthalene ring in the products. Further evidence to support the proton shift mechanism is that N-methylpyrrole quenches naphthalene fluorescence as efficiently as pyrrole, but the reaction does not take place.

The photoreaction of 1-cyanonaphthalene with tetramethylethylene in methanol and benzene have been studied. Substitution products were found in methanol solution but a cyclo-adduct was formed in benzene. Tetramethylethylene quenches fluorescence of 1-cyanonaphthalene both in

methanol and benzene.

In contrast, 2-cyanonaphthalene only reacts with tetramethylethylene in methanol to give substitution products with one mole of methanol incorporated. The failure of reaction in benzene is consistent with the absence of fluorescence quenching in that solvent; in methanol, quenching occurs at the diffusion controlled limit.

ACKNOWLEDGEMENT

The author wishes to express his gratitude to Dr. J.J. McCullough, his research supervisor under whose direction and encouragement this research was performed.

The author would also like to express his gratitude to Dr. B. Ramachandran and Dr. M. McClory for valuable discussions, also to Mr. and Mrs. H. Gillmeister for their assistance.

Special thanks to his wife, Marion, for her understanding and help which enabled the author to complete this thesis.

The financial assistance of the National Research Council of Canada for this research program is deeply appreciated.

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PART 1. INTRODUCTION

Photochemistry may be defined as the study of chemical changes induced by the action of light. There are many facets to the subject of photochemistry, such as the isolation and identification of new chemical compounds, the study of rates of reaction both in the gas phase and in solution, and the use of flash spectroscopic techniques to identify short lived intermediates, to mention only a few.

In the world around us, photochemistry is important in plant photosynthesis, in atmosphere and pollution chemistry, and in a few industrial processes such as vitamin D synthesis and nylon 6 production.

The work in this thesis has to do with the photochemistry of small aromatic compounds - naphthalene, cyanonaphthalene, and pyrrole, and is concerned with the nature of the products, and with the mechanism by which they are formed.

In this introduction, some principles of photochemistry needed later in the discussion are previewed. In particular, charge transfer processes, exciplexes, and some chemistry of aromatic molecules, are described.

Description of Excited States

In general, a ground state molecule has all electron spins paired and is a singlet state, often designated S_0. An electron in the highest occupied bonding orbital is promoted to an unoccupied anti-bonding orbital in a very fast process (10^{-15} sec) when light is absorbed by the molecule. This fast process is more rapid than the movement of nuclei (Franck - Condon

Principle), and spin multiplicity is conserved, giving the lowest excited singlet state S_1. Then the molecule rapidly loses excess vibrational energy and decays (10^{-13} to 10^{-14} sec) to the lowest vibrational level (ν_0') of S_1. The excited singlet may change to a triplet state (T_1, lowest triplet state) through intersystem crossing. However, this process is often slow (10^{-6} sec) in aromatic molecules.

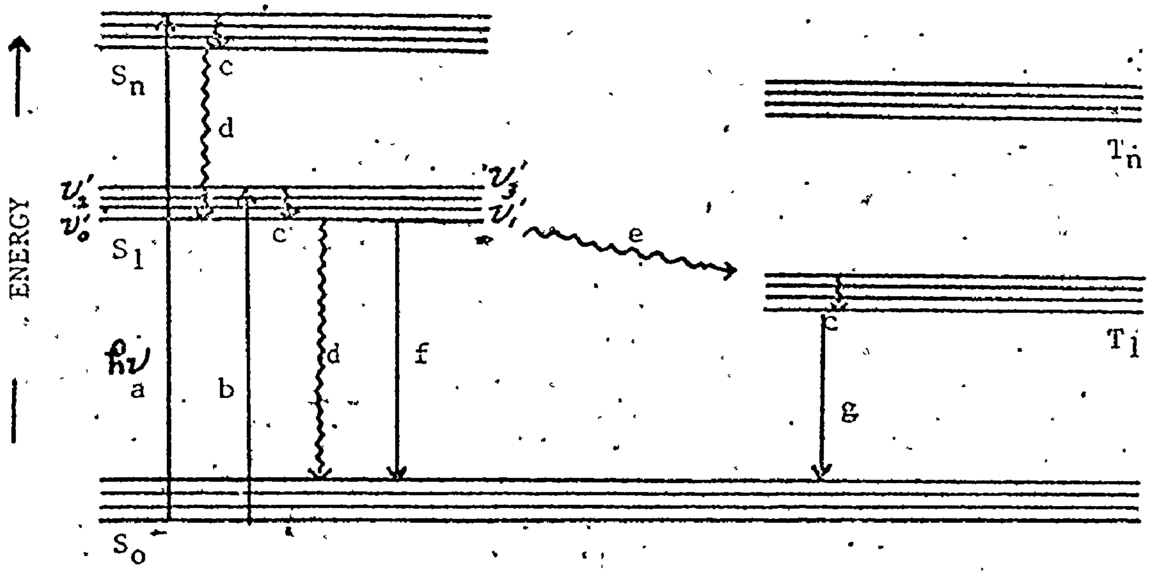
One of the important properties of the lowest excited state is luminescence emission. The light emitted during transition from lowest singlet state to ground state is called fluorescence. Since the transition retains spin multiplicity (transition allowed), it is a fast process (approx. 10^{-9} sec). On the other hand, the transition from lowest triplet to ground state (change in spin multiplicity, transition forbidden), the emission from which is termed phosphorescence, is considerably slower (10^{-3} to 1 sec). Hence, the lifetime of a singlet state is in general much shorter than that of a triplet state. The above concepts are illustrated by the Jablonski diagram(1) (Figure 1).

Quenching and Sensitization

If compound D is excited in a system containing only D and Q components, decrease of fluorescence or phosphorescence of D may be observed as shown in the following process.

	Rate
$D \xrightarrow{h\nu} D^*$	depends on light intensity
$D^* + Q \xrightarrow{k_q} D + Q^*$	$k_q\,[D^*]\,[Q]$

Here D is the sensitizer and Q is the quencher of D^*, and k_q is called the quenching rate constant.



The abscissa has no physical significance.

a,b: light absorption, $S_0 \longrightarrow S_1$ or S_n transition

c: vibrational decay

d: internal conversion

e: intersystem crossing

f: fluorescence

g: phosphorescence

Figure 1. Jablonski Diagram of Relations Between Ground and Excited States

A well known equation, the Stern - Volmer equation, which relates the fluorescence or phosphorescence intensity, or quantum yield and k_q is shown in equation (1).

$$I_0/I = 1 + k_q\tau[Q] \qquad (1)$$

I_0, I: fluorescence intensities, without and with quencher respectively

τ : lifetime of excited state

[Q]: concentration of quencher

Three categories of mechanism of fluorescence quenching can be distinguished:

a) Energy Transfer

As was mentioned before,

$$D^* + Q \longrightarrow D + Q^* \qquad (2)$$

b) Chemical Interaction of the Excited State

The quenching process often involves charge or electron transfer between excited and ground state molecules, eg.

$$D^* + Q \longrightarrow D^{\delta+} - Q^{\delta-} \qquad (3)$$

c) Enhancement of Intersystem Crossing

One example is if the solvent molecule contains a heavy atom(2)(3), ethyl iodide, and will promote the transition $S_1 \longrightarrow T_1$.

Mechansim b) leads to the formation of metastable excited complexes, called "exciplexes". These often have considerable charge separation, and many results in this thesis are interpreted in terms of them. Therefore, an outline of the nature of charge transfer processes, and exciplexes in particular, is given next.

Charge Transfer Complexes

The idea of charge transfer between the molecules was proposed by Mulliken(4) (1952). Suppose a charge donor, D, and an acceptor, A, closely approach each other. The new bond between A and D is formed because of a charge transfer taking place. Thus, a charge transfer complex (CT complex) is formed.

All the structures 1, 2, 3 could be classified as CT complexes although structure 3 is commonly called an ion radical pair.

$$\underset{}{D + A} \longrightarrow \underset{1}{(D - A)} \longleftrightarrow \underset{2}{(D^+ - A^-)} \longleftrightarrow \underset{3}{D^{\dagger} + A^{\overline{\cdot}}} \qquad (4)$$

The theory of charge transfer had not been understood very well until 1952 when Mulliken proposed his theory(4) based on quantum mechanical ideas. This theory will be discussed only briefly in this thesis.

In Mulliken's Theory(4)(5), when charge donor, D, forms a contact complex with acceptor, A, the configuration of D and A does not change. The wavefunction of contact state is ψ_0.

$$\psi_0 = \psi(D - A)$$

When there is a charge transfer from D to A, the wavefunction ψ_1 is,

$$\psi_1 = \psi(D^+ - A^-)$$

It should be noted that these two wavefunctions do not represent the true states and the two electronic configurations mix with each other. The true state wavefunctions are as follows:

$$\begin{aligned} \psi_G &= a\psi_0 + b\psi_1 \\ \psi_E &= -b^*\psi_0 + a^*\psi_1 \end{aligned} \qquad (5)$$

The coefficients a and b are the fractions of structures (D - A) and $(D^+ - A^-)$ at the ground state, ψ_G. Similarly, a* and b* are the fractions of $(D^+ - A^-)$ and (D - A) at excited state, ψ_E. The normalization condition is satisfied as,

$$a^2 + b^2 + 2abS_{01} = 1 \tag{6}$$

Here S_{01} is called the overlap integral which is

$$S_{01} = \int \psi_0 \psi_1 d\tau \tag{7}$$

The similar conditions are in the excited state, ψ_E.

$$a^{*2} + b^{*2} - 2a^*b^*S_{01} = 1 \tag{8}$$

The wavefunctions ψ_G and ψ_E are orthogonal to each other. Therefore,

$$\int \psi_G \psi_E d\tau = 0 = -ab^* + ba^* + (aa^* - bb^*)S_{01} \tag{9}$$

The energy of electronic configurations ψ_0, ψ_1, is given below, where H is the Hamiltonian operator.

$$\begin{aligned} E_0 &= \int \psi_0^* H \psi_0 d\tau \\ E_1 &= \int \psi_1^* H \psi_1 d\tau \end{aligned} \tag{10}$$

Strictly speaking, the energies of the ground and excited states, E_G and E_E, are the roots of the following secular determinant.

$$\begin{vmatrix} E_0 - E & E_{01} - S_{01}E \\ E_{01} - S_{01}E & E_1 - E \end{vmatrix} = 0 \tag{11}$$

where the exchange energy, E_{01}, is,

$$E_{01} = \int \psi_0^* H \psi_1 d\tau = \int \psi_1^* H \psi_0 d\tau \tag{12}$$

If $E_{01} - S_{01}E$ is very small compared to the difference of $E_1 - E_0$, the following equations are given to the second order perturbation.

$$E_G \cong E_0 - (E_{01} - S_{01}E_0)^2 \,/\, (E_1 - E_0)$$
$$E_E \cong E_1 + (E_{01} - S_{01}E_1)^2 \,/\, (E_1 - E_0) \tag{13}$$

The relations between a, b and a*, b* are,

$$b/a = (E_{01} - S_{01}E_0) \,/\, (E_1 - E_0)$$
$$b^*/a^* = (E_{01} - S_{01}E_1)^2 \,/\, (E_1 - E_0) \tag{14}$$
$$a^2 \approx 1, \text{ since } b/a \ll 1$$

This indicates that the wavefunction of ground state can be represented mainly as the structure (D - A) with slight mixing of $(D^+ - A^-)$. It is easy to derive that a = a* and b = b*. Thus the case is reversed for the excited state.

The ground state of complex mixes with a small fraction of $(D^+ - A^-)$ to lower the energy of the system. This stabilization energy is termed charge transfer force which is approximately given by,

$$E_G - E_0 = (E_{01} - S_{01}E_0) \,/\, (E_1 - E_0) \tag{15}$$

The term $(E_1 - E_0)$ can be related to the ionization potential of donor, $I_p(D)$, and the electron affinity of acceptor, $E_a(A)$, as shown in the following equation.

$$E_1 - E_0 = I_p(D) - E_a(A) - e^2/R_{AD} - \triangle \tag{16}$$

The term e^2/R_{AD} is the coulomb energy and R_{AD} is the distance between A and D, where $\triangle$ represents covalent bonding and repulsive energy. Thus, the ionization potential and electron affinity are the major criteria which determine the degree of charge transfer.

One can write a total wavefunction to represent all possible

$$\psi \cong \alpha\phi(A^- - D^+) + \beta\phi(A - D^*) \qquad (20)$$

Weller(6) proposed that molecule D, charge donor, and A, charge acceptor, formed an exciplex on the basis of the following evidence. It was observed that, when perylene (P) was irradiated in the presence of aniline (D, charge donor) in a non-polar solvent, a broad new fluorescence appeared at longer wavelength than perylene fluorescence (Figure 2). This new fluorescence spectrum is considered to arise from the CT exciplex and the process is as below.

$$P \xrightarrow{h\nu} P^*$$

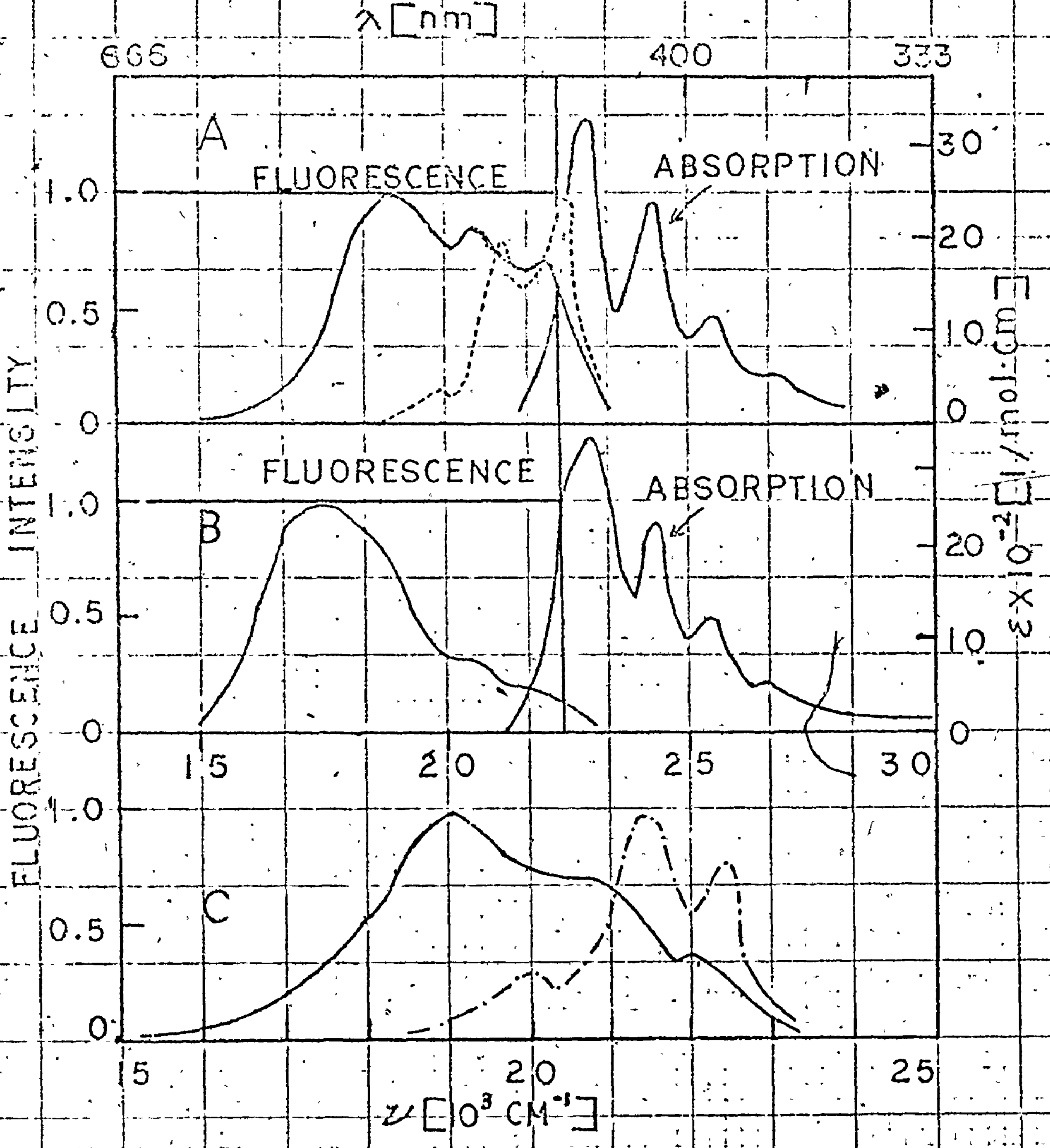
$$P^* + D \longrightarrow P^- - D^+ \longrightarrow P - D + h\nu_{CT}$$

However, this CT exciplex fluorescence band disappeared when a polar solvent such as acetonitrile was used. It seems that the excited perylene is not affected by solvent, but flash spectroscopic analysis shows that the perylene anion is formed when the exciplex solvated as an ion pair.

$$P^* + D \longrightarrow P^- - D^+ \longrightarrow P^-_{solv.} + D^+_{solv.}$$

Recombination of the ion pair in a very short time gives back the original materials. A similar phenomenon was found in the solutions of naphthalene with tetramethyl-p-phenylenediamine(7) and anthracene with N,N-dimethylaniline(8).

The above phenomenon had not been observed before. The reason for CT exciplex formation is that the capacity for donating or accepting is enhanced when either donor or acceptor is excited. If the excited molecule will contact the other molecule during its lifetime, a charge transfer complex can form. On the other hand, the case of contact charge



A ------- in Benzene (from perylene)

——— in Benzene - dimethylaniline (from perylene and charge transfer exciplex) (1.0 mol l^{-1})

B in Dimethylaniline (mainly from charge tranfer exciplex)

C -·-·- in Methylcyclohexane

——— in Methylcyclohexane - dimethylaniline (2.0 mol l^{-1})

Figure 2. Spe

transfer(9)(10)(11) is observed when either donor or acceptor (often it is donor) is in a very high concentration or serves as solvent, thus both acceptor and donor already are in contact with each other at the ground state. The charge transfer takes place immediately when excitation occurs.

It has been found that many aromatic hydrocarbons (A) in the excited state form a CT exciplex with amines (D) and the characteristic fluorescence exciplex spectrum is observed(12)(13)(14)(15). The ion radicals are formed when the solvent is very polar. The process of CT exciplex formation and its fluorescence emission are shown in Figure 3. The actual process of the scheme could be observed directly by analyzing the fluorescence spectra of aromatic hydrocarbon and CT exciplex, which varies with time.

$$\begin{aligned}
&A \xrightarrow{h\nu} A^* \\
&A^* \xrightarrow{k_1} A + h\nu_F \\
&A^* \xrightarrow{k_2} A \\
&A^* + D \underset{k_4}{\overset{k_3}{\rightleftarrows}} (A^* - D) \\
&(A^* - D) \xrightarrow{k_5} D + A + h\nu_{CT} \\
&(A^* - D) \xrightarrow[\text{polar solvent}]{k_6} D + A \\
&\qquad\qquad\qquad\qquad D^+ + A^- \\
&\qquad\qquad\qquad\qquad \ldots \\
&\qquad\qquad\qquad\qquad \ldots
\end{aligned}$$

$h\nu_F$, $h\nu_{CT}$: the fluorescence emission from excited A and CT exciplex

Figure 3. Process of CT Exciplex Formation and Fluorescence Emission

One example of pyrene and N,N-dimethylaniline in cyclohexane demonstrates this technique(16)(17). A very narrow band of pulse light for excitation is used in order to trace the variation of fluorescence spectrum since the process to form CT exciplex is very fast. The spectra variation with time is shown in Figure 4.

It can be seen in Figure 4 that the fluorescence spectrum is from pyrene (410 nm) after being excited for 3 nsec. As the time increases. the intensity of CT exciplex emission increases at about 440 nm, reaches a maximum at 60 nsec, then decreases as the time increases. From the relation between fluorescence intensity and time, k_3 is calculated as 9.8×10^9 sec^{-1}, k_4 is 1.8×10^7 sec^{-1}, $(k_5 + k_6)$ is 5.4×10^6 sec^{-1} at 20°C. It is noted that the formation of exciplex (k_3) is at the diffusion controlled rate.

The dipole moment of CT exciplex can also be obtained(18) by measuring the CT exciplex fluorescence shift in various slightly polar solvents. It was calculated to be about 10 Debye units in the above case.

benzene derivatives. Firstly, the photoproducts with naphthalene are more likely to be crystalline than those of benzene. This enables one to more readily purify and identify the products. Secondly, using naphthalene rather than benzene in the reaction allows one to answer the question of multiplicity more readily.(50)(51) These are some of the reasons for our extensive use of naphthalene in these studies.

PART II. RESULTS - STRUCTURES OF PHOTO-ADDITION PRODUCTS

SECTION A. NAPHTHALENE - PYRROLE SYSTEM

SECTION B. CYANONAPHTHALENE - TETRAMETHYLETHYLENE SYSTEM

SECTION A. NAPHTHALENE - PYRROLE SYSTEM

In this chapter, all the relevant NMR and mass spectra for the purpose of identification are listed in the Appendix.

Photo-addition of Naphthalene and Pyrrole and Products Identification

Irradiation of naphthalene and pyrrole$^{(52)(53)}$ with a pyrex filter and a medium pressure mercury lamp, in 95% ethanol, gave two major products identified as 2-(1,4-dihydro-1-naphthyl)-pyrrole (36), and 2-(1,2-dihydro-2-naphthyl)-pyrrole (37) in the relative ratio 50:35%, and two minor products, 3-(dihydronaphthyl)-pyrroles (total 15%). N-deuteriopyrrole and naphthalene were irradiated in the same manner as above but using solvent acetonitrile. This also gave the two major products, 2-(1-hydro-4-deuterio-1-naphthyl)-pyrrole (38) and 2-(1-deuterio-2-hydro-2-naphthyl)-pyrrole (39) in a ratio of 50:35%. The reactions are shown in Figure 24.

Both compounds 36 and 37 showed the parent peak at m/e 195 (M^+) corresponding to $C_{14}H_{13}N$.

The NMR spectrum of compound 36 had resonances at 3.03 τ (4H, benzenoid), 3.71 τ (1H) which was assigned to be H-5. The α and β hydrogens of unsubstituted pyrrole are at 3.38 and 3.95 τ. However, the α-methyl substituted pyrrole$^{(54)(55)}$ shows α'-H at 3.64 τ, β'-H at 4.11 τ and β-H at 4.28 τ. It appeared that pyrrole hydrogens in compound 36 were shielded by the dihydronaphthyl group. Hence, the resonance at 4.12 τ (4H, multiplet) should contain two hydrogens of pyrrole (C-3 and C-5) and the other hydrogens were apparently from C-2' and C-3'.

Both resonances at 5.50 (1H) and 6.70 τ (2H) were multiplets, consistent with ABX system. Irradiation of the resonance at 5.50 τ caused the methylene signal at 6.70 τ to simplify by elimination of a coupling with J=6.2 cps, thus pointing to a 1,4-dihydronaphthalene structure.(56)(57)(58) In the NMR spectrum of compound 37 resonances appeared at 3.05 τ (4H, benzenoid), 3.74 τ (2H, C-5 and C-3'(4')), 4.13 τ (3H, C-3, C-4 and C-4'(3')), 6.43 τ (1H, C-2') and 7.09 τ (2H, C-1'). The summary of NMR data is shown in Table 3.

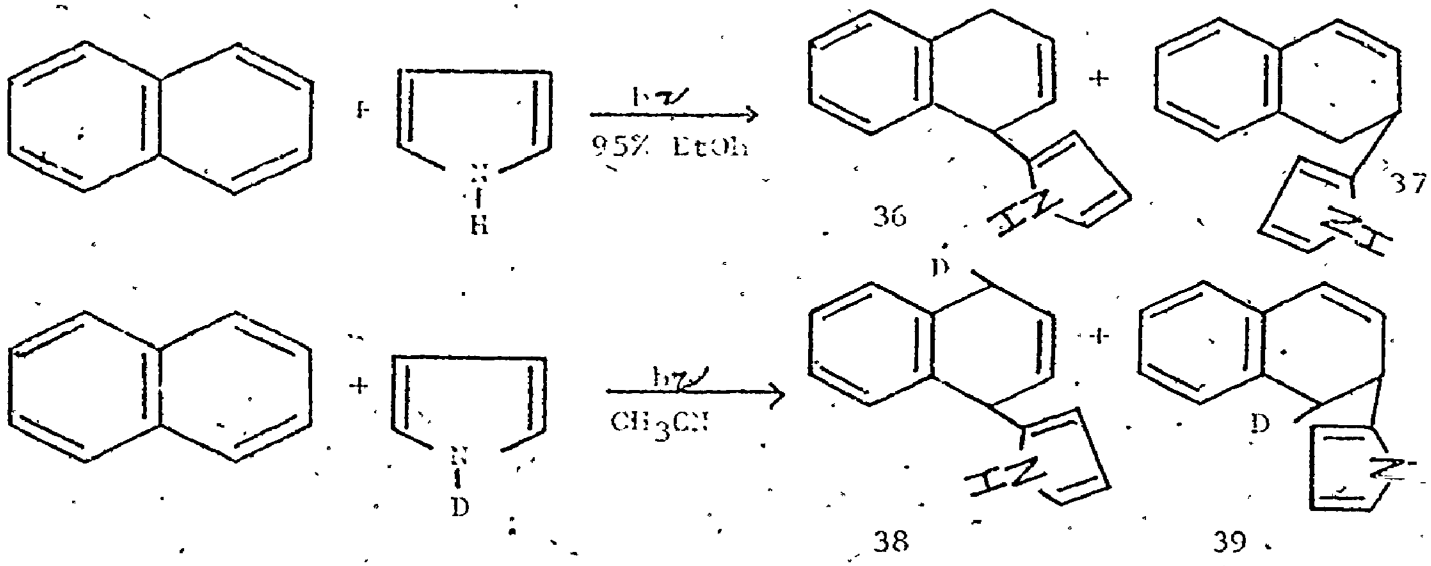
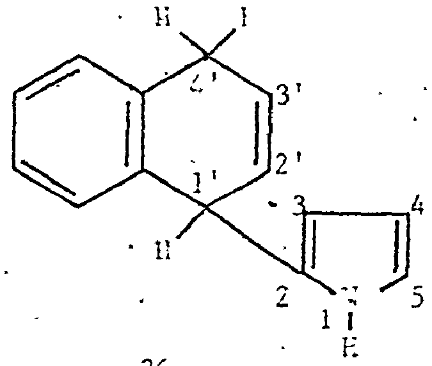
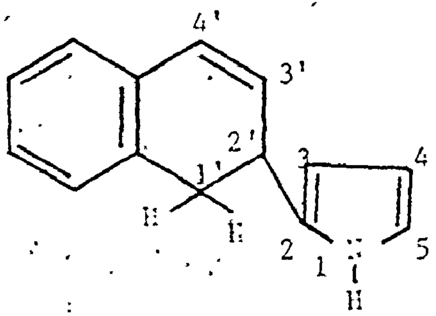


Figure 24. Photo-addition of Naphthalene and Pyrrole or N-deuteriopyrrole

The ultraviolet spectra(58) were consistent with the structure assignment of compounds 36 and 37. Compound 36 had λ_{max}^{EtOH} at 211, 265 and 274 nm with log ε of 4.44, 3.59 and 3.51 compared with 1,4-dihydronaphthalene which has λ_{max}^{EtOH} at 263, 267 nm with log ε of 2.6. Compound 37 had λ_{max}^{EtOH} at 209 and 270 nm with log of 5.39 and 3.80, while 1,2-dihydronaphthalene has λ_{max}^{EtOH} at 259 with log ε of 3.98.

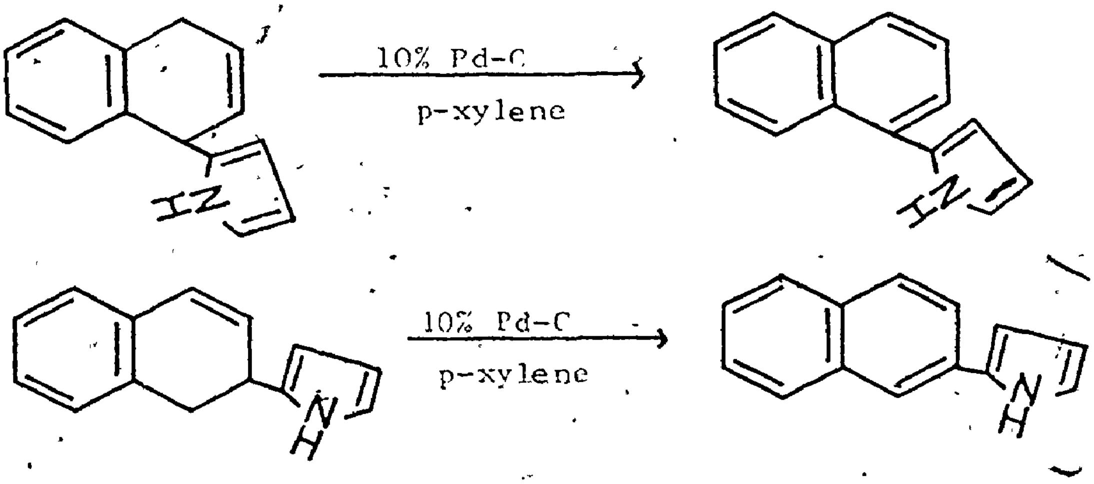
The structures of compounds 36 and 37 were further proved by de-

Hydrogen Compound	Benzenoid	Methylene	Methine	Others
	τ Value Multiplicity			
 36	3.03 (4H, m)	6.70 (2H,m)	5.50 (1H,m)	C-5 3.71 (1H,m) C-3, C-4, C-2', C-3' 4.12 (4H,m)
 37	3.05 (4H,m)	7.09 (2H,m)	6.43 (1H,m)	C-5, C-3'(4') 3.74 (2H,m) C-3, C-4, C-4'(3') 4.13 (3H,m)

m.= multiplet

Table 3. NMR Data of Compounds 36 and 37

hydrogenation. Both compounds were dehydrogenated using 10% palladium-charcoal in p-xylene solution at reflux. The unstable oily products were identified as naphthalene derivatives by NMR. Dehydrogenation of compound 36 is considerably slower than that of compound 37, possibly because the hydrogens on the former are in the 1,4-relationship (Figure 25).



38

39

Figure 25. Dehydrogenation of 36 and 37

Conversion of Compounds 36 and 37 to Ester Derivatives(58)

Since pyrroles with unblocked α-positions tend to be reactive, therefore, conversion of compounds 36 and 37 into derivatives was conducted. Both compounds were treated in the same way. N,N-dimethylaniline was added to carbonyl chloride in dry toluene and compounds 36 and 37 were added followed by absolute ethanol to give compound 40 or 41. These esters were stable crystalline compounds and gave satisfactory analyses (Figure 26).

The IR spectra of compounds 40 and 41 showed the $\nu_{max}^{CHCl_3}$ at 3430 (N-H); 1690 cm^{-1} (C=O) and 3310 (N-H); 1680 cm^{-1} (C=O) respectively.

The NMR spectra of compounds 40 and 41 were consistent with the assigned structures.(59) The ester protons of compound 41 gave signals at 8.77 (3H,t) and 5.28 τ (2H,q, J=7.0 cps). The two protons (C-3 and

C-4) of pyrrole nucleus gave signals at about 3.26 and 4.02 τ, which shifted down field relative to the analogous signals from compound 36(59). Similarly, the ester group of compound 41 showed signals at 8.36 (3H,t) and 5.46 τ (5.46,q). The two β-protons of pyrrole nucleus resonated at 3.06 and 2.90 τ. The methine proton and methylene groups comprised an ABX system, and the methylene group gave a doublet at 6.50 τ. This is in contrast to the corresponding signal for compound 37. The spectrum apparently belongs to the 'deceptively simple' type(60) for the ester of compound 37, meaning that the protons of the methylene group have almost the same chemical shift. The summary of NMR data for compounds 40 and 41 is shown in Table 4.

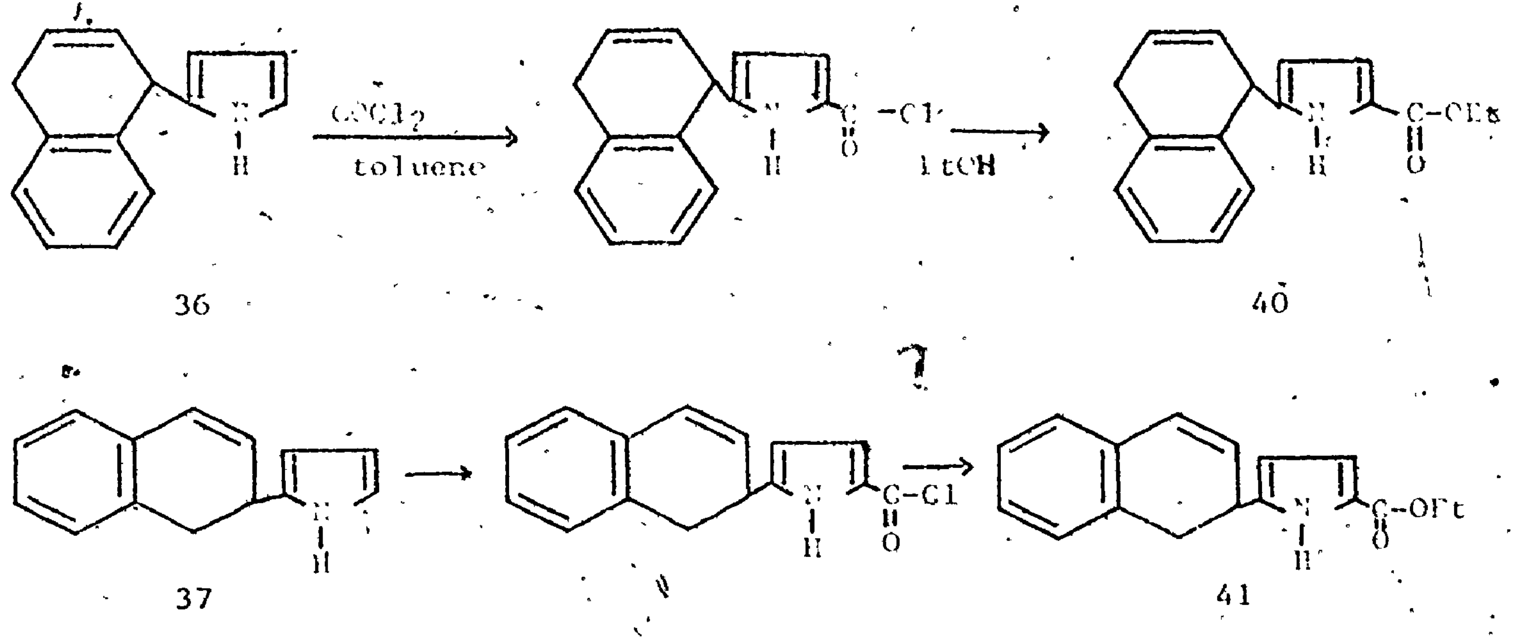
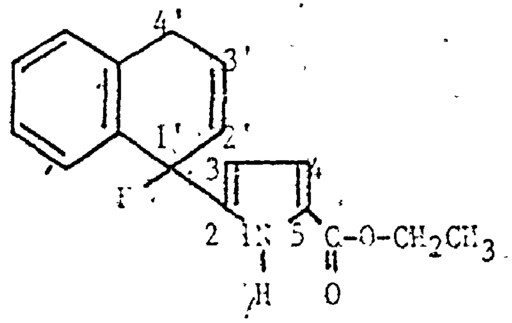
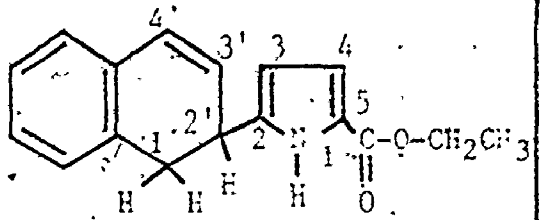


Figure 26. Conversion of Compounds 36 and 37 to Ester Derivatives

Hydrogen / Compound	CH_3 of Ethoxy	CH_2 of Ethoxy	Benzenoid	Methylene	Methine	Others
	τ Value Multiplicity Coupling Constants in cps Unit					
 40	8.77 (3H,t) J=7.0	5.82 (2H,q) J=7.0	2.94 (4H,m)	6.60 (2H,m)	5.32 (1H,m)	C-2', C-3', C-3(4) 4.02 (3H,m) C-4(3) 3.26 (1H,m)
 41	8.36 (3H,t) J=7.0	5.46 (2H,q) J=7.0	2.55 (4H,m)	6.50 (2H,d) $J_{1',2'}=5$	5.72 (1H,m)	C-4', C-4' 2.84 to 3.16 (2H,m) C-3, C-3' 3.48 to 3.70 (2H,m)

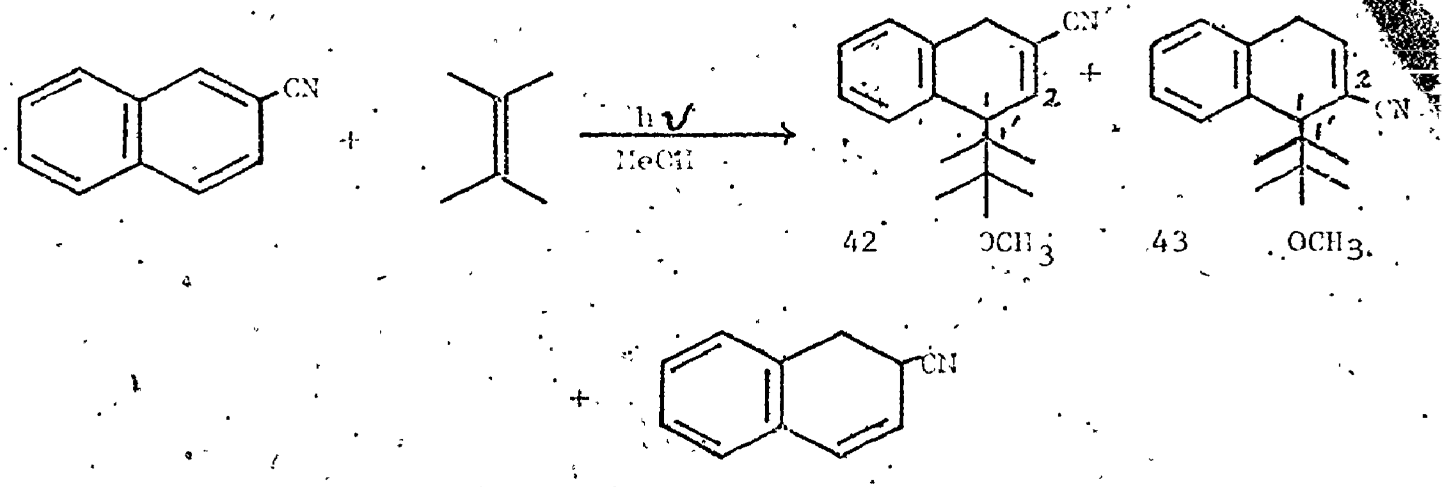
d = doublet t = triplet m = multiplet q = quartet

Table 4. NMR Data of Compounds 40 and 41

SECTION B. CYANONAPHTHALENE - TETRAMETHYLETHYLENE SYSTEM

Photoreaction of 2-cyanonaphthalene with TME in Methanol(61)

The 2-cyanonaphthalene and tetramethylethylene (TME) were irradiated (pyrex filter) in methanol to give two major products; 2'-methoxy-1',1',2',2'-tetramethylethyl-3-cyano-1,4-dihydronaphthalene (42) and 2'-methoxy-1',1',2',2'-tetramethylethyl-2-cyano-1,4-dihydronaphthalene (43) and a small amount of 1,2-dihydro-2-cyanonaphthalene (44). The relative ratio of these two major products is 60:40% in favour of compound 42 (Figure 27).



42 43 44

Figure 27. Photoreaction of 2-cyanonaphthalene with TME in Methanol

The infrared spectrum of compound 42 showed a band at 2223 (C≡N), and 1066 cm^{-1} (C-O-C) while 43 has the corresponding absorption at 2224 (C≡N) and 1065 cm^{-1} (C-O-C).

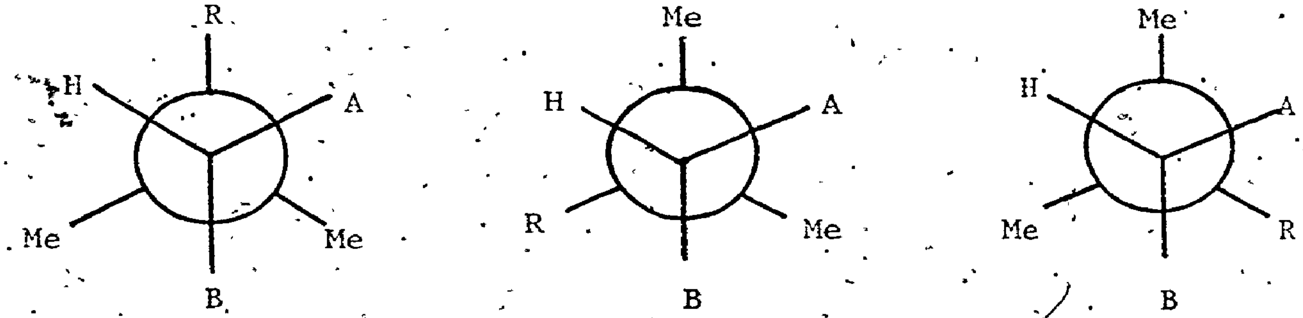
The ultraviolet spectra of both compounds 42 and 43 had λ_{max}^{EtOH} at 263 (log ε, 2.52) and 270 nm (log ε, 2.42). This indicates that both products could have the same basic structure. Both products also had m/e at 269 (M^+).

The NMR spectrum of compound 42 had resonances at 2.92 τ (4H, benzenoid), 6.76 τ (3H, methoxy group). The methylene and methine hydrogen resonated from 6.28 to 6.70 τ and slightly overlapped with methoxy signal. The vinyl proton resonated at 3.40 τ which overlapped with benzenoid hydrogens. The vinyl proton resonance should have a doublet structure due to coupling by the methine hydrogen. Thus, the NMR shift reagent, europium dipivaloylmethane, $Eu(DPM)_3$(62) was used (about 3 to 1 weight ratio in favour of europium dipivaloylmethane) and the doublet was shifted away from the benzenoid resonances. The coupling constant of $J_{1,2}$ is 5 cps. The four methyl groups all resonated differently at 8.74, 8.90, 9.18 and 9.44 τ.

The reason for the different resonances of methyl groups is due to the asymmetric center at C-1(63). The staggered rotational conformations of compound 42 are shown in Figure 28. The staggered conformations show that the two methyl and R groups are not equivalent with respect to other groups attached to C-1.

The NMR spectrum of compound 43 were at 2.92 τ (4H, benzenoid), 6.76 τ (3H, methoxy), 6.24 τ (1H, methine, almost singlet with a small splitting, J=1 cps). The methylene protons were at about 6.52 to 6.8 τ; and partially overlapped with methoxy protons. The vinyl proton in this structure should result in a doublet-doublet splitting caused by methylene hydrogens, and the resonance of this vinyl proton appeared at 3.25 τ in a doublet-doublet splitting with J=7 and 3 cps. The methyl group showed signals at 8.65, 8.88, 9.27 and 9.29 τ.

The NMR spectrum of compound 44, with typical 1,2-dihydronaphthalene pattern, showed resonances at 2.98 τ (4H, benzenoid), and two vinyl hydrogens at 3.50, 4,32 τ with coupling constant $J_{3,4}$=10 cps. The NMR spectra of compounds 42, 43 and 44 are summarized in Table 5. It should be mentioned here that the identification of compounds 42 and 43 by NMR spectra will be further discussed in the context of the deuterium labelling experiments.



A + B: 1,4-dihydro-3-cyanonaphthyl group

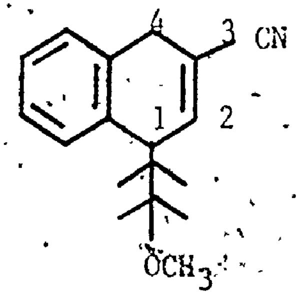
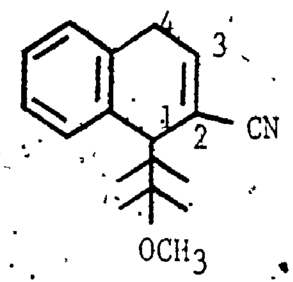
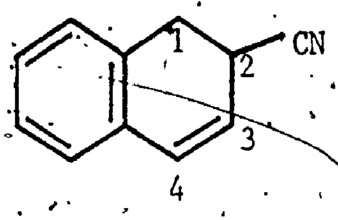
R: $-C(CH_3)_2(OCH_3)$

Figure 28. The Staggered Rotational Conformations of Compound 42

The irradiation of 2-cyanonaphthalene with TME was found not to yield any products when benzene was used as solvent. This is consistant with the lack of 2-cyanonapthalene fluorescence quenching by TME.

<u>Photoreaction of 2-cyanonaphthalene with TME in Deuteriomethanol</u>

To show that a methanol molecule participates in formation of compounds 42 and 43, a deuterium labelling experiment was conducted. On using methanol-O-D as solvent, it was found that deuterium appeared in the naphthalene ring of both compounds 45 and 46, a small amount of dideuterated reduced 2-cyanonaphthalene (47) also formed (Figure 29).

Compound	Hydrogen	Benzenoid	Methoxy	Methylene Methine	Vinyl	Methyl
		τ Value Multiplicity Coupling Constants in cps Units				
	42	2.92 (4H,s)	6.76 (3H,s)	from 6.28 to 6.70 (3H,m) slightly overlap with Methoxy	3.40 (1H,m) overlap with Benzenoid	8.74 (3H,s) 8.90 (3H,s) 9.18 (3H,s) 9.44 (3H,s)
	43	2.92 (4H,s)	6.76 (3H,s)	from 6.34 to 6.70 (3H,m) slightly overlap with Methoxy	3.25 (1H,d,d) $J_{C-2}J_{C-1} = 3.5$ $J_{C-2}J_{C-1'} = 1.5$	8.65 (3H,s) 8.88 (3H,s) 9.27 (3H,s) 9.29 (3H,s)
	44	2.98 (4H,m)			3.50 (1H,d) 4.23 (1H,d) $J_{C-3}J_{C-4} = 10$	

s = singlet d = doublet d,d = doublet of doublet m = multiplet

Table 5. NMR Data of Compounds 42, 43, and 44

The NMR resonances of compound 45 were at 2.89 τ (4H, benzenoid), 6.72 τ (3H, methoxy), 3.02 τ (vinyl proton, overlapped with benzenoid hydrogens), and four methyl groups were at 8.72, 8.88, 9.13 and 9.32 τ. The methine proton showed signal at 6.32 τ in doublet (J=6 cps) coupled by vinyl proton. The methylene proton resonated at 6.48 τ and partially overlapped with methoxy signal and the integration showed that the methylene group only contained one proton.

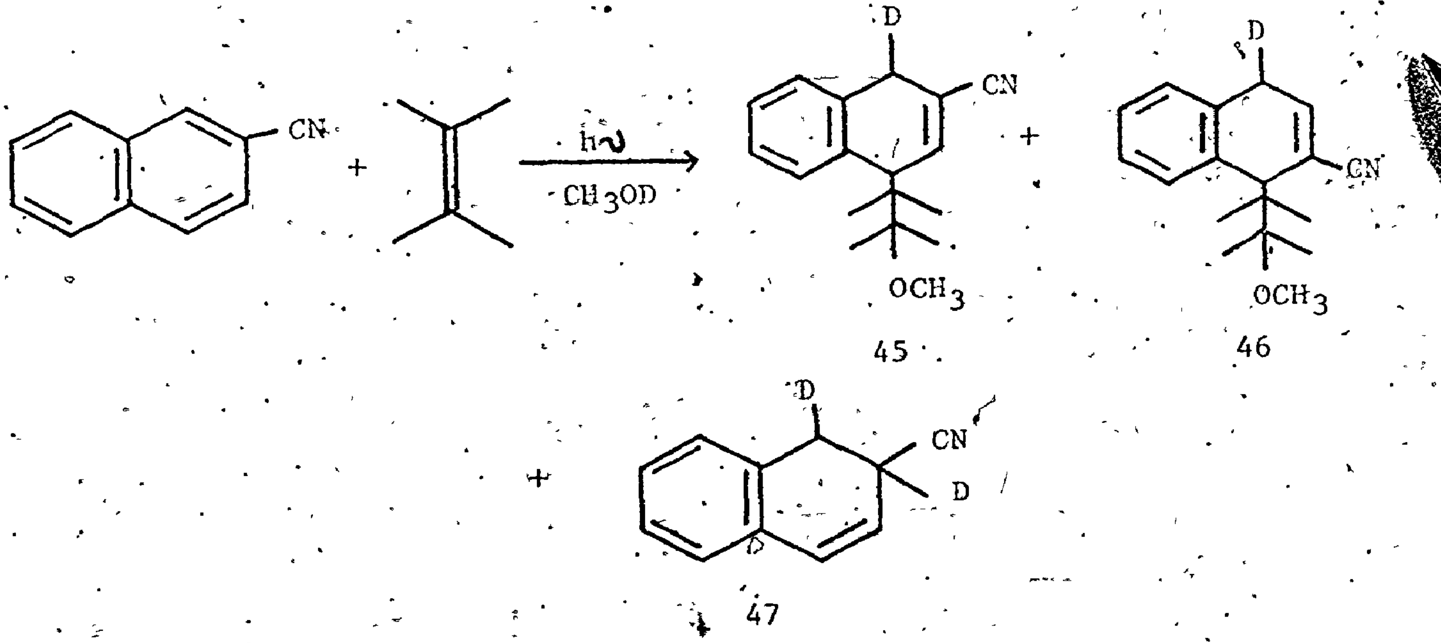


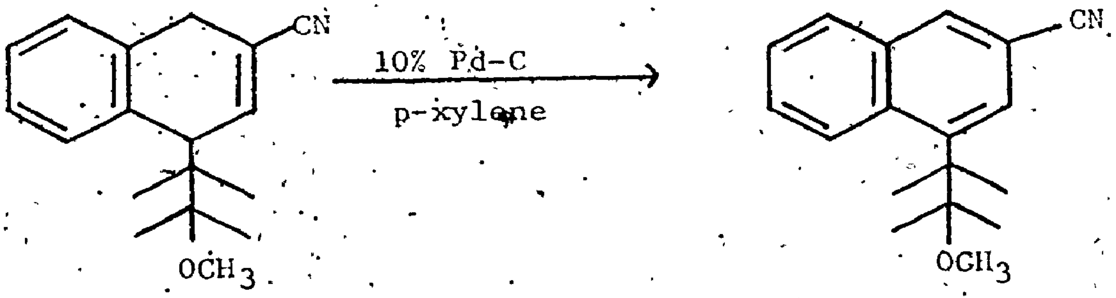
Figure 29. Photoreaction of 2-cyanonaphthalene with TME in Deuteriomethanol

The compound 46 had NMR signals at 2.93 τ (4H, benzenoid), 6.78 τ (3H, methoxy) and 8.67, 8.90, 9.28, 9.30 τ for four methyl protons. The vinyl proton resonated at 3.88 τ and was split by the methylene proton into a doublet with $J_{3,4}$=7 cps which indicated that one methylene proton of compound 46 was replaced by deuterium. The methine proton showed resonance at 6.30 τ and remained a singlet. The methylene proton resonance, however, completely overlapped with the methoxy signal. It is clear that the spectra of the deuterated derivatives agree with the structures 45, 46 as assigned.

Compound 47 had resonances at 2.98 τ (4H, benzenoid), two vinyl protons at 3.50 τ (1H, d) and 4.23 τ (1H, d) and coupled to each other with J=10 cps. The methylene proton appreared as a rather broad signal at 7.03 τ which was a singlet. Therefore, this compound has two deuterium atoms. The NMR data for compounds 45, 46 and 47 are summarized in Table 6.

Dehydrogenation of Compounds 42, 43, and 47

Dehydrogenation of compounds 42 and 43 provided more information about structures. Compound 42 was dehydrogenated using 10% palladium - charcoal to give 1-(2'-methoxy-1',1',2',2'-tetramethylethyl)-3-cyanonaphthalene (48) (Figure 30). The NMR spectrum of the latter showed(64) that the four methyl peaks of 42 had collapsed to a pair (8.34 and 8.88 τ) showing the asymmetric center of 42 is removed in the dehydrogenation.

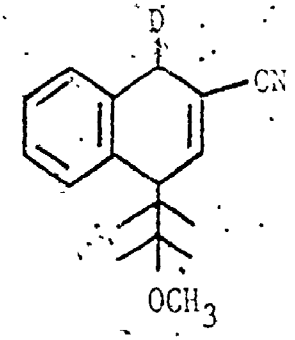
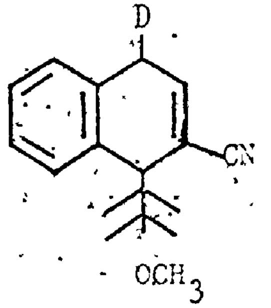
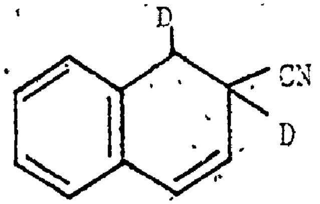


42

48

Figure 30. Dehydrogenation of Compound 42

The other NMR resonances of compound 48 were at 1.98 τ (1H, s, C-4 proton) and 1.20 τ (1H, s, C-8) which is called the 'peri' hydrogen(64). The peri hydrogen was deshielded, and this is attributed to a compression

Compound \ Hydrogen		Benzenoid	Methoxy	Methylene	Methine	Vinyl	Methyl
		τ Value Multiplicity Coupling Constants in cps Unit					
	45	2.89 (4H,s)	6.72 (3H,s)	6.26 to 6.60 (2H,m)		3.02 overlap with Benzenoid	8.72 (3H,s) 8.88 (3H,s) 9.13 (3H,s) 9.32 (3H,s)
	46	2.93 (4H,s)	6.78 (3H,s)	overlap with Methoxy	6.30 (1H,s)	3.88 (1H,d) $J_{3,4} = 4$	8.67 (3H,s) 8.90 (3H,s) 9.28 (3H,s) 9.30 (3H,s)
	47	2.98 (4H,m)		7.03 (1H,s)		3.50 (1H,d) 4.23 (1H,d) $J_{3,4} = 10$	

s = singlet d = doublet m = multiplet

Table 6. NMR Data of Compounds 45, 46, and 47

effect due to a bulky group at the C-1 position(64). The remaining aromatic hydrogens resonated from 2.16 to 2.62 τ (4H), and the methoxy protons signal appeared at 6.93 τ. The NMR data of compound 48 is shown in Table 7.

The dehydrogenation of compound 43, however, was not successful under the same conditions as applied for compound 42.

The NMR spectrum of the dehydrogenation product from compound 47 had the same general pattern as 2-cyanonaphthalene except that the H-1 had a resonance of area 0.5 H. Furthermore, mass spectrum of this cis-dehydrogenation product showed that both deuterated and undeuterated 2-cyanonaphthalene were formed in equal amount. This indicates that compound 47 is a mixture of cis- and trans-1,2-dideuterio-2-cyanonaphthalene (Figure 31).

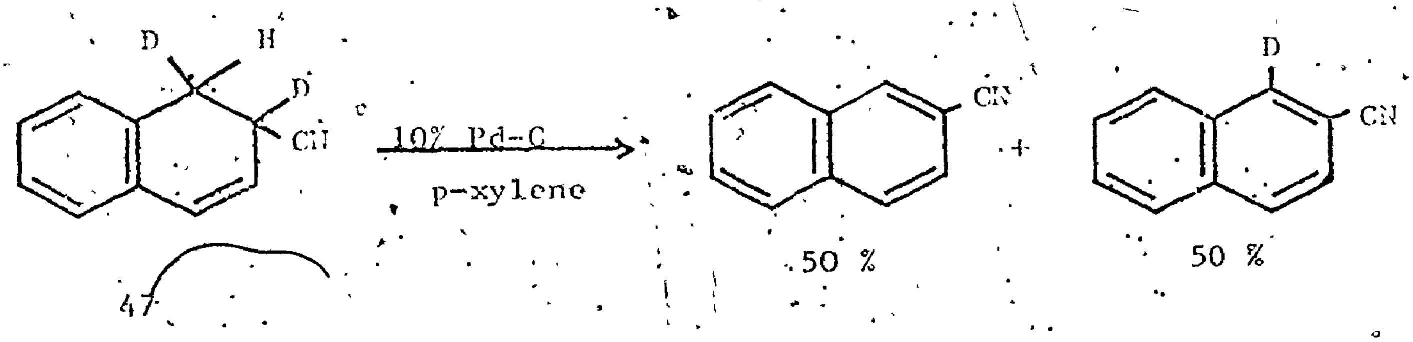
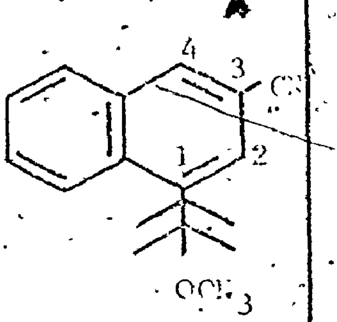


Figure 31. Dehydrogenation of 1,2-dideuterio-2-cyanonaphthalene

Photoreaction of 1-cyanonaphthalene and TME

The two major products 49 and 50 were formed in this reaction when methanol was used as solvent. These products were not positively identified. However, from the NMR and mass spectra and elementary analyses, it is believed that neither product is a primary photoreaction product.

The primary products are assumed to be substitution products which further react with excited 1-cyanonaphthalene, to give complicated structures.

Hydrogen / Compound	Aromatic Except C-4 C-8	C-4	C-8	Methoxy	Methyl
	τ Value Multiplicity				
 48	2.16 to 2.64 (4H,m)	1.98 (1H,s)	1.20 (1H,m)	6.93 (3H,s)	8.34 (6H,s) 8.88 (6H,s)

s = singlet m = multiplet

Table 7. NMR Data for Compound 48

When this reaction was carried out in benzene, it gave the cycloaddition product, 1-cyano-2,3-benzo-7,7,8,8-tetramethyl-bicyclo(4,2,0)oct-4-ene (51). (Figure 33).

The identification of product 51 was by NMR which showed resonances at 2.89 to 3.14 τ (4H, benzenoid), 8.60, 8.68, 9.00 and 9.19 τ for four methyl groups. The C-4 vinyl proton appeared at 3.69 τ with coupling constant of $J_{4,5}=10$ cps and $J_{4,6}=2$ cps. The C-5 vinyl proton resonated at 4.29 τ with coupling constant of $J_{5,4}=10$ cps and $J_{5,6}=4.5$ cps. Finally, the methine proton (C-6) showed the signal at 6.80 τ with $J_{6,5}=4.5$ cps and $J_{6,4}$=2 cps.. The NMR data for compound 51 is summarized in Table 8.

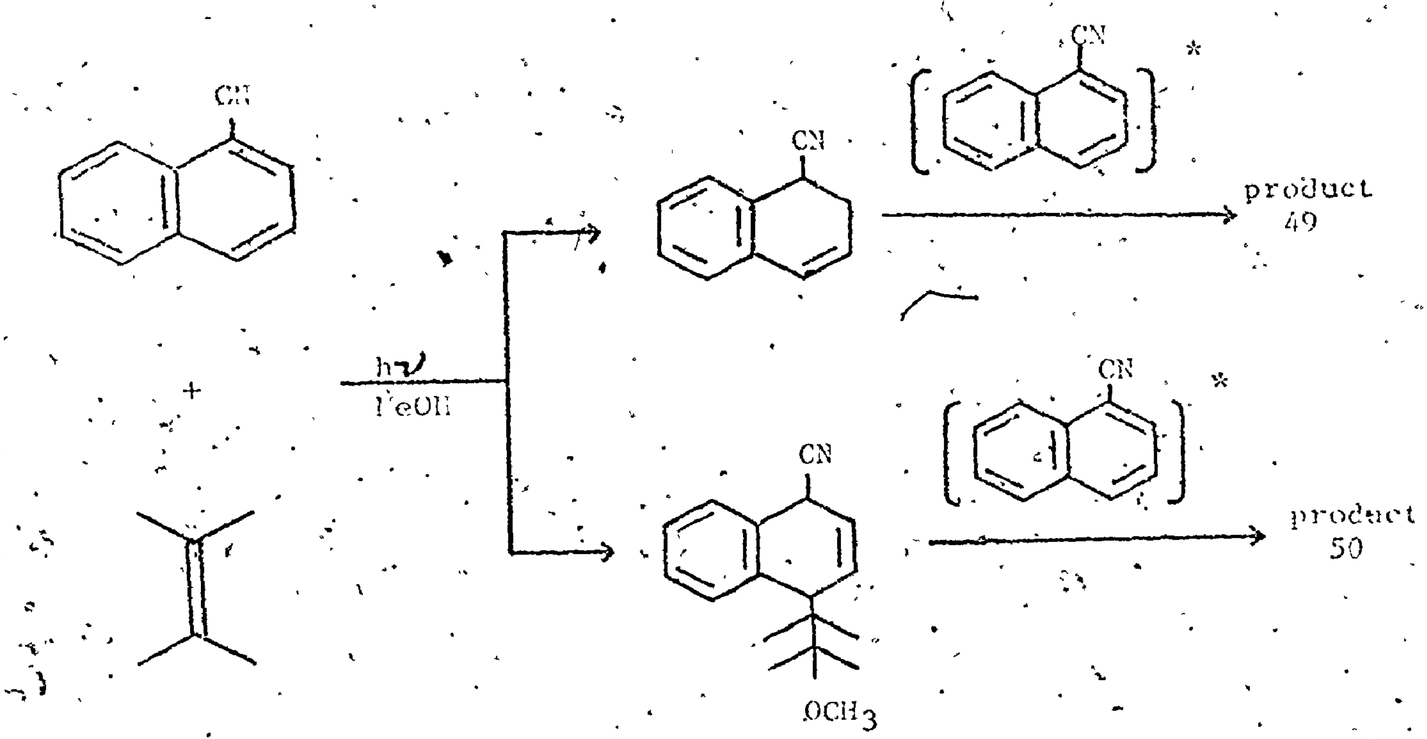
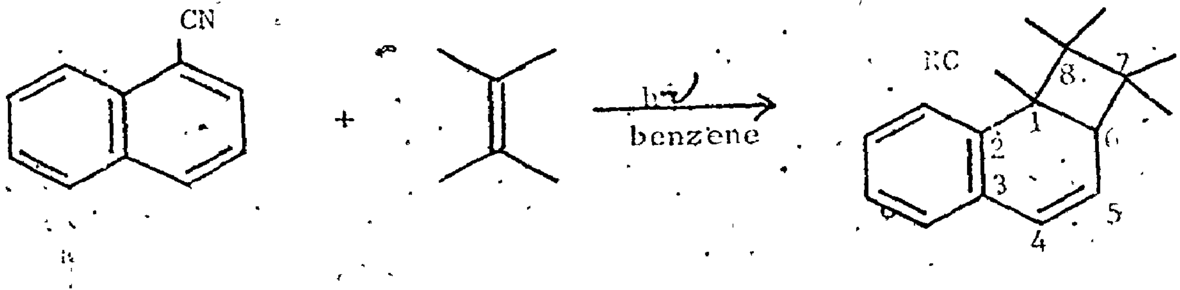
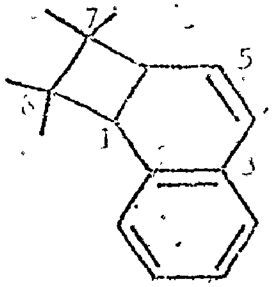


Figure 32. Photoreaction of 1-cyanonaphthalene and TME in Methanol



51

Figure 33. Photoreaction of 1-cyanonaphthalene and TME in Benzene

Hydrogen / Compound	Benzenoid	C-6	C-5	C-4	Methyl
	τ Value Multiplicity Coupling Constants in cps Units				
 51	2.80 to 3.14 (4H,m)	6.80 (1H,d,d) $J_{6,5}$ = 4.5 $J_{6,4}$ = 2	4.29 (1H,d,d) $J_{5,6}$ = 4.5 $J_{5,4}$ = 10	3.69 (1H,d,d) $J_{4,6}$ = 2 $J_{4,5}$ = 10	8.60 (3H,s) 8.68 (3H,s) 9.00 (3H,s) 9.17 (3H,s)

s. = singlet d,d = doublet of doublet

m = multiplet

Table 8. NMR Data for Compound 51

PART III. MECHANISTIC RESULTS

SECTION A. NAPHTHALENE - PYRROLE SYSTEM

SECTION B. CYANONAPHTHALENE - TETRA-METHYLETHYLENE SYSTEM

SECTION A. NAPHTHALENE - PYRROLE SYSTEM.

Attempted Triplet Sensatization Reaction of Naphthalene with Pyrrole

The lowest triplet (T_1) of naphthalene is 61 Kcal mol^{-1} above ground state$^{(65)}$, and the triplet sensitizers benzophenone, acetophenone and Michler's ketone have E_{T_1} of 68, 73, and 61 Kcal mol^{-1} respectively$^{(65)}$. These triplet sensitizers should sensitize efficiently the reaction of naphthalene with pyrrole if T_1 of naphthalene could react with pyrrole. However, no trace of products was found in these sensitization experiments.

The Fluorescence Quenching of Naphthalene with Pyrrole and N-methylpyrrole

The fluorescence quenching of naphthalene by pyrrole or N-methylpyrrole as quenchers was found to be near the diffusion controlled rate in ethanol, acetonitrile and benzene. The relative fluorescence intensities versus quencher concentration are shown in Tables 9 and 10. The relative intensity is directly proportional to the concentration of pyrrole or N-methylpyrrole. The Stern - Volmer plots for quenching of naphthalene fluorescence by pyrrole or N-methylpyrrole in acetonitrile, ethanol or benzene are shown in Figures 34 and 35. From the slopes of the Stern - Volmer plots, it is possible to calculate quenching rate constant, k_q, from the known fluorescence lifetime (Table 11).

Solvent Effect on Products Distribution$^{(66)}$

On irradiation of naphthalene and pyrrole in various solvents, the proportions of the two major products 36 and 37 were found to be solvent dependent, and the variation is shown in Table 12. The fractions of

Solvent	Concentration of Quencher (M x 10^{-2})	Relative Fluorescence Intensity I_0/I	Slope x 10^{-2} (l mol^{-1})
Ethanol	0.00	1.00	2.07
	0.80	2.59	
	1.60	4.44	
	2.39	6.03	
	2.79	6.66	
	3.19	7.45	
Acetonitrile	0.00	1.00	3.85
	0.80	4.49	
	1.60	7.09	
	2.00	8.47	
	2.40	9.84	
	3.20	12.71	
Benzene	0.00	1.00	2.43
	0.85	3.05	
	1.70	4.85	
	2.55	7.28	
	3.40	9.36	
	4.26	11.29	

Table 9. The Fluorescence Quenching of Naphthalene by Pyrrole

Solvent	Concentration of Quencher ($M \times 10^{-2}$)	Relative Fluorescence Intensity I_0/I	Slope $\times 10^{-2}$ ($l\ mol^{-1}$)
Ethanol	0.00	1.00	0.86
	0.80	1.63	
	1.60	2.30	
	2.39	2.66	
	2.79	3.09	
	3.19	3.83	
Acetonitrile	0.00	1.00	1.95
	0.80	2.39	
	1.60	3.93	
	2.00	4.86	
	2.40	5.80	
	3.20	7.34	

Table 10. The Fluorescence Quenching of Naphthalene by N-methyl Pyrrole

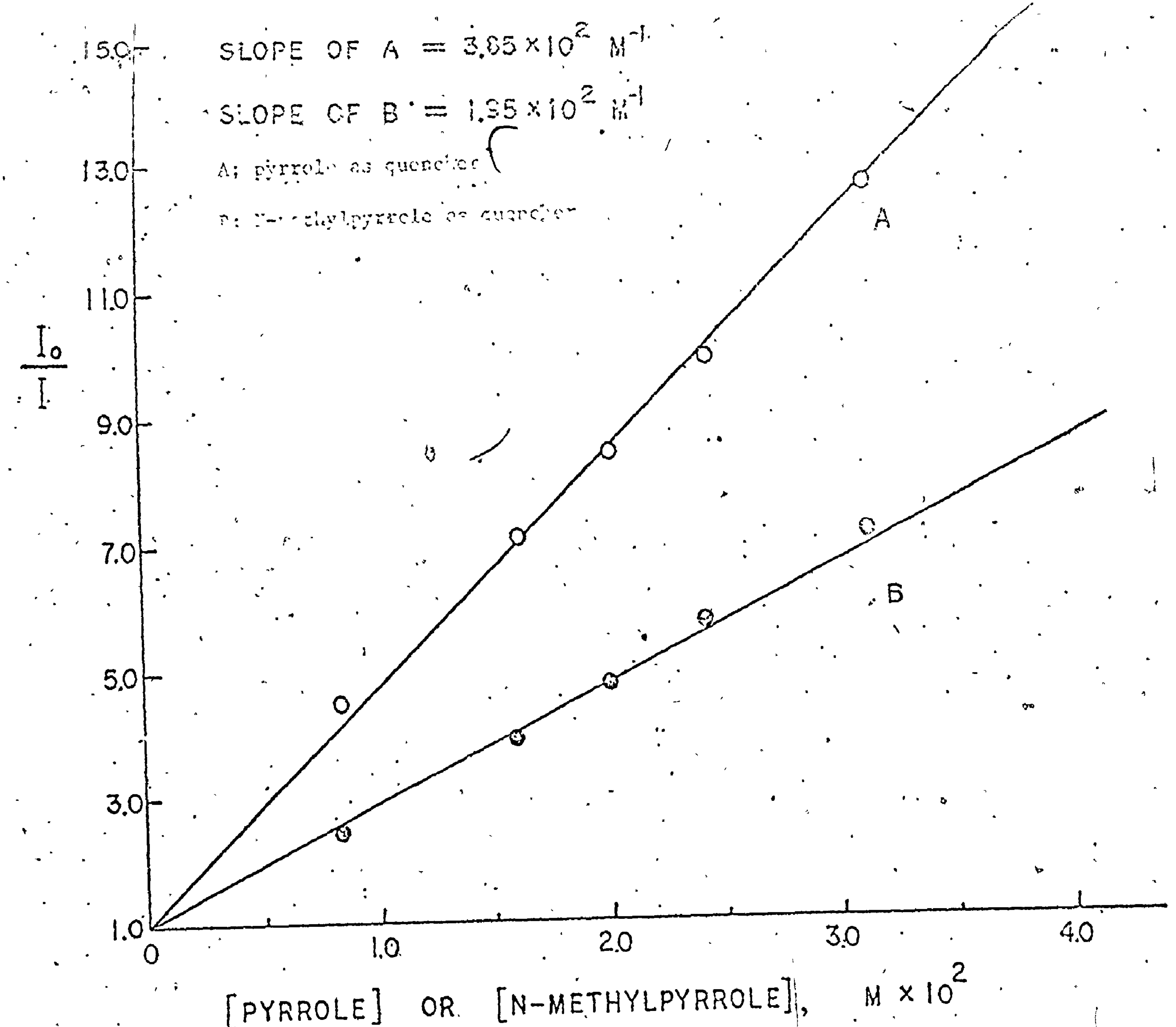


Figure 34. Plot of Relative Fluorescence Intensity Versus Pyrrole or N-methylpyrrole in Acetonitrile

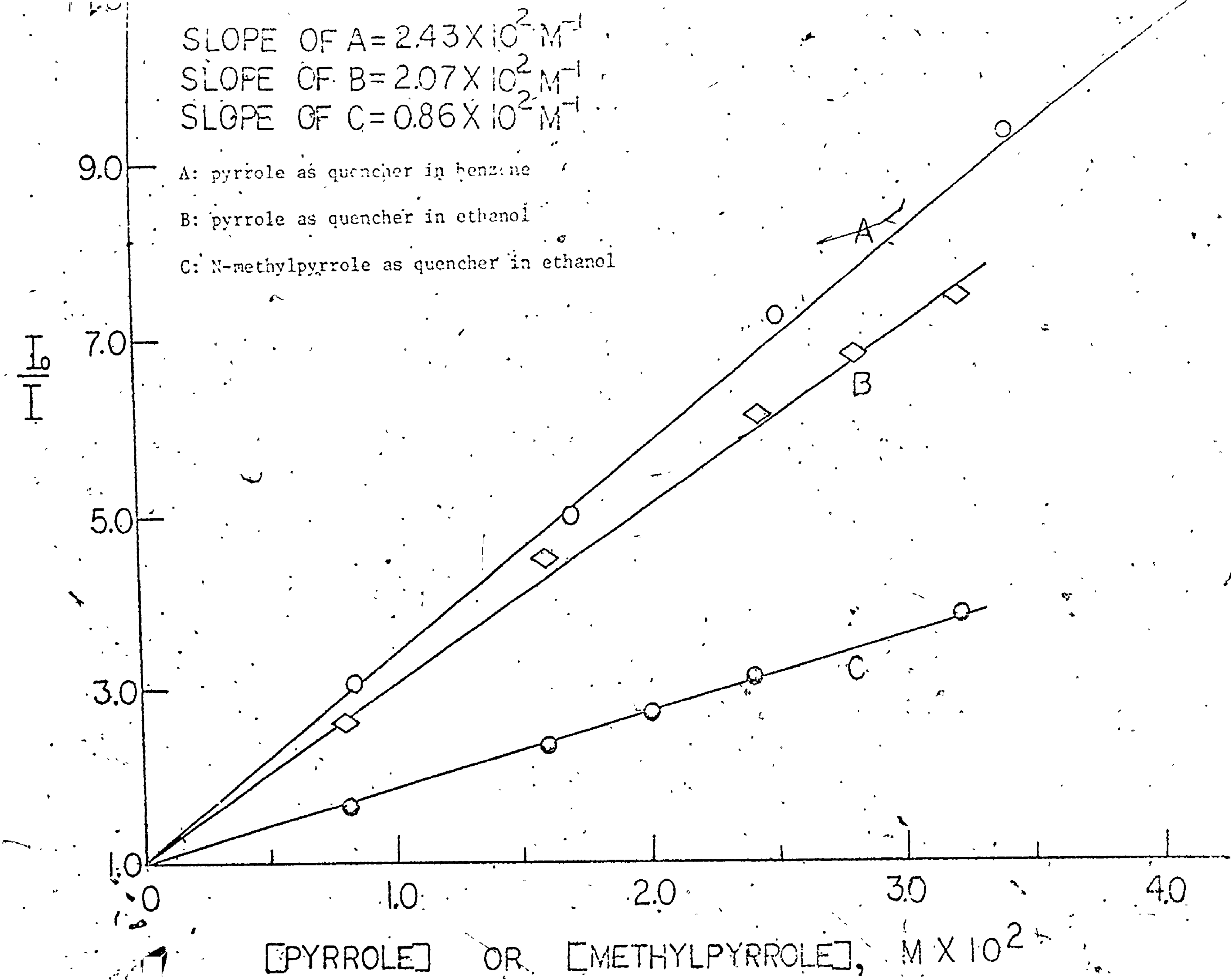


Figure 33. Plot of Fluorescence Intensity Versus Pyrrole or N-methylpyrrole in Ethanol and

Solvent	Quencher	$k^a \times 10^{-9}$ $1\ mol^{-1}s^{-1}$	Fluorescence Lifetime (ns)	Slope $\times 10^{-2}$ $1\ mol^{-1}$	[illegible] $\times 10^{-9}$ $1\ mol^{-1}s^{-1}$
Ethanol	Pyrrole	8.5	85^b	2.07	2.43
	N-methylpyrrole			0.86	1.01
Acetonitrile	Pyrrole	10.0	118^c	3.85	3.26
	N-methylpyrrole			1.95	1.65
Benzene	Pyrrole	5.0	96^b	2.43	2.53

[a] P.J. Wagner and A.E. Kemppainen, J. Amer. Chem. Soc., 1969, 91, 3085. [b] D. Schulte - Frohlinde and R. Pfefferkorn, Ber. Bunsengesellschaft Phys. Chem., 1968, 72, 330.

[c] N. Mataga, M. Tamura, and H. Nishimura, Mol. Phys., 1965, 9, 367.

Table 11. Fluorescence Quenching Rate Constants of Naphthalene with Quenchers Pyrrole and N-methylpyrrole

the two minor products in all the reactions was a constant, 15%. The results show that when the least polar solvent is used, then compound 36 is formed in the greatest amount.

Solvent	Dielectric Constant (D)[a]	Fraction[c] (%) of 36	Relative Reaction Rate
Hexane	1.9	82	–
Benzene	2.3	74	1.45
Dichloromethane	9.1	66	1.08
95% Ethanol[b]	24.3	60	1.04
Acetonitrile	37.5	62	1.00
Methanol[b]	32.6	52	0.89
80% Methanol[b]	32.6	49	0.59

[a] A.A. Maryott and E.R Smith, "Table of Dielectric Constants of Pure Liquids", National Bureau of Standards, Circular 514, Washington, 1951.

[b] The effects of these solvents are probably due in part to their hydrogen bonding properties.

[c] Given by (36/(36 + 37)) x 100; minor products were present in all runs, total 15%.

Table 12. Solvent Effect on Products Distribution of Naphthalene-Pyrrole Reaction

The relative reaction rate in hexane could not be determined due to the products not being very soluble; hence the result would be unreliable.

Quantum Yield of Products 36 and 37

The quantum yields of the two major products with fixed concentrations of naphthalene (5.8×10^{-2} mol l^{-1}) and pyrrole (0.11 mol l^{-1}) in benzene and 95% ethanol are shown in Table 13.

Solvent	Amount of Light Absorbed in Einstein x 10^5	Amount of Products (36 + 37) Produced mg	mole x 10^5	Products Quantum Yield mole/Einstein
95% EtOH	16.33	7.159	3.709	0.23
	14.49	7.014	3.634	0.25
Benzene	12.37	7.162	3.711	0.30
	11.09	6.782	3.514	0.32

Table 13. Quantum Yield of Products 36 and 37

SECTION B. CYANONAPHTHALENE - TETRAMETHYLETHYLENE SYSTEM

Acid Effect in the Photoreaction of 2-cyanonaphthalene with TME

It was found that addition of acetic acid or formic acid to the reaction mixture increased the total yield of compounds 42 and 43. It was also found that the products ratio of compounds 42 and 43 changes according to the concentration of acid used (Table 14).

(42/(42 + 43))	Relative Rate of Formation of 42,43	Concentration of Acetic Acid (N)
61.6	1.00	0.00
63.9	1.27	0.24
73.6	1.15	0.48
75.8	1.58	1.02
76.0	1.77	1.30
78.7	1.63	2.08
80.8	1.72	2.60

Table 14. Acid Effect on the Formation of Compounds 42 and 43

A small amount of a new product identified as 3,4-dihydro-2-cyanonaphthalene (52) by NMR, mass spectra and molecular weight analysis, was isolated when the reaction proceeded in 5% formic acid.

Fluorescence Quenching of 2-cyanonaphthalene with TME

Fluorescence quenching experiments were conducted in methanol, acetonitrile, and hexane for 2-cyanonaphthalene in TME. The Stern - Volmer quenching plots are shown in Figure 36. As an example of the quenching rate in methanol, using the lifetime of 2-cyanonaphthalene in methanol,

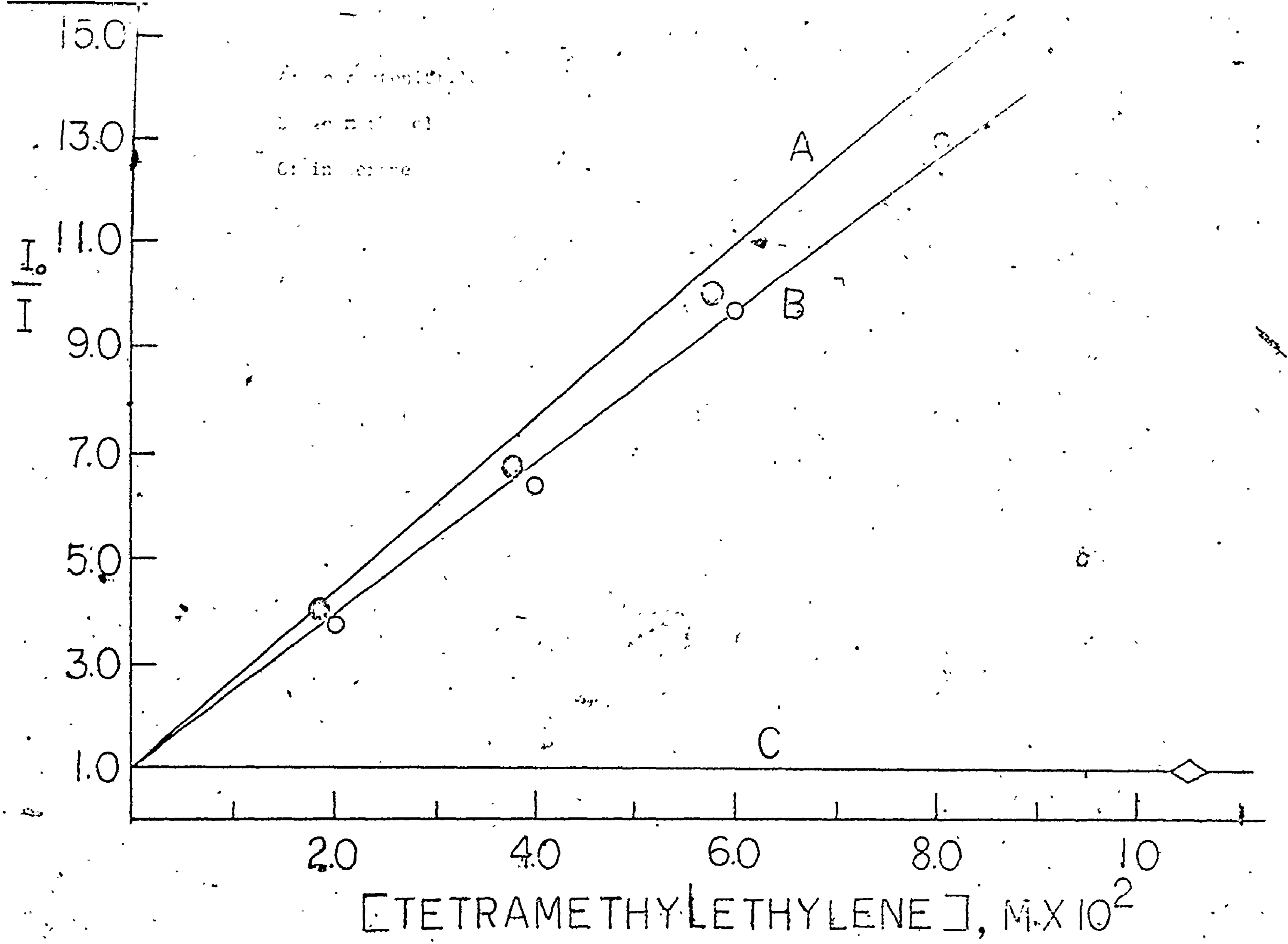


Figure 36. Plot of Fluorescence Intensity Versus Tetramethylethylene in Acetonitrile, Methanol, and Benzene

11.3 nsec (67) and the slope of 1.48 x 10^2 M^{-1} from the Stern - Volmer quenching plot, the quenching rate constant is calculated to be 1.13 x 10^{10} M^{-1} sec.$^{-1}$ (Table 15). However, it was found that no fluorescence quenching took place in hexane or benzene. It was confirmed that neither glacial acetic acid nor 90% formic acid affected the fluorescence quenching efficiency, hence the quenching rate appears to be determined prior to the involvement of the proton donor. Also, added acid did not cause quenching in hexane or benzene, nor did acid change the quenching efficiency in methanol.

The fluorescence quenching of 1-cyanonaphthalene by TME in benzene or in hexane is very efficient (47), in contrast to 2-cyanonaphthalene with TME case; 0.1 M of TME quenches the 1-cyanonaphthalene fluorescence almost completely in methanol, benzene, or hexane.

Solvent	Concentration of TME ($M \times 10^{-2}$)	Relative Fluorescence Intensity I_0/I
Methanol	0.0	1.00
	2.0	3.73
	4.0	6.55
	6.0	9.83
	8.0	13.20

Slope = $1.48 \times 10^2\ M^{-1}$

Solvent	Concentration of TME ($M \times 10^{-2}$)	Relative Fluorescence Intensity I_0/I
Acetonitrile	0.0	1.00
	1.9	3.92
	3.8	6.54
	5.7	10.05
	7.6	14.60
	9.5	18.50

Slope = $1.67 \times 10^2\ M^{-1}$

Table 15. The Fluorescence Quenching of 2-cyanonaphthalene by TME

PART IV. DISCUSSION

Mechanism of Pyrrole - Naphthalene Reaction

Naphthalene has the lowest excited singlet (S_1) energy of 88 kcal, whereas pyrrole has S_1 energy of about 112 kcal (obtained from absorption spectra). Since pyrrole has a higher E_{S_1} level than that of naphthalene, fluorescence quenching of naphthalene by pyrrole could not result from energy transfer from excited naphthalene to pyrrole as previously shown in equation (2). This, of course, indicates an exciplex is formed between naphthalene S_1 state and pyrrole S_0 state (equation (3)), and the fluorescence quenching is due to chemical interaction.

The triplet energy of triplet sensitizers(65) such as acetophenone, benzophenone or Michler's ketone is higher than that of triplet naphthalene (T_1) energy but these sensitizers fail to sensitize the reaction. This strongly indicates that the reacting species is not the T_1 state of naphthalene. Moreover, T_1 can be eliminated on kinetic arguments, since the rate constant, k_q, of bimolecular reaction between naphthalene S_1 and pyrrole S_0 states gives a rate at the pyrrole concentration used (0.2M) much higher than the intersystem crossing rate constant, k_{ic} (2×10^6), of naphthalene S_1 state to T_1 state(68). The following calculation shows that the relative reaction rate (r) for the singlet and triplet reactions must be at least one-hundred-fold larger for the former.

$$r = k_q[\text{pyrrole}]/k_{ic} = (10^{10} \times 0.2)/(2 \times 10^6) = 100$$

Since the reaction is from S_1 state of naphthalene, the preferred reaction scheme comprises the following processes.

If the quenching of naphthalene fluorescence is a bimolecular process involving pyrrole according to the reaction scheme, then the

	Rate
$N \longrightarrow N_{S_1}$	light intensity, I
$N_{S_1} \xrightarrow{k_{d_1}} N$	$k_{d_1}[N_{S_1}]$
$N_{S_1} + P \xrightarrow{k_q} \text{exciplex-}S_1$	$k_q[N_{S_1}][P]$
$\text{exciplex-}S_1 \xrightarrow{k_p} \text{products}$	$k_p[\text{exciplex-}S_1]$
$\text{exciplex-}S_1 \xrightarrow{k_{d_2}} N + P$	$k_{d_2}[\text{exciplex-}S_1]$

N: naphthalene

P: pyrrole

exciplex-S_1: exciplex formed between N_{S_1} and pyrrole S_0 state

following relation known as the Stern - Volmer equation describes the concentration dependence of the quenching.

$$I_0/I = 1 + k_q\tau[P]$$

The experimental results for fluorescence quenching in benzene, acetonitrile and ethanol all show a linear relationship between the concentration of pyrrole and the ratio of fluorescence intensities without and with pyrrole. The rate constants, k_q, are of course obtained from these plots (Figures 34 and 35).

The experiment with deuterium labelled pyrrole has shown that deuterium is incorporated from the N-position of pyrrole into the naphthalene ring. Since N-methyl pyrrole quenches naphthalene fluorescence but does not react, this indicates a proton shift takes place after exciplex formation. The failure of N-methyl pyrrole to react with naphthalene, thus results from the absence of an acidic -NH proton.

It is significant that the products ratio of this reaction changes with solvent polarity which indicates that the reaction is ionic rather than radical. The ratio of more stable, 37, to less stable isomer(68),(69), 36, increases in more polar solvents in a fashion resembling some ground state ionic reactions. An example is the ionic addition of bromine to 1,3-dienes. The more stable 1,4-dibromide is favoured over 1,2-dibromide in polar solvent(70). A second example is the silver ion-catalyzed solvolysis of allyl halides to generate carbonium ions. The product of kinetic control is often the major one and is decreased in amount by the effect of more polar solvents(71).

From the quenching of fluorescence, solvent effects on reaction products, and the deuterium labelling experiment described above, the reaction mechanism shown in Figure 37, can be proposed. This consists of the following steps; i) formation of a naphthalene and pyrrole exciplex at naphthalene S_1 state, ii) a hydrogen shift from pyrrole to naphthalene, iii) ionic reaction between 53 and 54 to give products, and possibly iv) electron transfer from pyrrole to naphthalene to give radical ions (53' and 54').

The formation of products 36 and 37 can be explained as ionic bonding of naphthalene cation (53) with pyrrole anion (54) through path (a) or (b) as shown in Figure 38.

The proton shift, of course, takes place after the formation of exciplex since the naphthalene fluorescence quenching only involves the exciplex formation as already mentioned. The question of whether the proton shift occurs at excited or ground state (involving, for example, radical ions) is not known. If the proton shift occurs after the radical ions diffused apart, a radical reaction rather than ionic would produce the products. This is shown in path iv) in Figure 37. In this case

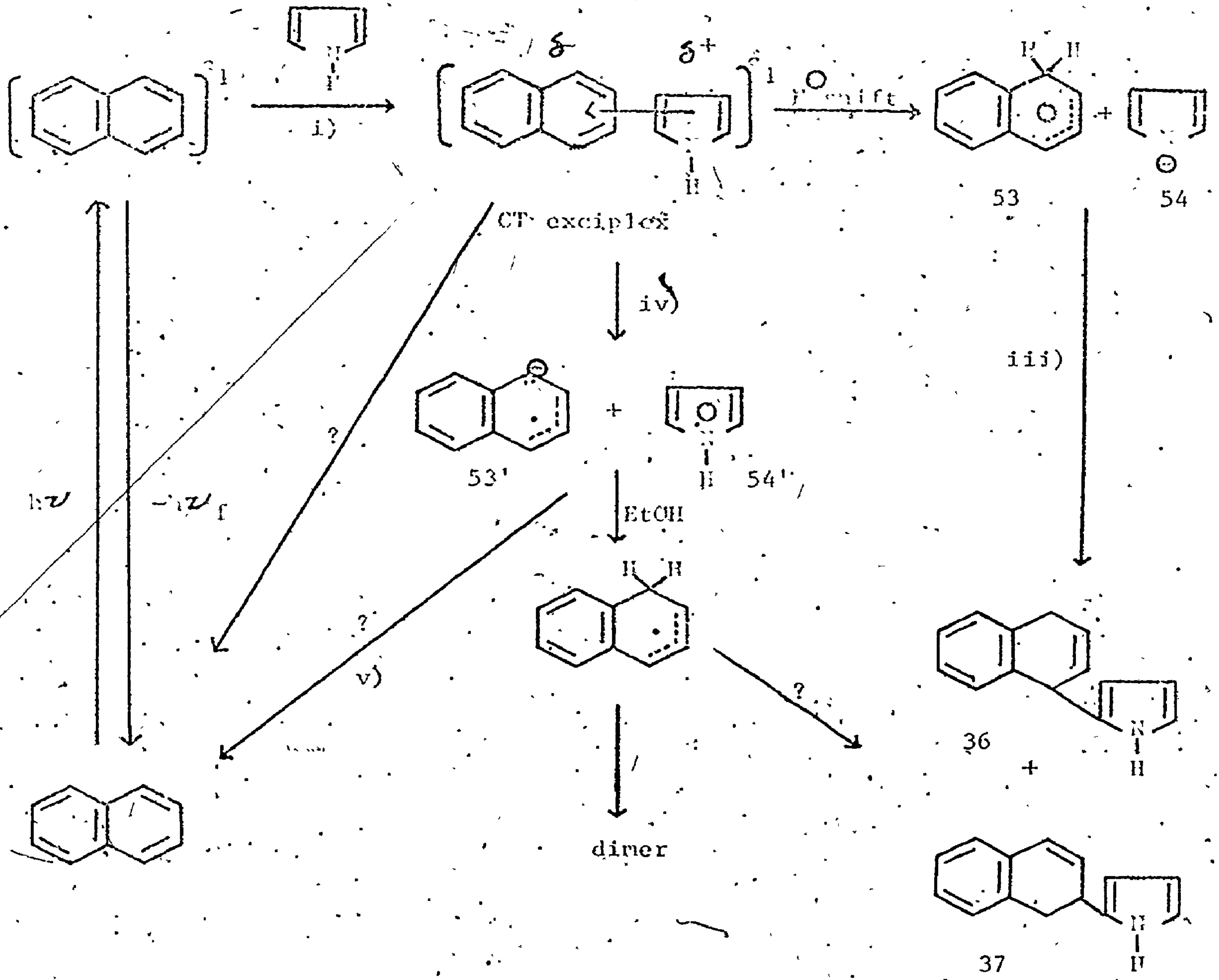


Figure 37. Reaction Mechanism for the Photoreaction of Naphthalene and Pyrrole

the products should contain some reduced naphthalene dimer which has not been found in this reaction. However, it it not possible to conclude the above argument with certainty at the present stage.

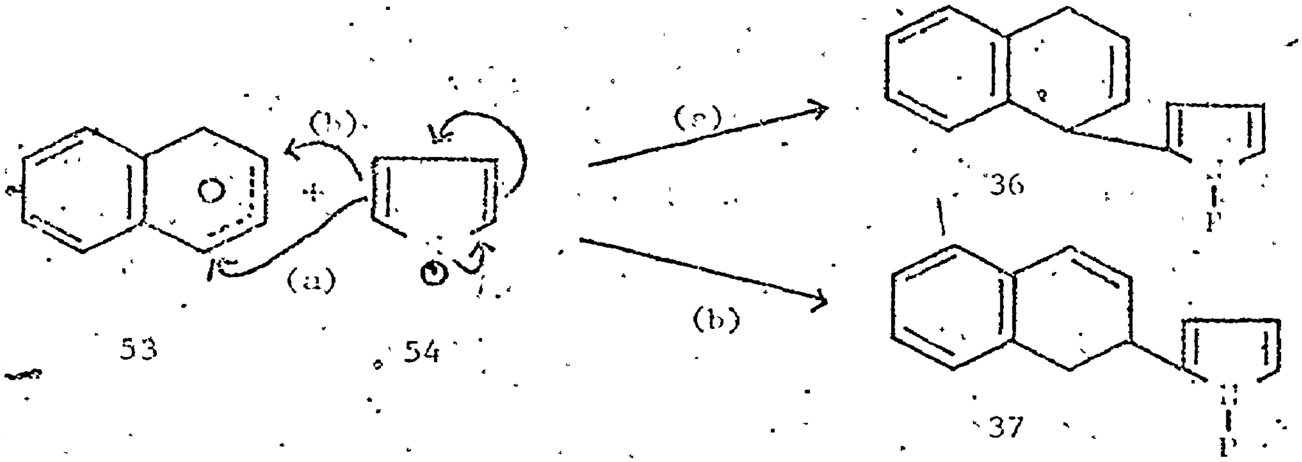


Figure 38. Ionic Reaction of Pyrrole Anion and Naphthalene Cation

Benzene - Pyrrole Reaction

The photoreaction of benzene and pyrrole is proposed to involve benzene T_1 state rather than S_1 by Bryce - Smith(37)(38). However, it is unlikely that there are any fundamental differences between the benzene and naphthalene reactions. If the photoreaction of benzene with pyrrole involves the same reaction mechanism as proposed for naphthalene with pyrrole, the products 18 and 55 should be formed rather than 18 alone (Figure 39).

Two reactions of benzene and pyrrole were conducted in benzene and in absolute methanol. Two products in both runs were observed on gas chromatography with 130 x 0.3 cm of 5% SE-30 column at 103°C. The retention times of these two products were 4.8 and 5.5 min. The products distribution in benzene and methanol is shown in Table 16.

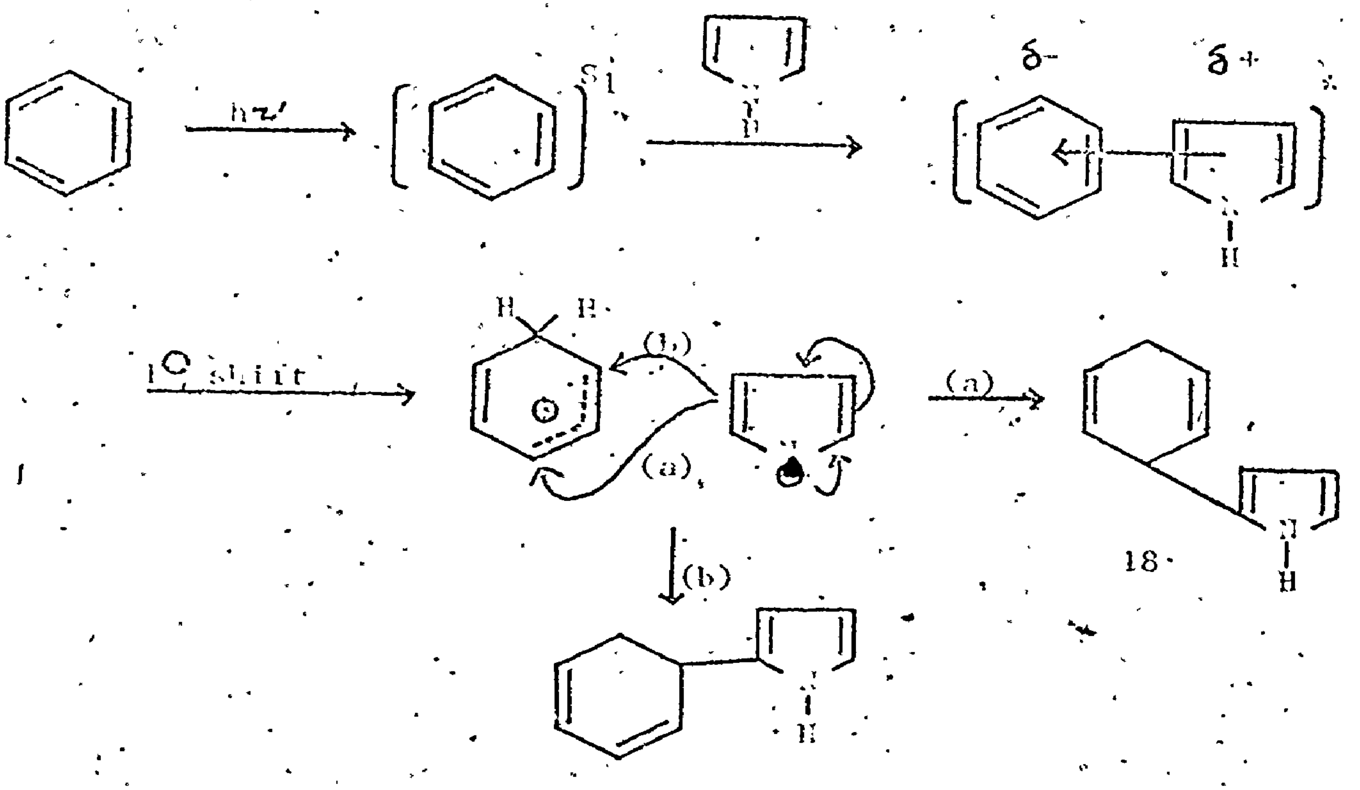


Figure 39. Charge Transfer Mechanism for the Photoreaction of Benzene and Pyrrole

However, both products have not been identified but isomer B probably is compound 18 and A may be 55. The photoreaction of benzene and pyrrole seems to be worth reinvestigating.

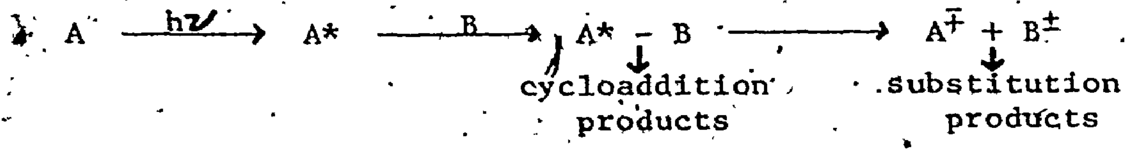
Solvent	Relative Yield of Products* A%	B%	Relative Reaction Rate
Benzene	33	67	1.8
Methanol	25	75	1.0

*both products were not identified, hence isomers A and B are so termed in this table.

Table 16. Products Distribution for the Reaction of Benzene with Pyrrole

Cyanonaphthalene and Tetramethylene Reactions

It is clear that S_1 state energy of TME is higher than that of 1-, or 2-cyanonaphthalene (both have E_{S_1} about 91 kcal, calculated from absorption spectra). Therefore, the quenching of cyanonaphthalene fluorescence by TME must be a result of exciplex formation. The products formation 1- and 2-cyanonaphthalene and tetramethylethylene reactions greatly depend upon solvent polarity. The reaction of 1-cyanonaphthalene and TME in methanol was believed to give substitution products 49 and 50, although the primary photo-products which led to 49 and 50 were not isolated. In contrast, only cycloaddition product 51 was produced when benzene was used as solvent in the reaction of 1-cyanonaphthalene and TME. It should be recalled that the photoreaction of naphthalene and acrylonitrile gives both substitution and cycloaddition products, but the relative amount of the substitution product increases over the cycloaddition product when the reaction is carried out in more polar solvent. A similar situation was also observed in the reaction of benzene and TME(52). The latter reaction gave 60% substitution product (30) when benzene was used as solvent, which increased to about 80% when in 50:50% benzene and methanol. The photoreaction of 1-cyanonaphthalene and TME serves as an excellent reaction model to relate the solvent polarity and type of products. This may be rationalized in terms of solvated ion pair and exciplex the former giving substitution and the latter giving cycloaddition. These two processes would compete with each other as the reaction proceeds (Figure 40).



Fluorescence Data

It was clear that the quenching of cyanonaphthalene fluorescence by TME and pyrrole was due to exciplex formation. Now the ionization potential values of these quenchers may be considered. TME has about the same ionization potential as pyrrole(72) (I_p of TME: 8.30 - 8.40 eV; I_p of pyrrole: 8.20, 8.61, 8.97 eV), but is lower than that of aliphatic amine (I_p of ethylamine: 9.32 eV). This indicates that TME is more readily ionized than an aliphatic amine which in many cases involves charge transfer mechanism in the photoreaction of aromatic hydrocarbons. Thus a large charge transfer component in exciplex formation between TME and excited cyanonaphthalene would be reasonable.

It was mentioned in the results that TME quenches the fluorescence of 2-cyanonaphthalene in methanol, acetonitrile but not in hexane or benzene. The following points concerning the fluorescence quenching are noteworthy.

1) The fluorescence quenching does not depend upon the solvent viscosity (η) since methanol and benzene have about the same η values and which are about twice that of hexane(73).

2) The proton of a protic solvent is not a major factor in causing fluorescence quenching, since the quenching in acetonitrile is just as efficient as in methanol. In other words, the hydrogen bonding between 2-cyanonaphthalene and methanol apparently is not important in this process.

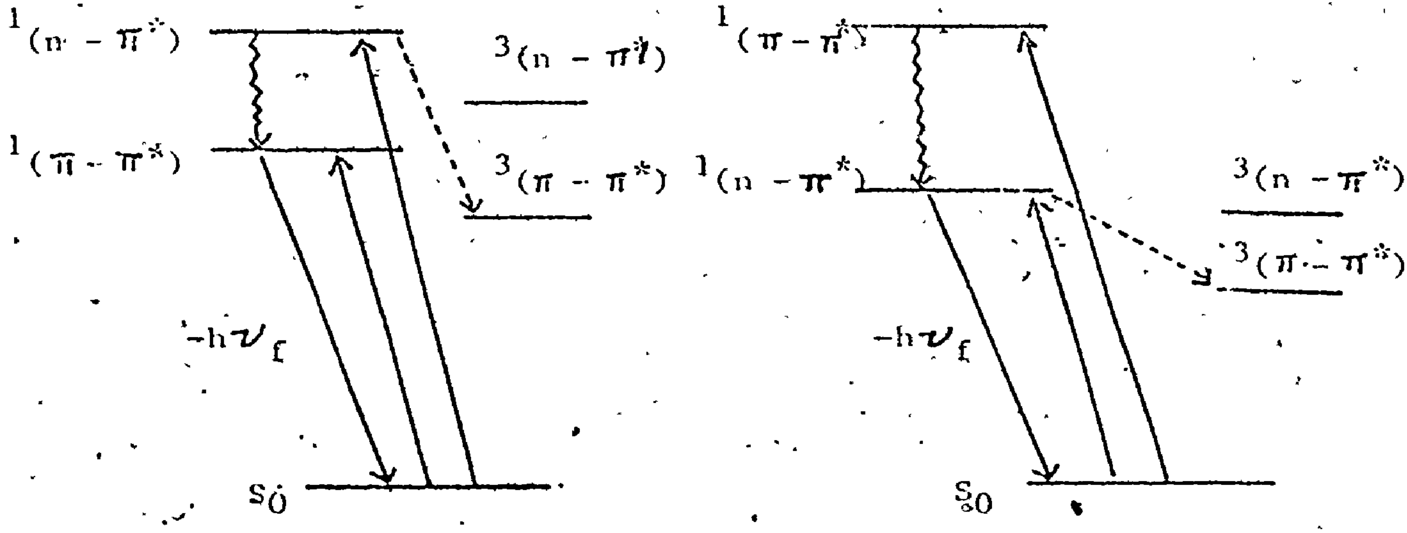
3) There is no exciplex formed between 2-cyanonaphthalene and methanol or acetonitrile since the 2-cyanonaphthalene fluorescence is still observed in those solvents and the relative fluorescence intensity, I_0/I, in the Stern - Volmer plot is linearly related to the concentration

The only major factor influencing quenching of the fluorescence of 2-cyanonaphthalene by TME seems to be solvent polarity. That is, the fluorescence is quenched in polar solvents such as methanol and acetonitrile, at diffusion controlled rate, but in non-polar solvents such as benzene and hexane, quenching fails. The interesting question is why 2-cyanonaphthalene behaves so differently from 1-cyanonaphthalene, the latter showing fluorescence quenching by TME in both polar and non-polar solvents. This is baffling at the present stage and further work needs to be done.

One possibility concerning the role of solvent polarity towards excited states is worth mentioning. The excited 2-cyanonaphthalene may involve a $(n - \pi^*)$ state since the cyano group is conjugated with the naphthalene π-system. In polar solvents, the energy level of n to π^* singlet transition, $^1(n - \pi^*)$, may be higher than that of π to π^* singlet, $^1(\pi - \pi^*)$. The energy levels of $^3(n - \pi^*)$ and $^3(\pi - \pi^*)$ are supposed to lie as shown in (a) of Figure 41(74). The intersystem crossing from $^1(n - \pi^*)$ to $^3(\pi - \pi^*)$ may be inefficient if there is a large energy gap between these two levels. The efficiency of intersystem crossing is not a major factor, however, if the triplet species is not reactive. On the other hand, the energy levels of $^1(n - \pi^*)$ and $^1(\pi - \pi^*)$ could be reversed(75)(76) in a non-polar solvent (case (b) in Figure 41). It is possible that the lowest excited singlet state which is $^1(n - \pi^*)$ does not form a exciplex with TME, which the $^1(\pi - \pi^*)$ does. However, the cyano group usually has high energy for both singlet and triplet $(n - \pi^*)$ states. Therefore, the excited states of 2-cyanonaphthalene should have the excitation localized in the ring. Hence, the above action of the solvent is unlikely but nevertheless is possible.

The many products from the reaction of 2-cyanonaphthalene and TME in acetonitrile were not identified.[7] A reaction did occur, however, in contrast to the case of the non-polar solvent, benzene, and this is a further demonstration of the importance of solvent polarity.

The fluorescence quenching results also suggest that both 1- and 2-cyanonaphthalenes and TME reactions proceed via S_1 of the cyanonaphthalenes. This is demonstrated by the fact that 2-cyanonaphthalene fails to react with TME in benzene or hexane and no fluorescence quenching occurs. However, as in the naphthalene - pyrrole reaction, the rate of intersystem crossing, k_{ic}, of cyanonaphthalene should not be much different from naphthalene (the intersystem crossing process involves a spin inversion which requires $\sim 10^{-6}$ sec in ($\pi - \pi^*$) system). Therefore, at 0.2 M TME concentration, the reaction from cyanonaphthalene triplet state could not occur when the fluorescence quenching is at diffusion controlled ~~rate~~.



(a) in polar solvent (b) in non-polar solvent

Figure 41. Solvent Effect of Energy Levels of Singlet and Triplet ($n - \pi^*$) and ($\pi - \pi^*$)

Mechanism of Reaction of 2-cyanonaphthalene and TME

The evidence from the products structures, fluorescence quenching and deuterium experiment suggest this reaction also involves a charge transfer mechanism which consists of the following processes:

i) formation of exciplex between excited 2-cyanonaphthalene and TME

ii) electron transfer within the exciplex from TME to cyanonaphthalene giving the charged speeies (56 and 57) solvated ion pairs

iii) solvent attack on the ion pairs, followed by radical combination between 56 and 57 to give products.

The scheme of the reaction mechanism is shown in Figure 42.

The species 56 can be protonated by solvent methanol. The product then results from radical combination between 56,56',57 and 58 the latter be formed by nucleophilic attack of methanol on the TME radical cation. This is an unprecedented process which is excellent evidence for the proposed ionic nature of the intermediates 56 and 57. The formation of products 42 and 45 seems to be under kinetic control. The almost equal distribution of products 42 and 43 in methanol, of course, indicates two resonance forms of 56 giving an electron distribution which leads to products 42 and 43.

It is quite clear that acid (acetic acid, formic acid) or protic solvent (methanol) would also protonate the 2-cyanonaphthalene radical anion. When the reaction is conducted in methanol containing 2.8 M acetic acid, the rate of products formation increases by a factor of about 2 over the system without acid. This can be explained by the fact that the protonation by acid is faster than that of methanol. The protonation by both methanol and acid could conceivably take place prior to or after the

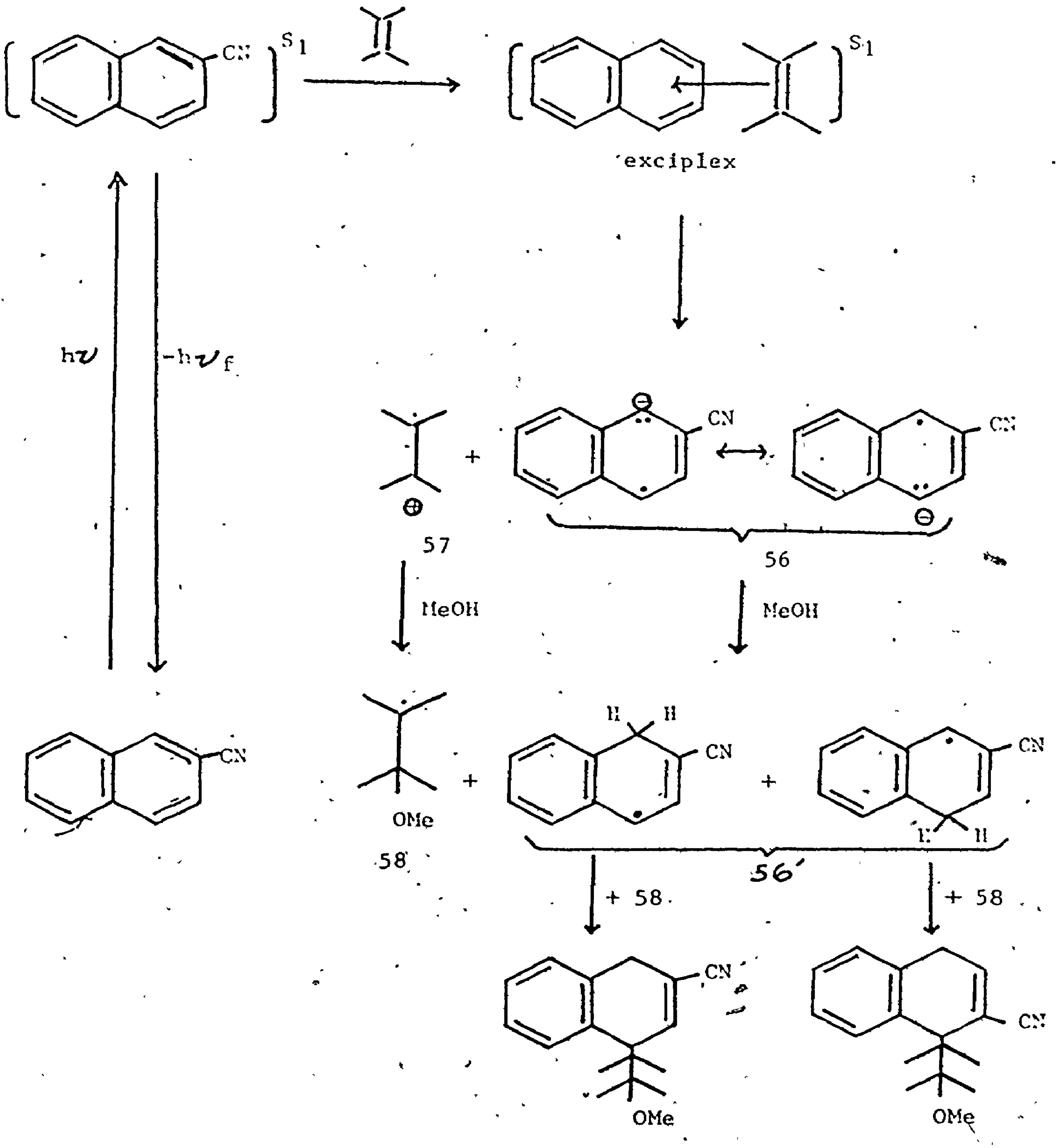


Figure 42. Reaction Mechanism for 2-cyanonaphthalene with TME in Methanol

[illegible] cyanonaphthalene radical anion by TMT radical cation, but the increase in rate of product formation with the presence of an acid shows that, in fact, protonation occurs prior to the bonding attack of the radical centers. The efficiency of 2-cyanonaphthalene fluorescence quenching by TMT in methanol is not promoted by the presence of an acid. Thus the formation of exciplex which results in fluorescence quenching does not involve action of the acid.

Suggestion for Further Studies

Although the photoreaction of naphthalene and pyrrole, and cyanonaphthalene with TMT have been suggested to follow a charge transfer mechanism from various experimental results, the attempted direct observation of charge transfer species ie. radical ions by physical methods such as ESR, CIDNP (77)(78) or flash photolysis has not been seriously undertaken. Probably these physical techniques can be applied with likelihood of success.

The naphthalene (or other aromatic hydrocarbons) fluorescence quenching by pyrrole can be explained to include many other pyrrole-like heterocyclic aromatic compounds such as thiophene, furan, imidazole, pyrazole, oxazole, thiazole, etc., which may behave as pyrrole. The ionization potentials of heterocyclic aromatic compounds may correlate with the fluorescence quenching constant (k_q) if quenching, resulting from charge transfer, takes place. Thus, these studies might be expanded into the area of physical chemistry, in the cause of the search for new photoreactions.

Further experiments for the photoreaction of 2-cyanonaphthalene and TMT system certainly should use some other polar protic solvents with poor nucleophilicity such as β-trifluoroethanol (CF_3CH_2OH). This should give new, possibly elimination products (Figure 43) if the reaction resembles the one in methanol.

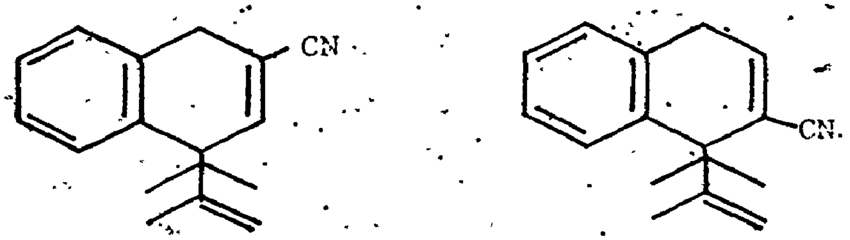


Figure 43. Possible Products from the Reaction of 2-cyanonaphthalene and TME in Solvent of Trifluoroethanol

The products formed in the same reaction but using acetonitrile as solvent as well as in the photoreaction of 1-cyanonaphthalene with TME in methanol are worth identifying.

General Conclusions and Significance of the Results

Two photoreactions have been studied. The first, pyrrole with naphthalene, gave products which were 1:1 adducts, and were 1,4-dihydronaphthalene derivatives. It is believed that the pyrrole acts as the donor in a charge transfer exciplex with naphthalene S_1, and a proton shift followed by ionic reaction leads to the products. The ionic nature of the final step is suggested by the medium effects.

The second case (cyanonaphthalene and tetramethylethylene) also involves the TME as a donor. 2-cyanonaphthalene gave an interesting reaction in which solvent methanol was incorporated and the products were 1,4-dihydronaphthalene derivatives. 1-cyanonaphthalene gave simple cyclobutane adducts with TME in benzene, a reaction which 2-cyanonaphthalene does not undergo.

The pyrrole and TME reactions show certain similarities in the products formed and mechanism of reaction. Clearly, these results may be precedent for the course of many photoadditions, and could lead to a scheme having predictive power. Such scheme does not exist at present for photoadditions of aromatic molecules.

PART V. EXPERIMENTAL

SECTION A. INSTRUMENTATION AND MATERIALS

SECTION B. NAPHTHALENE - PYRROLE SYSTEM

SECTION C. CYANONAPHTHALENE - TETRAMETHYLETHYLENE SYSTEM

SECTION A. INSTRUMENTATION AND MATERIALS

Instruments

The nuclear magnetic resonance spectra were obtained with a Varian HA-100 or A-60 spectrometer. The chemical shifts are given as τ values and tetramethylsilane (τ = 10) was used as internal standard. Infrared and ultraviolet spectra were determined with a Perkin - Elmer 521 or Cary Model 14 spectrophotometer respectively. Mass spectra were recorded on Hitachi Perkin - Elmer RMU 6A or a CEC 21-110B instrument. The gas-liquid chromatography (g.l.c.) was performed unless if specified, with a Varian 204B dual column instrument with the flow rate of helium about 30 ml/min. The exact conditions of g.l.c. with be stated in each experiment. For thin layer chromatograph (t.l.c.), Eastman plastic sheet precoated with silica gel was used. Celite was supplied by the Eagle - Picher Co. (type, Celatom F-W 80). Melting points were measured on a Kofler hot stage and uncorrected. The fluorescence spectra were obtained with an Aminco - Bowman spectrofluorimeter. Nitrogen was Canadian Liquid Air certified grade. Two kinds of silical gel (Grace, 923, 100-200 mesh, and MN-Silica Gel G) were used as adsorbents in the adsorption column chromatography.

Microanalyses were determined by the Spang Microanalytical Laboratory, Ann Arbor, Michigan or by the Cygli Microanalysis Laboratory, Toronto. Molecular weight determination was by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Chemicals

All the solvents for reactions and fluorescence quenching experiments were distilled before use.

Naphthalene, Fisher Scientific Co., was recrystallized from ethanol, m.p. 78.5 - 80°.

Pyrrole, Baker or Aldrich Chemical Co., was freshly distilled under nitrogen atmosphere, b.p. 104° at 20 mm Hg, before each run.

N-methylpyrrole, Columbia Organic Chemicals, was freshly distilled before use.

Acetophenone, from Eastern Chemical Corp., had b.p. 52° at 0.5 mm Hg.

Benzophenone was also from Eastern Chemical Corp. and had m.p. 47.5 - 48°.

Michler's ketone was from Aldrich Chemical Co., recrystallized from benzene, had m.p. 172 - 172.5°.

p-Bromobenzophenone was from Eastern Chemical Corp. and was recrystallized from light petroleum, m.p. 78 - 80°.

N-deuteriopyrrole was prepared according to literature(79) and freshly distilled before use.

Carbonyl chloride was supplied by Matheson of Canada Ltd.

N,N-dimethylaniline was from Eastern Chemical Corp. and was freshly distilled before use.

1-Cyanonaphthalene was from Eastman Organic Chemicals and was recrystallized from light petroleum, m.p. 36.5 - 37°.

2-Cyanonaphthalene was also from Eastman Organic Chemicals and was crystallized from 95% ethanol, m.p. 67 - 68°.

Tetramethylene was from Columbia Organic Chemicals and was distilled at atmospheric pressure, b.p. 70.5°.

Deuterium Oxide was from Columbia Organic Chemicals, and was specified at 99.7% D_2O.

Dimethyl carbonate was from BDH Chemicals and was specified as [illegible]% pure.

Dimethyl sulfate was supplied by Matheson Coleman & Bell.

Methanol-OD was prepared according to literature(80).

Formic acid, 90%, was from BDH Chemicals.

Acetic acid from CIL, c.p. reagent, was specified as > 99.8% pure.

SECTION B. NAPHTHALENE - PYRROLE SYSTEM

Photo-addition of Naphthalene and Pyrrole

Naphthalene (12.0 g, 0.094 mole) and pyrrole (14.0 g, 0.21 mole) in 450 ml 95% ethanol were irradiated using a pyrex filter with a Hanovia type L 540 W lamp in a water-cooled immersion apparatus fitted with a means of withdrawing portions by a syringe. The progress of the reaction was followed by analysis of portions by g.l.c. The irradiation was continuous for 16 hrs, with nitrogen passing through the solution. Gas-liquid chromatography on a 150 x 0.3 cm of 5% F-1 on a 60/80 Chromasorb W column at 153°C showed two major products, 36 and 37, with retention times 3.5 min. and 3.9 min. respectively. The two minor products had retention times of 5.2 and 5.9 min. and are tentatively identified as 3-(dihydronaphthyl)-pyrroles, present in 15% yield. The solvent was evaporated and most of the excess pyrrole was distilled with a vacuum pump with slightly gentle heating (about 40°C). The mixture was decolorized and naphthalene removed by passage through a silica gel column (Grace 923, dimension: 80 x 3 cm) and eluted with 50:50% hexane and benzene; 200 ml fractions were collected. Each fraction was checked by t.l.c. on silica gel. A total of 6.8 g of naphthalene was recovered (56.4% recovery) in the early fractions: continued elution with about 500 ml of 95:5% ether and methanol and recovered the products' mixture. The solvent was evaporated and the weight of crude mixture which contained the products was 6.5 g.

This residue was introduced into a celite supported liquid-liquid partitioning column$^{(81)}$ (130 x 5 cm). The column was equipped with water-jacket and the temperature was maintained at 25°C during the elution. The stationary phase is dimethylformamide-water-ethyl acetate on Celite with cyclohexane as the mobile phase. The fractions (200 ml) were collected, as the separation shown below.

Fractions 1 to 18, essentially nothing eluted.

Fractions 19 to 20 had a combined weight of 1.15 g of which about 90% was compound 36. Fractions 21 to 24 had a combined weight of 3.00 g which contained both compounds 36 and 37 (51.3% of 36, 43.0% of 37). Fraction 25 contained about 61% of compound 37, 5% of compound 36 and a total of 34% of the two minor products. The weight of this fraction was 0.40 g. The combined fractions 21 to 24, after the solvent was removed, were introduced again on to the same celite column under the same conditions; 250 ml fractions were collected, whose content was as follows.

Fractions 8 to 10 had a combined weight of 0.69 g of which 99% was compound 36. Fractions 11 to 12 had a combined weight of 1.45 g of which 50.4% was compound 36 and 49.6% was compound 37. Fraction 18 contained 0.43 g of which 95% was compound 37.

Compound 36 (fractions 8 to 10), crystallized from ethanol, had m.p. 149 - 154 °C with ν_{max} at 3484 cm^{-1} (N-H), and compound 37 (fraction 13) was oily with ν_{max} also at 3484 cm^{-1}.

Conversion of Compound 36 to the Ester Derivative(63)

A 100 ml, 3 necked round bottom flask which contained 20 ml freshly distilled dry toluene (12 hrs over $CaCl_2$, and distilled) was cooled in ice and carbonyl chloride passed through toluene until 1 g was absorbed and the unabsorbed one was destroyed with KOH solution. A 1.5g of fres ly distilled N,N-dimethylaniline was added and then 10 ml of a toluene solution of compound 36 (1.15 g, 6.1 mole). The mixture was stirred overnight. At this point, 1.5 g of N,N-dimethylaniline was added, followed by 10 ml absolute ethanol and the mixture was refluxed for 2 hrs. The solvent was distilled and the residue was introduced into a silica gel column (Grace 923, 40 x 2 cm) and eluted with 50:50% benzene and hexane, and 250 ml fractions were collected. From fraction 7, the eluting solvent was 75:24:1% benzene, hexane, methanol. Fraction 8 showed one spot on t.l.c. Fraction 8 was washed twice with 5% HCl, three times with a total of 150 ml of water. The organic layer was filtered through anhydrous Na_2SO_4 and evaporated. The residue was crude crystalline compound 40. It was washed with cold ether and weighed 0.33 g. The crude crystal was purified by crystallization fromethanol (charcoal), m.p. 160.5 - 162.5°C.

Anal. Calcd. for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.20; H, 6.41; N, 5.06.

Conversion of Compound 37 to the Ester Derivative(63)

The photo-adduct 37, 868 mg (containing 78% of 37), (3.47 mmole) was treated with carbonyl chloride (600 mg) in toluene and then with ethanol as described above. The residue obtained on evaporation of the toluene, was chromatographed on a silica gel column (Grace, 923, 30 x 2 cm) and eluted with benzene: hexane (75:25%, 4.5 liter), then with benzene: hexane: methanol (74:25:1%) and 450 ml fractions were collected. The four consecutive fractions (1 to 4) all had one identical t.l.c. spot and NMR showed to be the carboethoxy derivative. These four fractions were combined and the solvent was removed; the oily residue failed to crystallize. It was then introduced into another silica gel column (Grace, 923, 30 x 2 cm) and eluted with 75:25% benzene and hexane. 450 ml fractions were collected, and fractions 18 to 20 contained the carboethoxy derivative. The combined crude product weighed 350 mg and was crystallized with hexane water, m.p. 84 - 85°C.

Anal. Calcd. for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.21; H, 6.41; N, 5.55.

Photolysis of Naphthalene and N-deuteriopyrrole

Naphthalene (6.0 g) and N-deuteriopyrrole (3.0g) in acetonitrile (distilled from phosphorus (V) oxide) were irradiated through a pyrex filter with a 450 W Hanovia lamp for 5 hrs. The adducts 38 and 39 were isolated as before (reference compounds 36 and 37, page 84). In the NMR spectra, the incorporation of deuterium in the methylene group was shown by the 50% reduction in the areas of the peaks at 6.70 and 7.09 τ respectively. Also the mass spectra showed that one deuterium atom had been incorporated into the adducts.

Attempted Sensitization of the Naphthalene - Pyrrole Reaction

Irradiation of the following solutions of naphthalene, pyrrole, and sensitizers for 2.5 or 25 hrs with the Hanovia 450 W lamp (pyrex filter) gave no measurable yield of adducts 36 or 37.

a) naphthalene (0.0235 M), pyrrole (0.0448 M), and benzophenone (0.033 M)

b) naphthalene (0.0235 M), pyrrole (0.0448 M), and acetophenone (0.0416 M)

c) naphthalene (0.0235 M), pyrrole (0.0448 M), and Michler's ketone (0.045 M)

Attempted Reaction of Naphthalene with N-methylpyrrole

Irradiation of naphthalene and N-methylpyrrole in the same way [illegible] for the conditions [illegible] pyrrole adds, [illegible] no detectable amounts [illegible] (g.l.c. monitoring) after short (2.5 hrs) or long (25 hrs) irradiation.

[illegible] of Fluorescence by Pyrrole or N-methylpyrrole

Measurements were made on an Aminco - Bowman spectrofluorimeter. Excitation was carried out at 32[illegible] nm and monitoring at 3[illegible]3 nm. Naphthalene concentration was 1.48×10^{-2} mol l^{-1}. Sample solutions were deoxygenated by purging with argon. The results are given in Tables 9 and 10. Stern - Volmer quenching plots are shown in Figures 38 and 39.

Solvent Effects

Solutions containing naphthalene (0.0237 mol l^{-1}) and pyrrole (0.54 mol l^{-1}) in each of the following solvents; hexane, benzene, dichloromethane, 95% ethanol, acetonitrile, methanol and 80% methanol, were placed in pyrex tubes (11 x 3.5 cm). The samples were degassed by the freeze-pump-thaw method, and sealed. The tubes were irradiated for 2.5 hrs in a Rayonet Photochemical Reactor (Southern New England Ultraviolet Company) using 16 RPR 300 nm lamps, and a "merry-go-round" turntable to average the light intensity. The relative rates in each of the solvents were estimated by g.l.c., using p-bromobenzophenone as internal standard. The product ratios were also measured, and the results are given in Table 12.

Dehydrogenation of Compounds 36 and 37

The adduct 36 or 37 (0.5 g) and 10% palladium - charcoal (0.45 g, Matheson, Coleman, and Bell) were heated under reflux in p-xylene (15 ml). The solution was filtered and evaporated, and the unstable oil was ex-

[illegible] g.l.c. (150 x 0.3 cm, 5% [illegible], [illegible] 160°C) [illegible]. The two [illegible] adducts to naphthalene [illegible], which had different retention times on g.l.c. and different NMR spectra, but both were α-substituted pyrroles. This indicates that the pyrrole substituent is [illegible] position. In the adducts 36 and 37, in agreement with the [illegible] structures. The dehydrogenations proceed at different rates, [illegible] 36 requiring 2 days, but isomer 37 only 3 hrs.

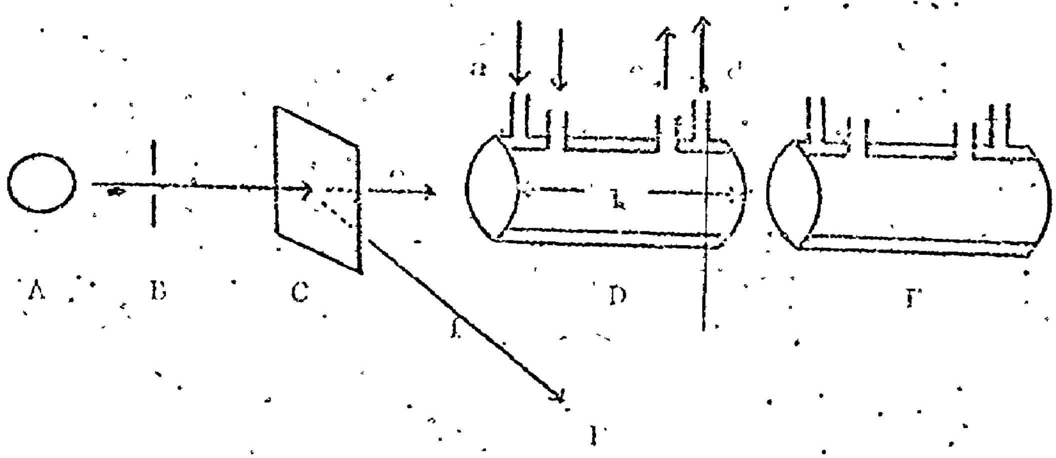
Investigation of Ground State Charge Transfer Interaction by Ultraviolet Absorption between Naphthalene and Pyrrole

Solutions of naphthalene (5.33×10^{-3} mol l^{-1}) and pyrrole (1.23×10^{-2} mol l^{-1}) in ethanol and of naphthalene (5.12×10^{-3} mol l^{-1}) and pyrrole (2.12×10^{-2} mol l^{-1}) in hexane were found to have u.v. absorption equal to the sum of the absorbances of the separate constituents. The path length was 0.1 mm. No evidence for charge - transfer interaction was found.

Quantum Yield of Product Formation(82)

The irradiation was performed using the monochromator set-up shown in Figure 44. The light intensity was measured using the beam splitting technique, and the products were assayed by g.l.c. analysis (150 x 0.3 cm, 5% SE-30 at 167°C) using p-bromobenzophenone as internal standard. The relative areas of g.l.c. peaks were integrated with an Aerograph Model 475 Electronic Digital Integrator with Victor printer.

The procedures to obtain the products quantum yield is shown below.



A: light source, a high pressure mercury lamp

B: wavelength selector

C: pyrex glass plate, transmitting and partially reflecting the light in e and f directions

D,F: cylindrical reaction cell, with outer water jacket (a,d) to keep the reaction temperature constant, the deoxygenated jacket to permit argon to enter b, pass through reaction mixture, leaving through c, the volume capacity of this cell is 26 ml

F: the same design as D, but the volume capacity is 13 ml, and the length of the cell is exactly half of D, (The size of these reaction cells can vary depending upon the reaction involved.)

Figure 44. Products Quantum Apparatus for Photoreaction of Naphthalene and Pyrrole

a) Light intensity measurement

The ratio (r) of the amount of light transmitted (e path, Figure 44) and reflected (f path, Figure 44) by the quartz plate was determined as follows.

The potassium ferrioxalate system developed by Parker and Hatchard is the best solution-phase chemical actinometer for photochemistry(83). A 0.006 M potassium ferrioxalate, $K_3Fe(C_2O_4)_3\cdot2H_2O$, solution was placed in both cells D (26 ml) and F (13 ml), and irradiated at 300 nm for 20 min. The photoreaction is based on the reduction of ferric ion to ferrous ion. The ratio of ferrous ion produced in D and F cells gives the splitting ratio γ , and was found by measuring the ratio of the absorbances of the coloured complex of Fe^{2+} with 9,10-phenanthroline at 510 nm. The ratio was 10.1 in this experiment. The absorbances were measured on a Bausch and Lomb Precision spectrophotometer, calibrated with standard solutions of ferrous ion - phenanthroline complex..

b) Products quantum yield determination

The reaction solution (26 ml) containing 0.7498 g of naphthalene and 0.7525 g of pyrrole in 100 ml of 95% ethanol was placed in cell D, the potassium ferrioxalate solution was placed in cells E and F. The solution was irradiated at 300 nm for 4 hrs. A preliminary run was performed to set the approximate irradiation time to yield 15 to 20% conversion to products. The temperature was 25° and all solutions were purged with argon.

The reaction solution in cell D was then mixed with a known amount of g.l.c. internal standard solution of p-bromobenzophenone, and the weight of products was determined from the g.l.c. calibration plot.

	(36 + 37) wt % by g.l.c. response	(36 + 37) wt %*	Total amount of products mg	mol × 10^{-5}
Run 1	30.7	27.2	7.20	3.71
Run 2	30.0	26.7	7.01	3.63

*The data was obtained by the calibration of g.l.c. weight response to true weight. The method was as follows. Two stock solutions (in ethylacetate) were prepared by weighing the exact amounts of p-bromobenzophenone (p-BBP, internal standard) and product 36. Then, they were combined in varying ratios. The g.l.c. weight response ratios were plotted against the true weight ratios, 36/(36 + p-BBP) wt % by g.l.c. versus 36/(36 + p-BBP) wt %,to obtain a straight line.

The absorbance of ferrous ion in cell E which was produced during the irradiation was negligible showing that all the light incident on the naphthalene - pyrrole solution was absorbed.

The number of Fe^{2+} ions ($n_{Fe^{2+}}$) in cell F formed during photolysis is calculated by the following equation.

$$n_{Fe^{2+}} = 6.023 \times 10^{20} V_1 V_3 \log(I_0/I)/V_2 l \epsilon \qquad (34)$$

V_1: the volume of actinometer solution in cell F irradiated (ml)

V_2: the volume of aliquot in cell F taken for analysis (ml)

V_3: the final volume to which the aliquot V_2 is diluted (ml)

$\log(I_0/I)$: the measured absorbance of the solution at 510 nm

l: the path length of the spectrophotometer cell used (cm)

ϵ: the experimental value of the molar extinction coefficient of the Fe^{2+} complex as determined from the slope of the calibration plot

From these data, equation 34 gives

$$n_{Fe^{2+}} = 6.023 \times 10^{20} \times 26 \times 25 \times 0.7 / 2 \times 1 \times 1.125 \times 10^{4}$$
$$= 1.22 \times 10^{19}$$

Since the quantum yield of Fe^{2+} formation is known to be 1.24 at 300 nm, from the definition of quantum yield (Φ), the total amount of light absorbed by solution in cell F (I_F) can be calculated from the following equation.

$$\Phi = \text{moles of } Fe^{2+} / I_F \text{ (Einstein)} = 1.24 \qquad (35)$$

Thus I_F is calculated to be 1.61×10^{-5} Einstein.

The amount of light absorbed by the reaction solution in cell D (I_D) can be calculated from the splitting factor (γ).

$$I_D = I_F \cdot \gamma = 1.61 \times 10.15 = 1.63 \times 10^{-4} \text{ Einstein}$$

Finally, the products' quantum yield of compound 36 and 37 was calculated as,

$$\Phi_{36+37}^{95\%\ EtOH} = 3.7 \times 10^{-5} / 1.63 \times 10^{-4} = 0.23$$

The measured quantum yields for ethanol and benzene solvents are given in Table 13.

Photoreaction of Benzene and Pyrrole

Two benzene - pyrrole solutions were prepared by mixing 0.3 ml benzene and 0.5 ml pyrrole and diluting to 20 ml with benzene and methanol respectively, were degassed by the freeze-pump-thaw method, and sealed in quartz tubes. The solutions were irradiated for 4 hrs, using 16 RPR 350 nm lamps and a merry-go-round turntable to average the light intensity. Two products were apparent by g.l.c. analysis with retention times of 4.8 and 5.9 min on 150 x 0.3 cm, 5% SE-30 column at 103°. The relative rate in methanol or benzene was estimated by g.l.c. using acetophenone as internal standard. The results are shown in Table 16.

SECTION C. CYANONAPHTHALENE - TETRAMETHYLETHYLENE SYSTEM

Photolysis of 2-Cyanonaphthalene and Tetramethylethylene in Methanol

A 400 ml methanol solution of 2-cyanonaphthalene (6 g, 0.015 mole) and tetramethylethylene (18 g, 0.214 mole) was irradiated (pyrex filter) with the Hanovia type L 450 W lamp for 36 hrs under a nitrogen atmosphere. The extent of reaction was checked by NMR (aromatic protons resonated at different position for 2-cyanonaphthalene and products). The major products 42 and 43 were observed by g.l.c. (150 x 0.3 cm, 5% QF-1 column, at 200°; retention time: compound 43, 8.3 min, and compound 42, 10 min). The relative products ratio for compounds 43 and 42 was about 60:40 in favour of 43. The reaction mixture (8.14 g) was cleaned by passing it through a silica gel column (Grace, 923, dimensions, 27 x 3 cm) in 30% ether in light petroleum and 400 ml fractions were collected. The contents of the various fractions were as follows.

Fraction	Component	Weight (g)
1 - 2	unidentified	0.136
3 - 4	2-cyano-naphthalene	3.34
5 - 10	mainly compounds 42 and 43	4.20

It can be seen that 45% of the 2-cyanonaphthalene had reacted.

The combined residue from fractions 5 to 10 was introduced into a second silica gel (MN-Silica Gel G) column (65 x 4 cm) and eluted with 10:10:80 ether, benzene, light petroleum. The first liter of effluent was discarded and the remainder collected as 25 ml fractions. The results of the separation are shown below.

Fraction	Component	Weight (g)
1 - 8	unidentified	0.235
9 - 12	75:25% unidentified compound and compound 42	0.120
13 - 23	50:50% of compounds 42, 43	2.128
24 - 25	mixture of 42 and 43	0.198
26 - 37	compound 43 in 88%	1.184

The residue from evaporation of fractions 13 to 23 was chromatographed on a silica gel (MN-Silica Gel G) column (25 x 3 cm) with 3% ether in light petroleum ether. The oily compound 42 (1.064 g, 23.4% yield) was obtained and purified from ethanol (0.387 g, 8.5% yield) with m.p. 89.5 - 91.5°.

Anal. Calcd. for $C_{18}H_{23}NO$: C, 80.25; H, 8.61; N, 5.31. Found: C, 80.31; H, 8.55; N, 5.31.

The combined fractions 26 to 37 (1.12 g) consisted of 43 (82% pure, 19.6% yield) and gave crystals from ethanol, m.p. 96.5 - 98°, (0.351 g, 7.1%).

Anal. Calcd. for $C_{18}H_{23}NO$: C, 80.25; H, 8.61; N, 5.31. Found: C, 80.38; H, 8.62; N, 5.22.

The mother liquor of compound 42 was distilled at 0.05 mm (oil bath at 130°) to afford 0.723 g (28.9%) compound 44.

For the deuterium labelling experiment, this reaction was run in methanol-O-D. The deuterated products 45 and 46 were separated in the same way as above and identified by NMR and mass spectra.

Attempted Deuterium Exchange for 2-Cyanonaphthalene Without Tetramethylethylene

A 200 ml, 5% CH_3CO_2D, methanol-O-D solution containing 0.2 g 2-cyanonaphthalene in a pyrex tube was irradiated in a Rayonet Photochemical Reactor, using 16 RPR 300 nm lamps, for 10 hrs. No deuterium exchange between 2-cyanonaphthalene and solvent was found by comparison of the mass spectra of isolated and authentic 2-cyanonaphthalene.

Irradiation of 2-Cyanonaphthalene and Tetramethylethylene in Formic Acid - Methanol

A 400 ml, 5% formic acid, methanol solution containing 5 g 2-cyanonaphthalene and 15 g tetramethylethylene was irradiated in the same way as in the above methanol case for 40 hrs. The products ratio was about 90:10 of compound 42 over 43. The reaction solution was concentrated to about 100 ml, transferred to a 1 liter separatory funnel with 500 ml of benzene, and washed with 1% NaOH solution followed by water. The benzene layer was dried over sodium sulfate. The residue remaining after filtration and evaporation was chromatographed on a silica gel (Grace, 923) column (25 x 3 cm) with 1% ether in light petroleum ether. The 2-cyanonaphthalene was removed in the first 2 liters (2.632 g, 56.2%). The column was further eluted with 2 liters of 20% ether in light petroleum ether. The oily residue (3.65 g) contained about 75% compound 42, corresponding to a 65.8% yield. This residue was crystallized from ethanol-water (0.7 g, m.p. 89.5 - 91.5°). The mother liquor was evaporated and distilled at 125°, 0.05 mm, to afford 0.5 g distillate, which crystallized, m.p. 63 - 67°. It was recrystallized from 95% ethanol to yield 0.1 g compound 52, m.p. 57 - 58.5°. This product (52) has not been positively identified, but is assigned as 3,4-dihydro-2-cyanonaphthalene.

Molecular weight Anal. Calcd. for $C_{11}H_9N$: 155. Found: 149.

The deuterium labelling experiment of this reaction was carried out in methanol-O-D which contained 5% CH_3CO_2D and compound 45 was isolated in the same way as above.

Photoreaction of 2-Cyanonaphthalene and Tetramethylethylene in Acetonitrile

A 400 ml acetonitrile solution of 2 g 2-cyanonaphthalene and 6 g of tetramethylethylene was irradiated the same way as in methanol solution for 12 hrs. A complex mixture of products with two being major were detected by g.l.c. analysis (150 x 0.3 cm, 5% SE-30 at 185°). However, the separation of products by a variety of methods was unsuccessful.

Dehydrogenation of Compound 42

A mixture of 0.2 g compound 42 and 0.15 g 10% palladium-charcoal in 15 ml p-xylene were refluxed for 3 days. The catalyst was filtered and the solution distilled under aspirator pressure. The residue was crystallized from ethanol-water. The dehydrogenation product 48, m.p. 124 - 126°, was obtained (0.06 g, 30% yield).

Anal. Calcd. for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.88; H 7.99; N, 5.24.

Dehydrogenation of Compound 47

Compound 47 (0.26 g) and 10% palladium-charcoal (0.2 g) in 10 ml toluene were refluxed for 8 hrs. The solvent was removed and the residue chromatographed on a silica gel (MN-Silica Gel G) column (7 x 3 cm). First elution was with 0.5 liter light petroleum and this was discarded.

[illegible] was dissolved in light petroleum (1 liter) and the residue [illegible] crystallized (m.p. 65 - 66°) when solvent was removed. The product contained about 50:50 of 2-cyanonaphthalene and 1-deuterio-2-cyanonaphthalene according to NMR and mass spectra analyses.

Irradiation of 1-Cyanonaphthalene and Tetramethylethylene in Methanol

A 400 ml methanol solution containing 3.0 g of 1-cyanonaphthalene and 5.0 g of tetramethylethylene was irradiated in the same way as 2-cyanonaphthalene - tetramethylethylene in methanol, for 48 hrs. An NMR spectrum [illegible]d when the amount of products was a maximum. After solvent evaporation, the residue was chromatographed on a silica gel (CN-Silica Gel G) column (50 x 4 cm) in 15:15:70 ether, benzene, light petroleum. A forerun of 400 ml contained only 1-cyanonaphthalene, in a very small amount. On continued elution of the column in 25 ml fractions, the results of the separation are shown below.

Fraction	Wt. in g	Contents
1 - 24	1.086 (including fore-run)	1-cyanonaphthalene (32.6% recovery)
25 - 34	0.277	m.p. 175 - 179°
35 - 44	0.251	m.p. 162 - 173°
45 - 54	0.225	m.p. 176 - 181°
55 - 64	0.221	large range of m.p.
65 - 80	0.281	large range of m.p.

The residues from fractions 25 to 34 and 35 to 44 (total wt 0.528 g) were combined and crystallized from ethanol, m.p. 177 - 178°. The NMR and mass spectra indicated this is a secondary photoreaction product.

[illegible] The structure of the compound is not [illegible], but the [illegible] empirical formula [illegible].

Anal. Calcd. for [illegible]: C, 8[illegible].43; H, 7.08; N, 6.73. Found: C, [illegible]2; H, 7.[illegible]; N, 6.63.

The combined crystals from fractions 45 to 50 were crystallized [illegible] and had m.p. 18[illegible] - 186.5°. NMR and mass spectra also indicated this compound is not a primary product, but possibly a photo-induced 1-cyanonaphthalene [illegible]. The empirical formula for this secondary product is $C_{22}H_{16}N_2$ (42).

Anal. Calcd. for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.29. Found: C, 85.6[illegible]; H, 5.51; N, 9.29.

Photoreaction of 1-Cyanonaphthalene and Tetramethylethylene in Benzene

1-cyanonaphthalene (3.0 g) and tetramethylethylene (8 g) in 420 ml benzene were irradiated in the same way as in methanol, for 50 hrs. The completion of reaction was determined from the NMR spectrum. The reaction mixture was cleaned by passing it through a silica gel (Grace, 923) column (7 x 2 cm) in benzene (about 1 liter), and evaporated. The residue was introduced into a second silica gel (MN-Silica Gel G) column (35 x 3 cm) and eluted with 15:15:70 ether, benzene, light petroleum. Discarded the first 300 ml fraction and then collected each fraction by 25 ml. The results of the separation are shown below. The residue from fractions 11 to 70 was distilled at 0.1 mm with an oil bath temperature of 110°. The distillate (0.621 g) was identifies as 1-cyanonaphthalene. Hence, the total amount of recovered 1-cyanoanphthalene was 1.495 g (50% recovery). The undistilled residue was filtered through a silica gel (Grace, 923) column (10 x 3 cm) and t.l.c. was used to check for complete recovery.

Fraction	Wt. in g	Contents
1 - 5	0.574	1-cyanonaphthalene
6 - 10	0.331	mainly 1-cyanonaphthalene with 5-10% product
11 - 70	1.449	mixture of 1-cyanonaphthalene and product 51

The filtrate was evaporated and analyzed by g.l.c. (Varian - Aerograph model 200 dual column, 300 x 0.6 cm, with column temperature at 210°, retention time of 7.5 min). A sample of product 51 was isolated by g.l.c. under the same conditions as above. This sample crystallized on colling in ice. This was used to seed the remaining material, which had m.p. 60 - 61.5° from methanol (0.420 g, 20% yield).

Anal. Calcd. for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.22; H, 8.29; N, 5.90.

Fluorescence Quenching of 1- and 2-Cyanonaphthalene by Tetramethylethylene

This was prepared in methanol solution and the 2-cyanonaphthalene was irradiated at 313 nm and fluorescence emission recorded at 358 nm. The concentration of 2-cyanonaphthalene was 4.35×10^{-3} mol l^{-1} and the concentrations of tetramethylethylene were 0, 2×10^{-2}, 4×10^{-2}, 6×10^{-2}, 8×10^{-2} mol l^{-1} respectively. The quenching results are shown in Table 15. The addition of formic acid (concentration, 4.56×10^{-2} mol l^{-1}) to the solution did not affect the quenching rate. The same concentrations of 2-cyanonaphthalene and tetramethylethylene in acetonitrile also showed very effective quenching (Table 15).

[illegible] in a range of [illegible] concentration [illegible] and [illegible] tetra[illegible] [illegible] at [illegible] (2.2) [illegible] concentration, the fluorescence was not quenched. [illegible] the [illegible] was also not affected by addition of formic acid [illegible] 0.17 mol l^{-1}) in the solution.

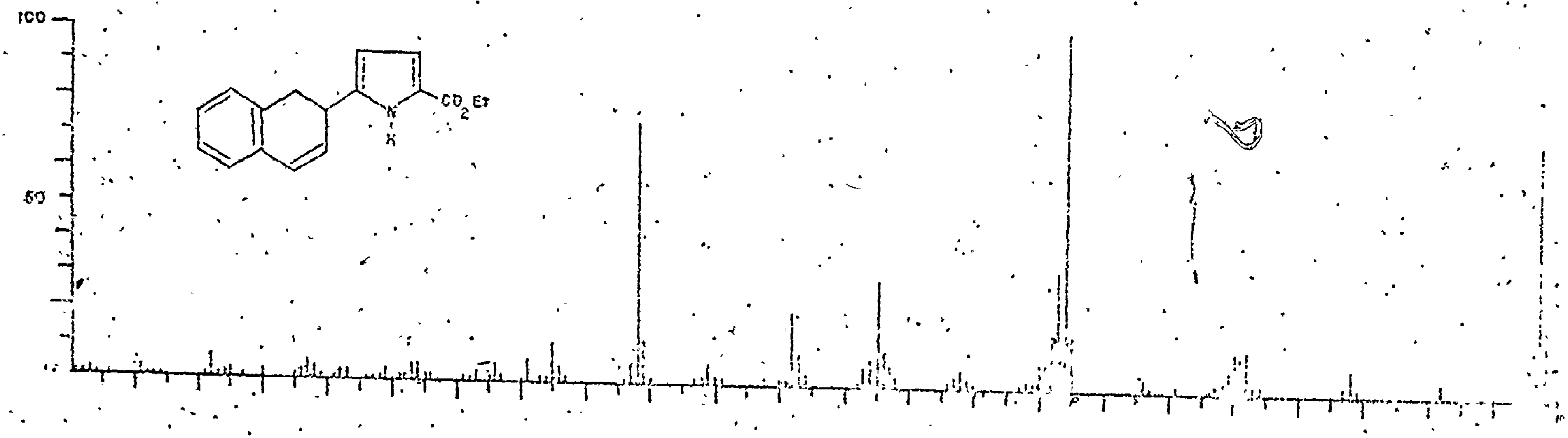
The fluorescence of [illegible] was quenched efficiently [illegible] in [illegible] ethanol, [illegible], and [illegible] 4.4 x 10^{-3} [illegible] these solution showed the fluorescence was almost [illegible] quenched by 0.1 mol l^{-1} tetrachloroethylene in these three [illegible], consistent with the results of Taylor$^{(47)}$.

APPENDIX

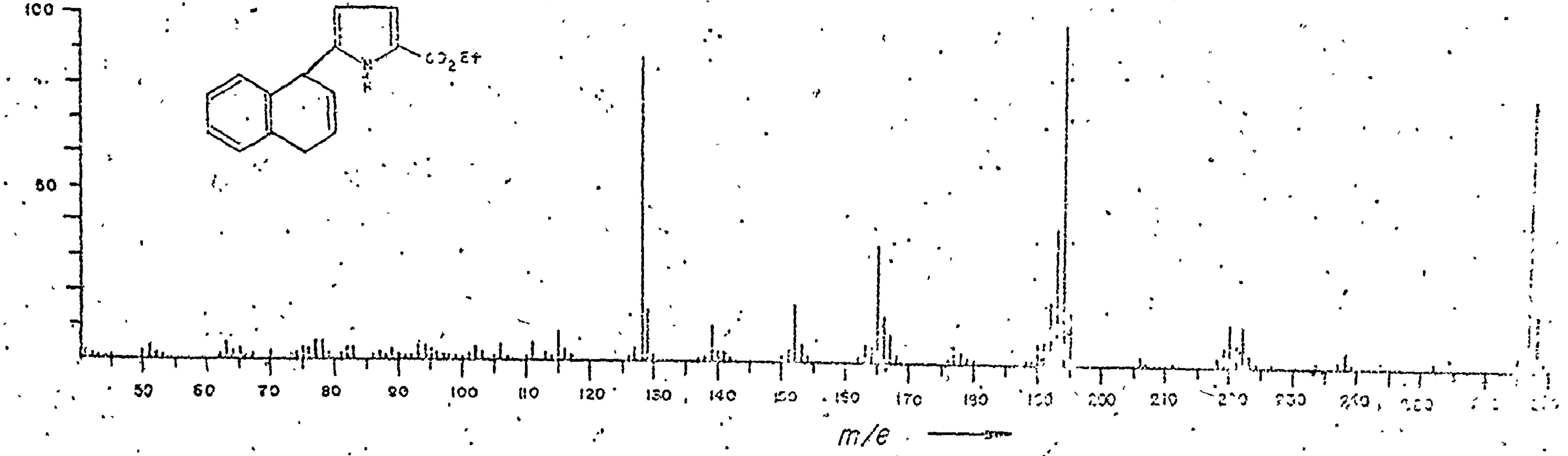
SECTION A. MASS SPECTRA

SECTION B. NMR SPECTRA

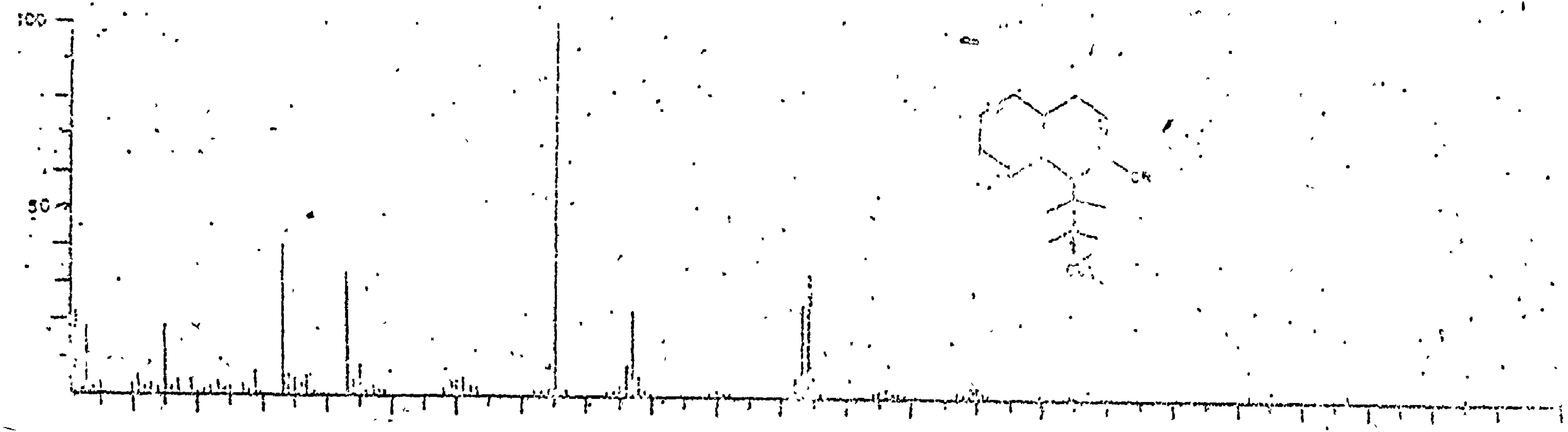
SECTION A. MASS SPECTRA



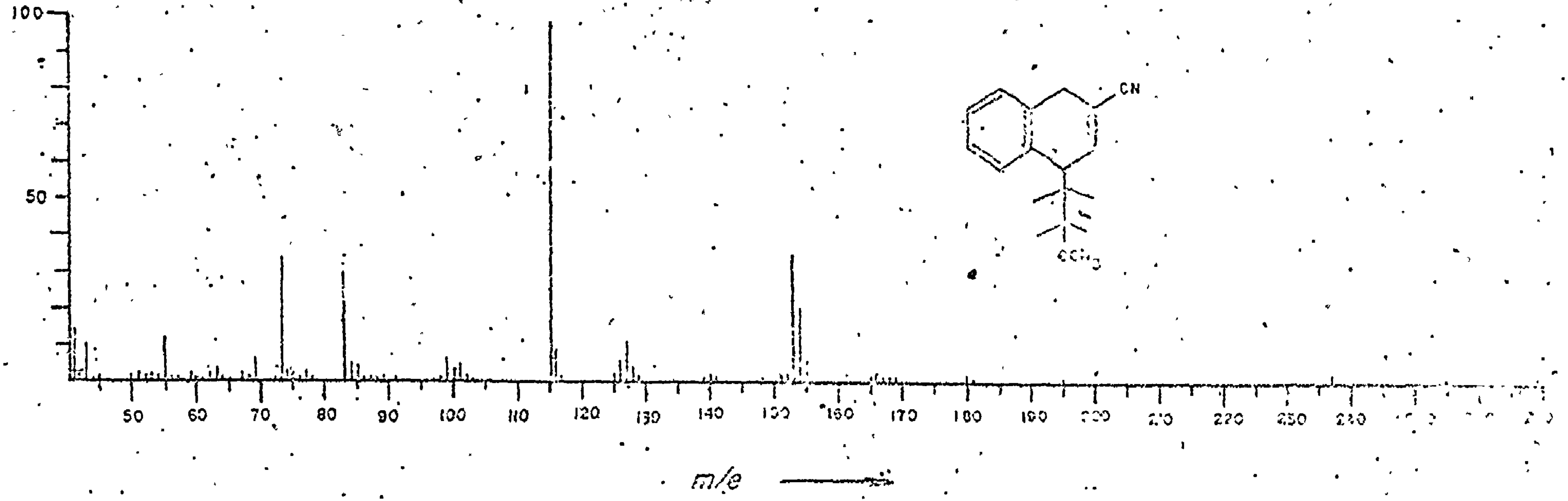
Mass Spectrumof Compound 41



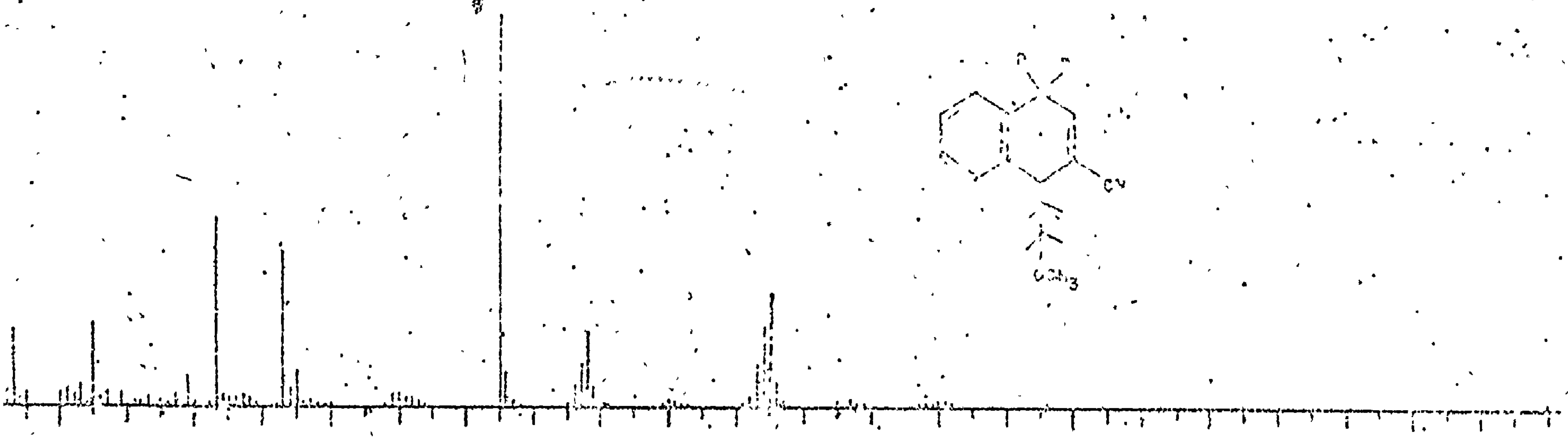
Mass Spectrumof Compound 40



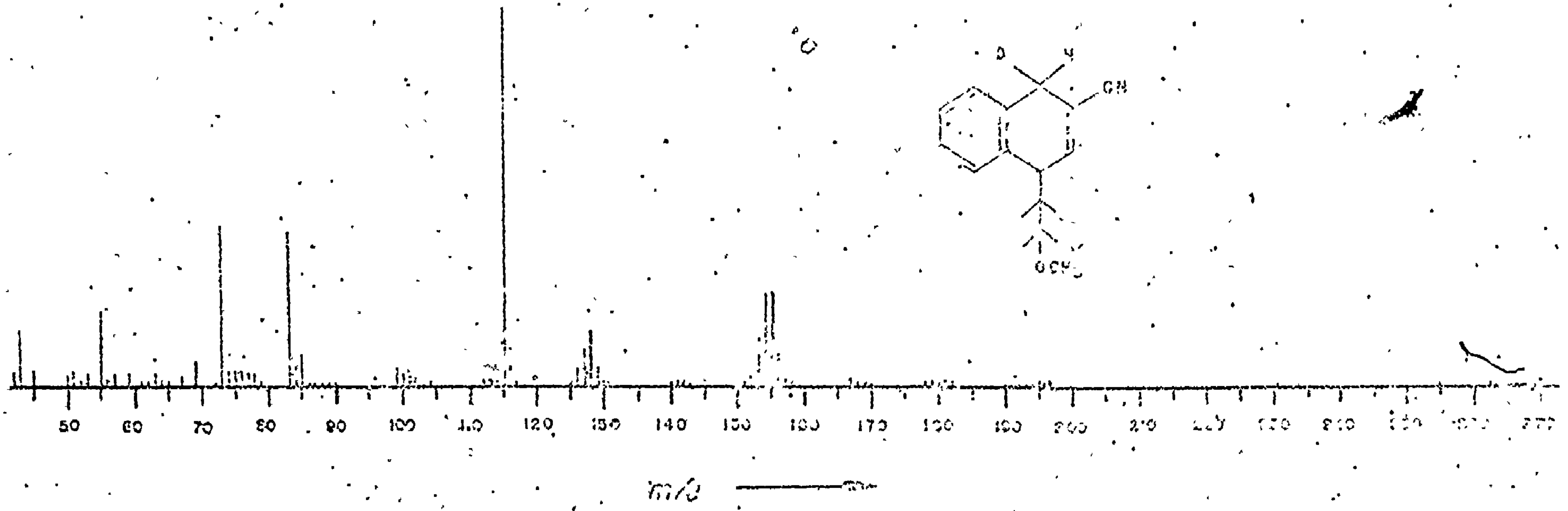
Mass Spectrum of Compound 43



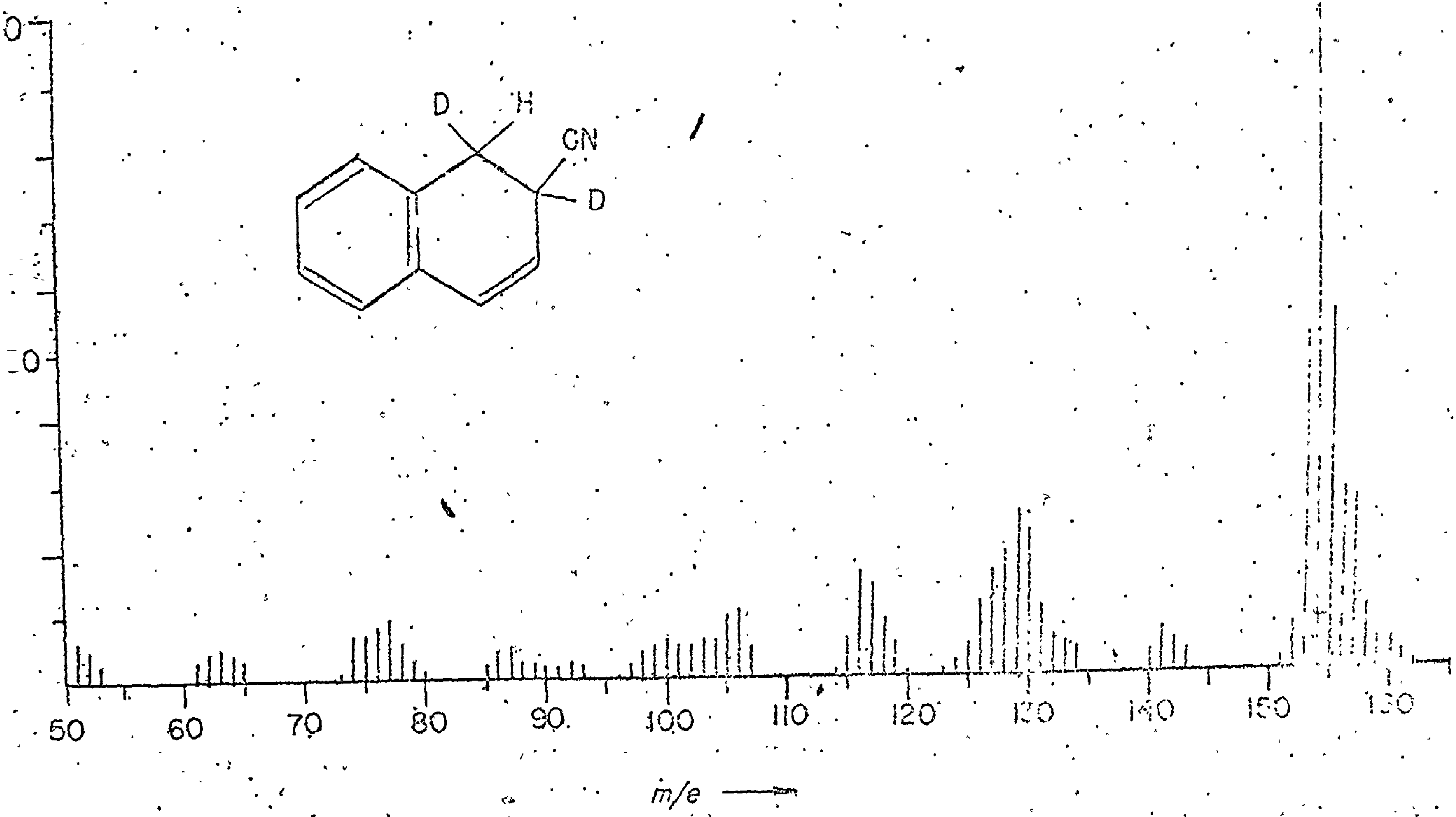
Mass Spectrum of Compound 42



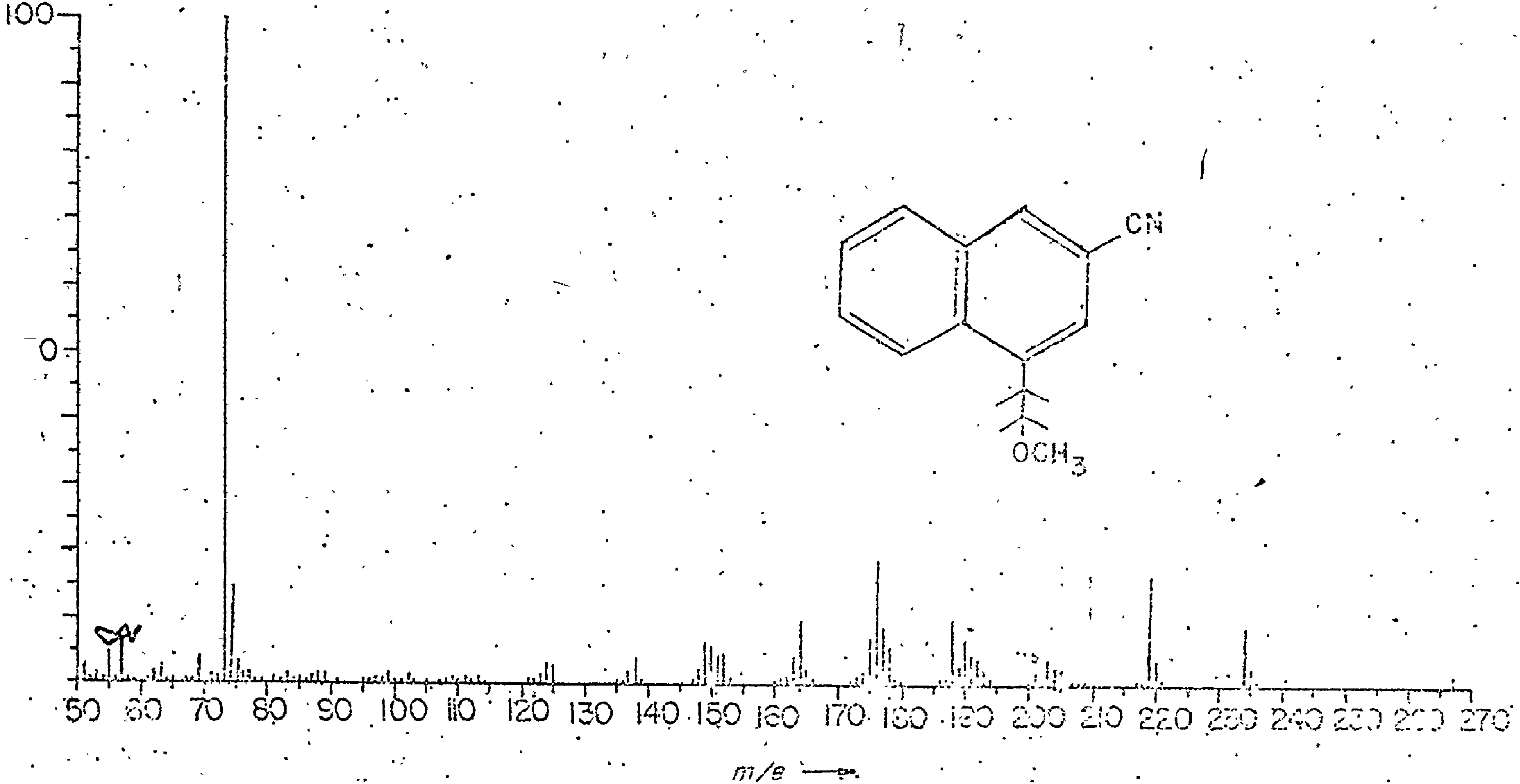
Mass Spectrum of [illegible]



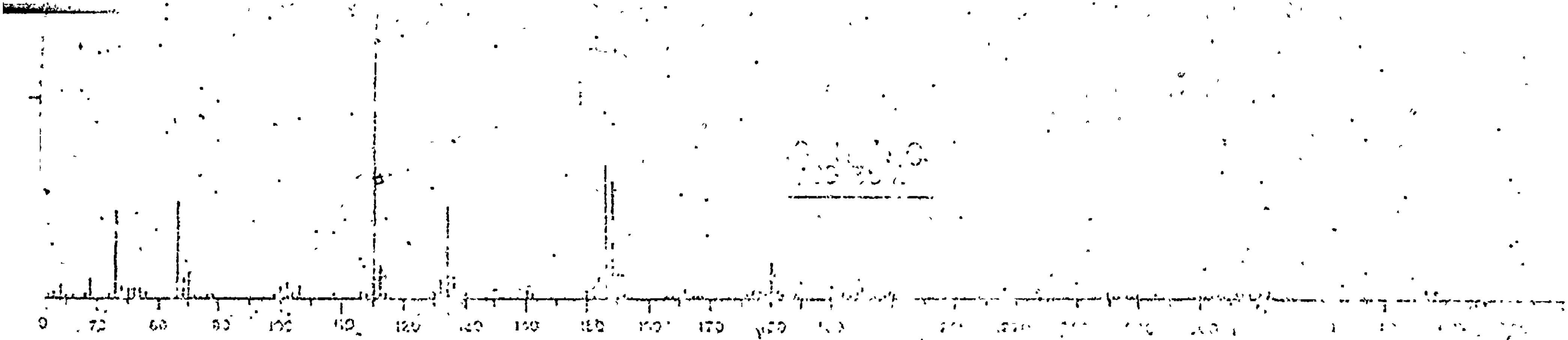
Mass Spectrum [illegible]



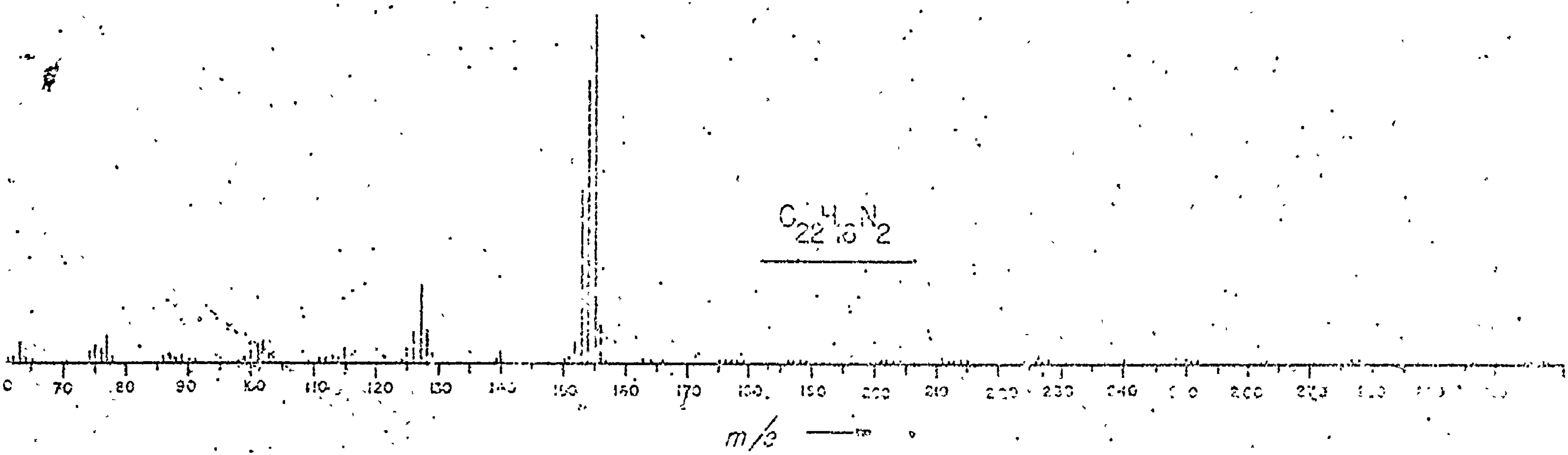
Mass Spectrum of Compound 47



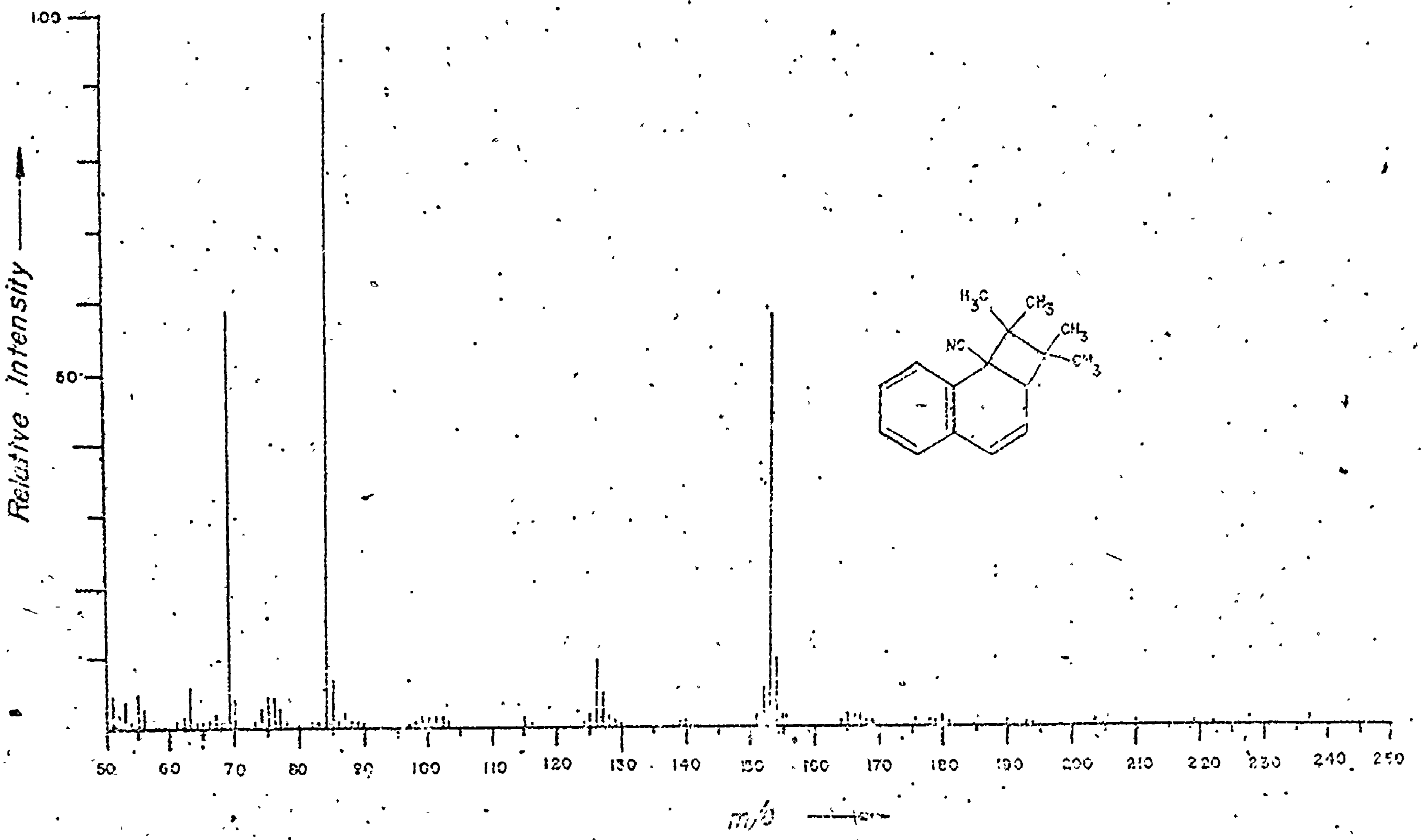
Mass Spectrumof Compound 48



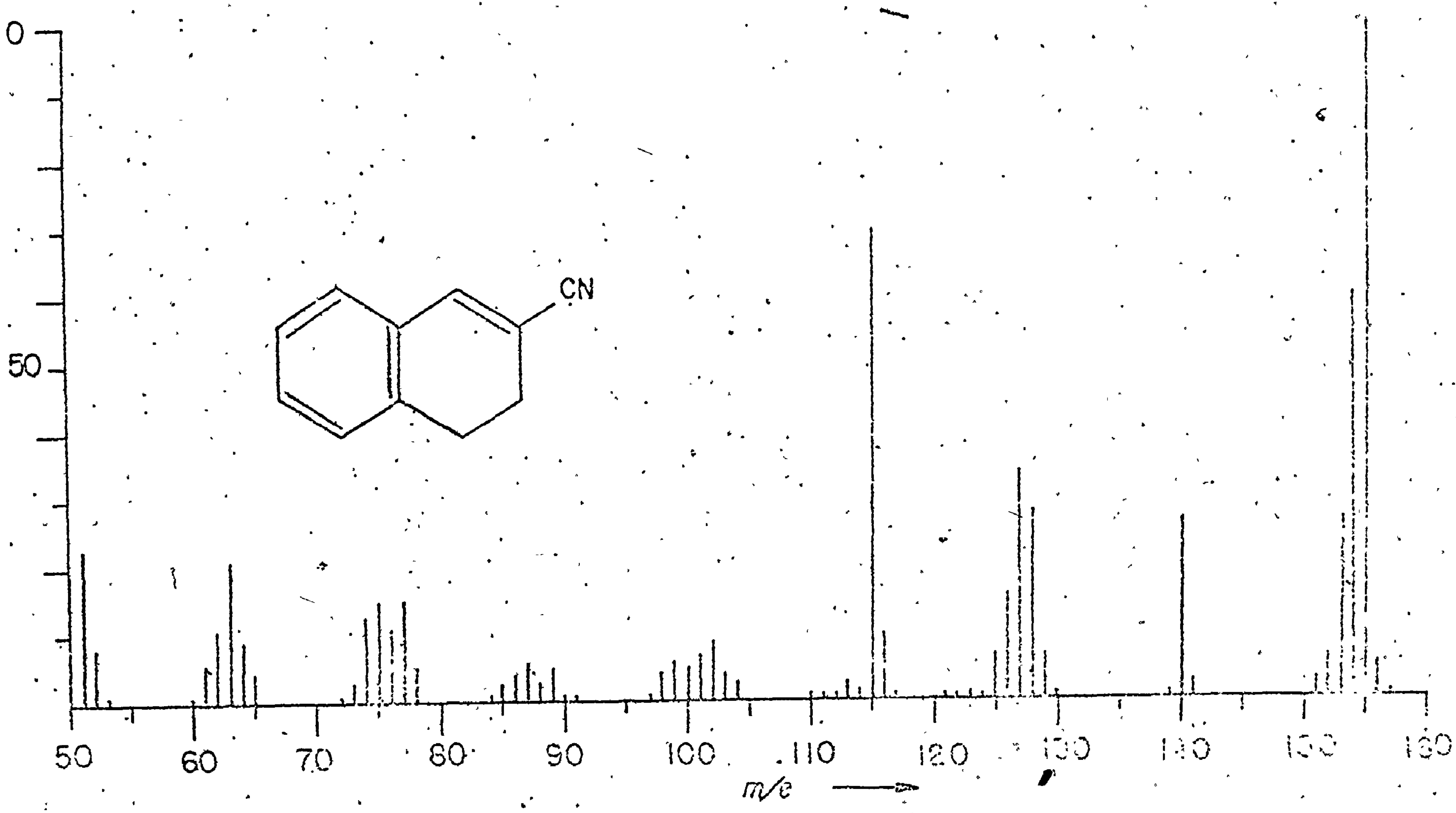
Mass Spectrum of Compound [illegible]



Mass Spectrum of Compound [illegible]



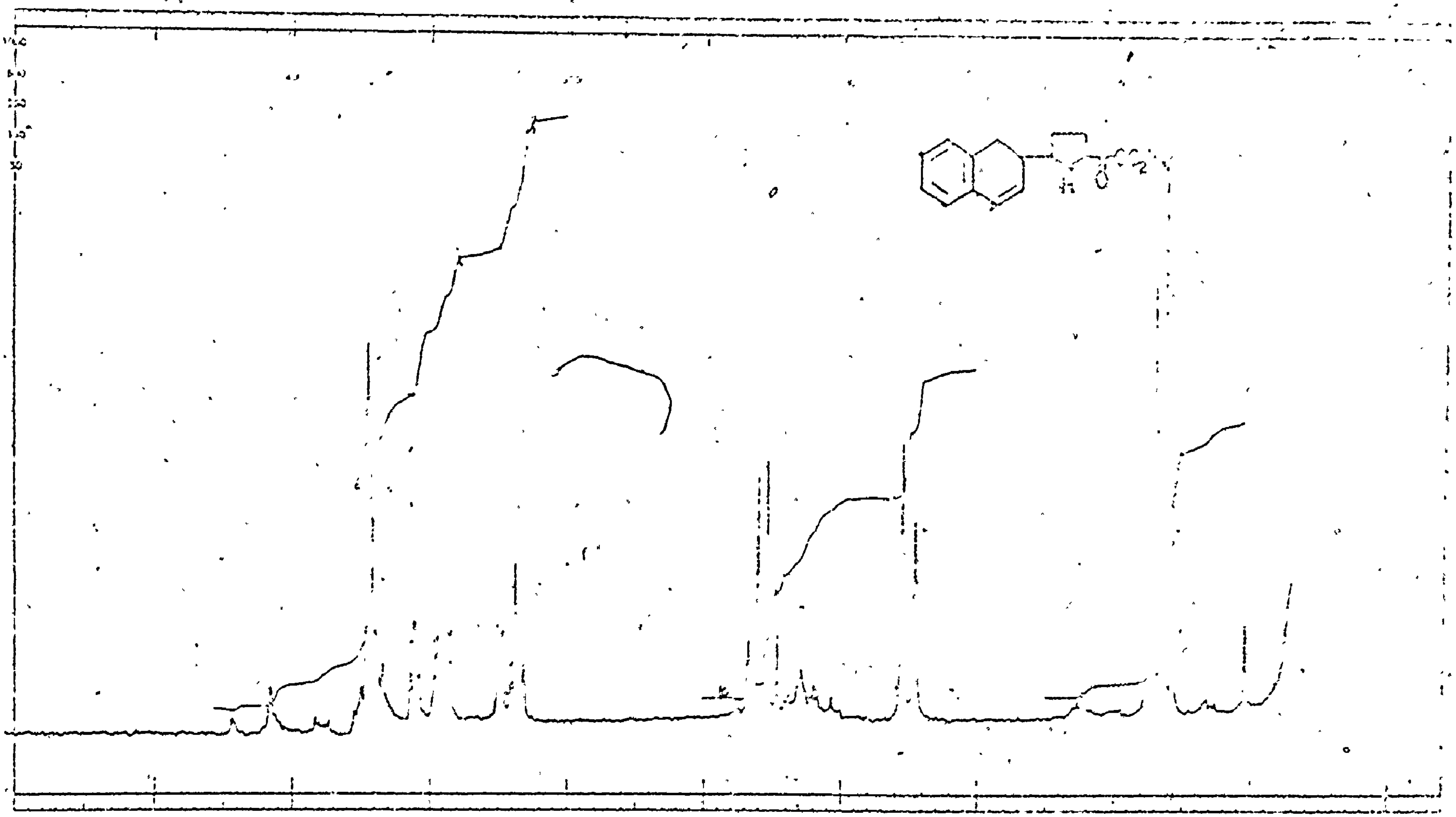
Mass Spectrum of Compound 51



Mass Spectrum of 'Compound' 52

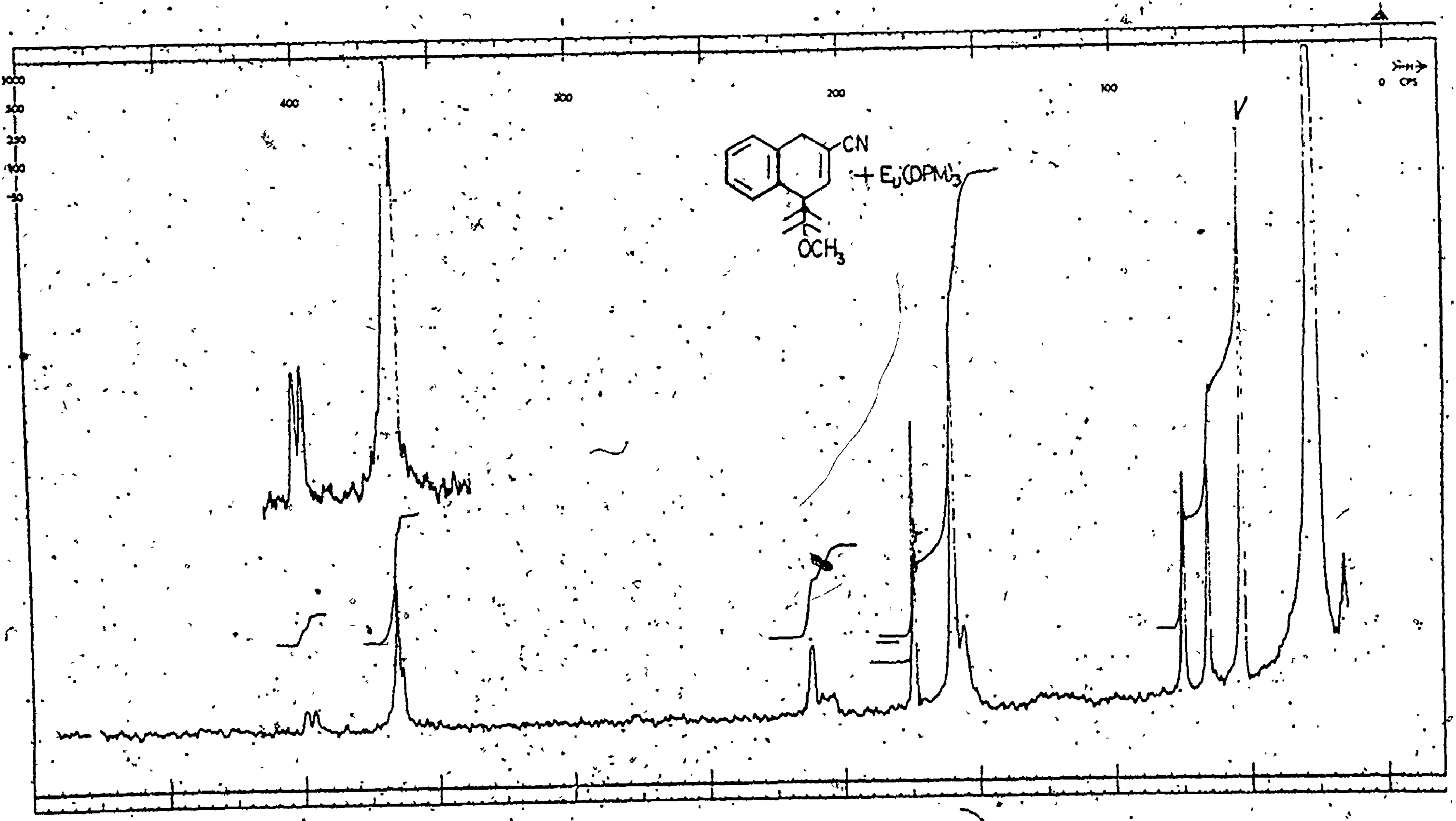
SECTION B. NMR SPECTRA

NMR Spectrum of Compound 40

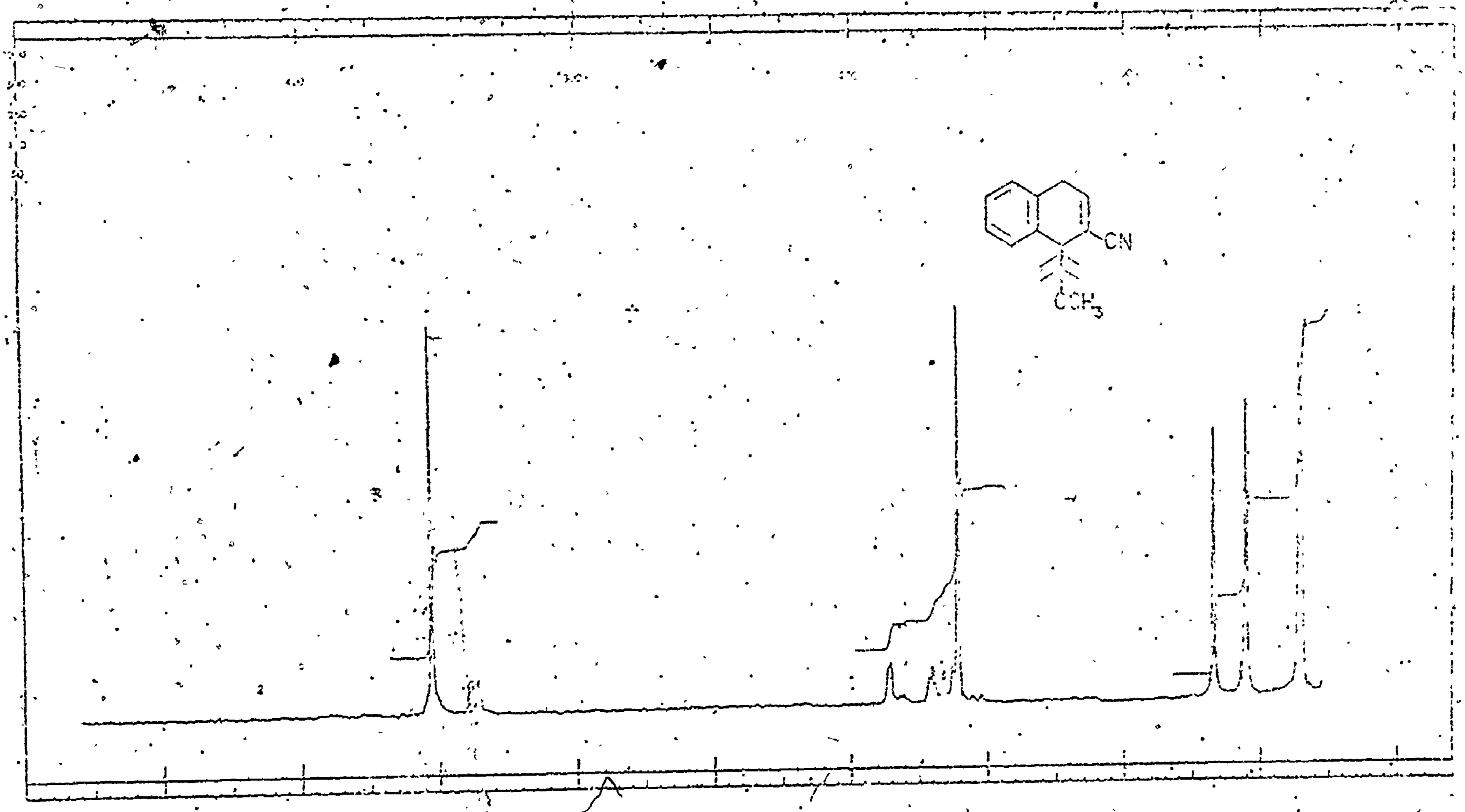


NMR Spectrum of Compound 41

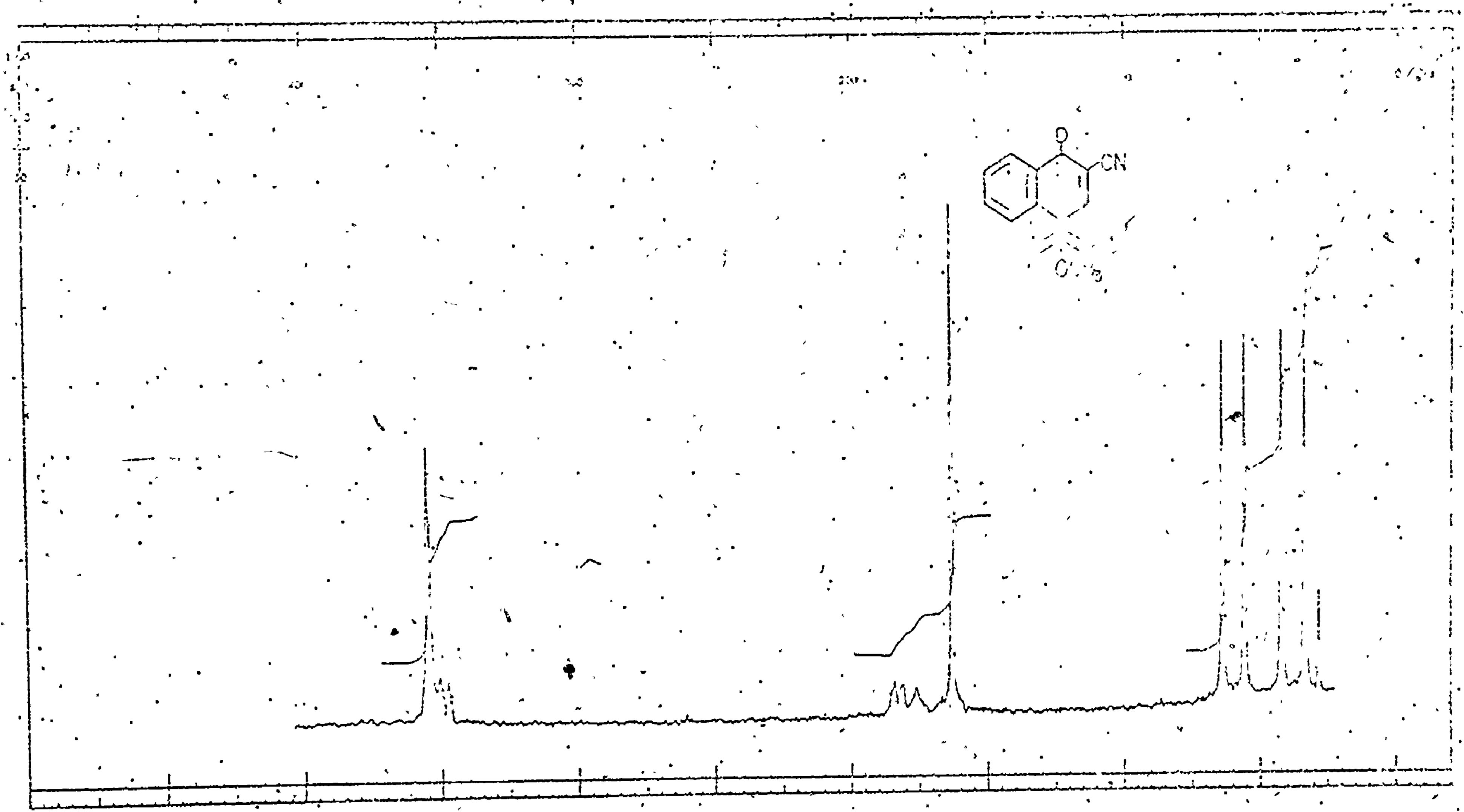
NMR Spectrum of Compound 42



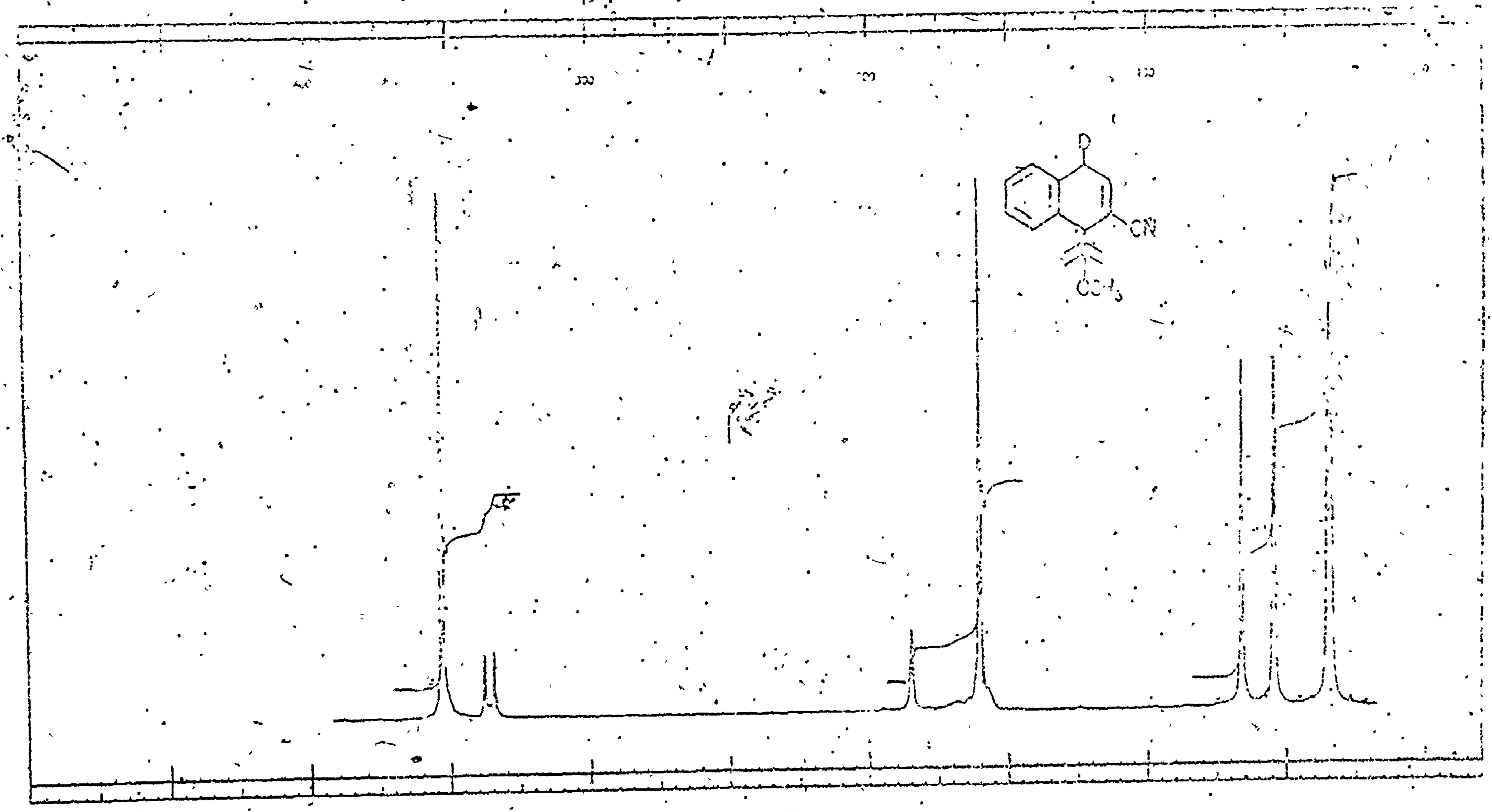
NMR Spectrum of Compound 42 with Europium Dipivaloylmethane



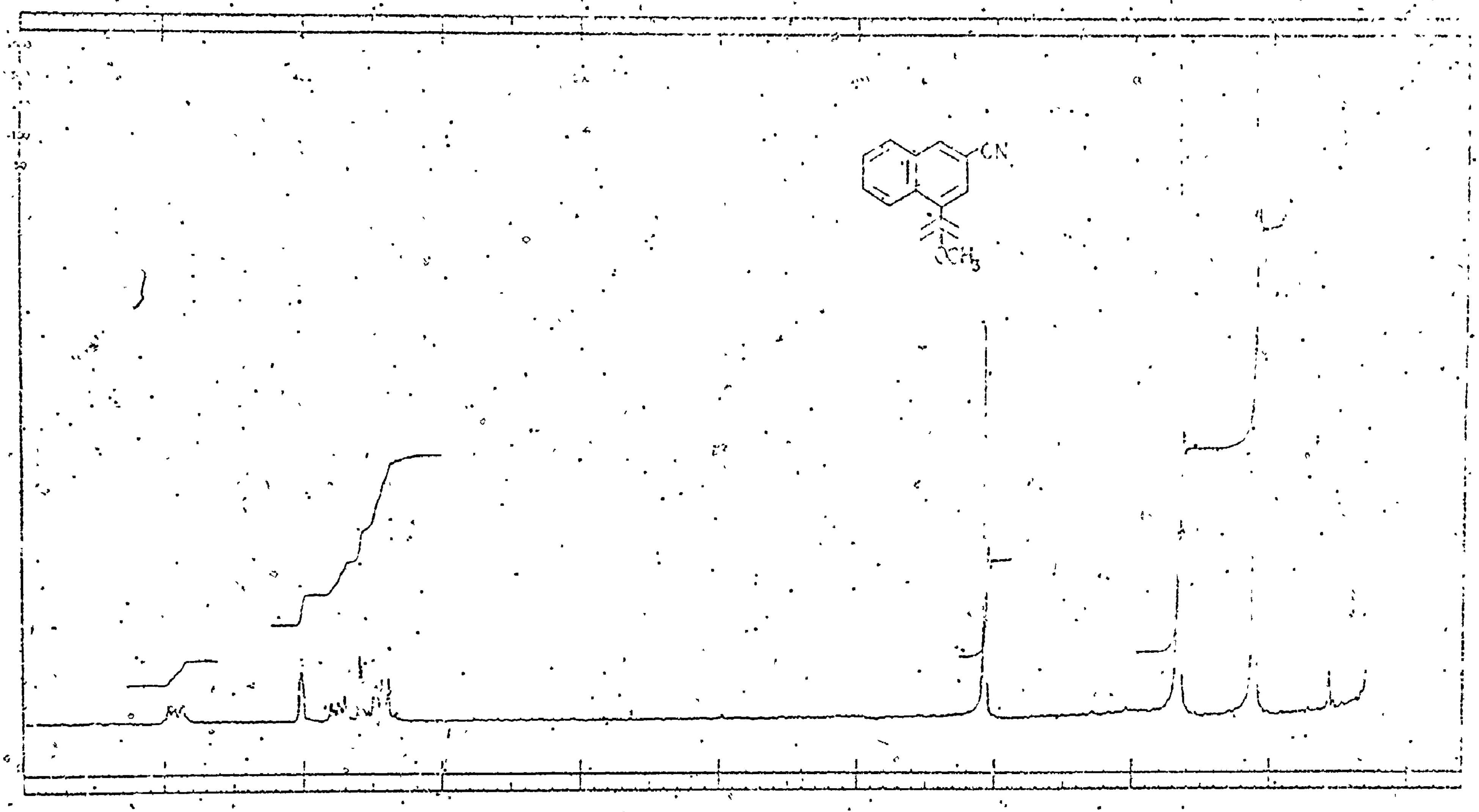
NMR Spectrum of Compound 43



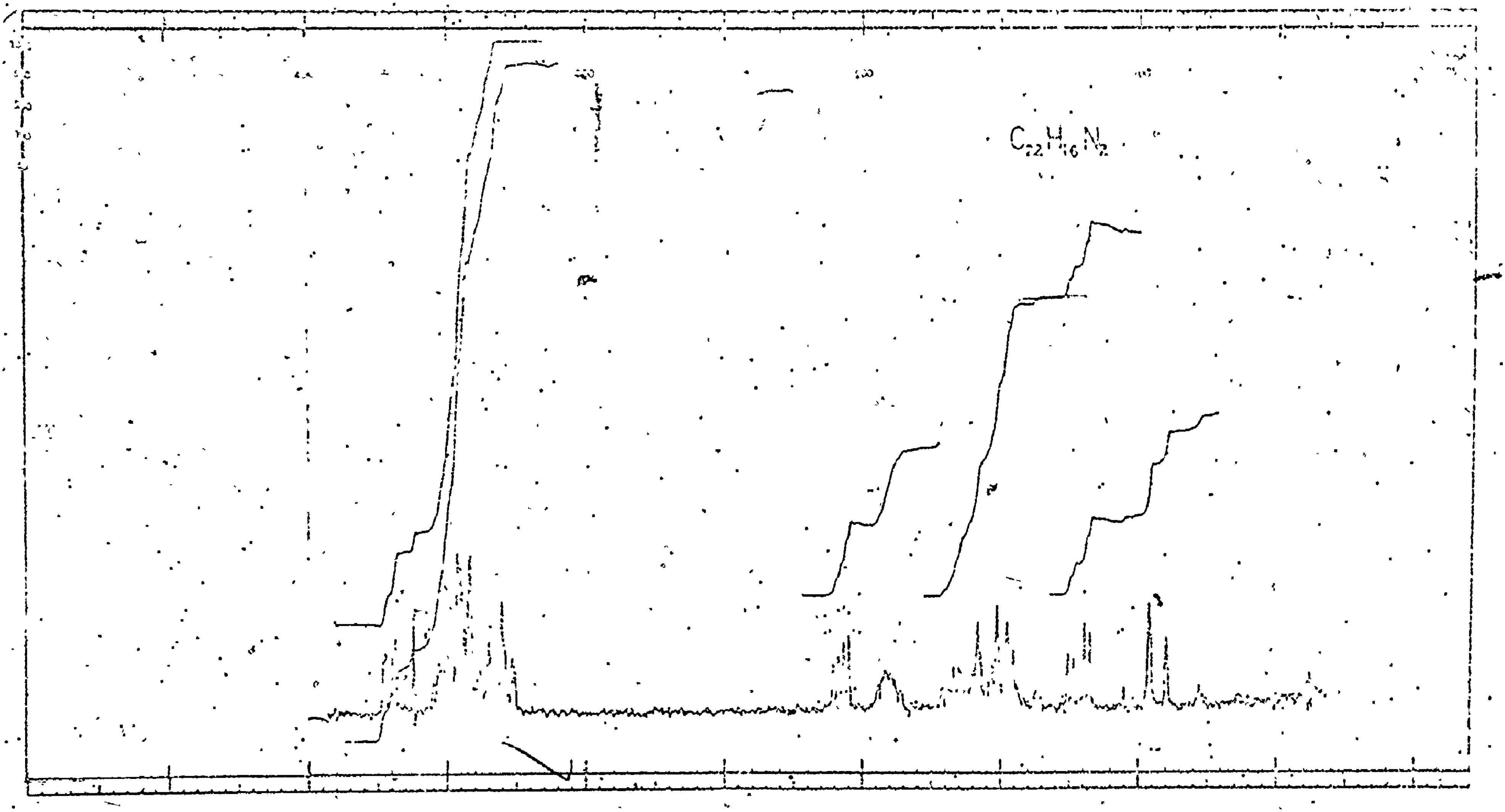
NMR Spectrum of Compound 45



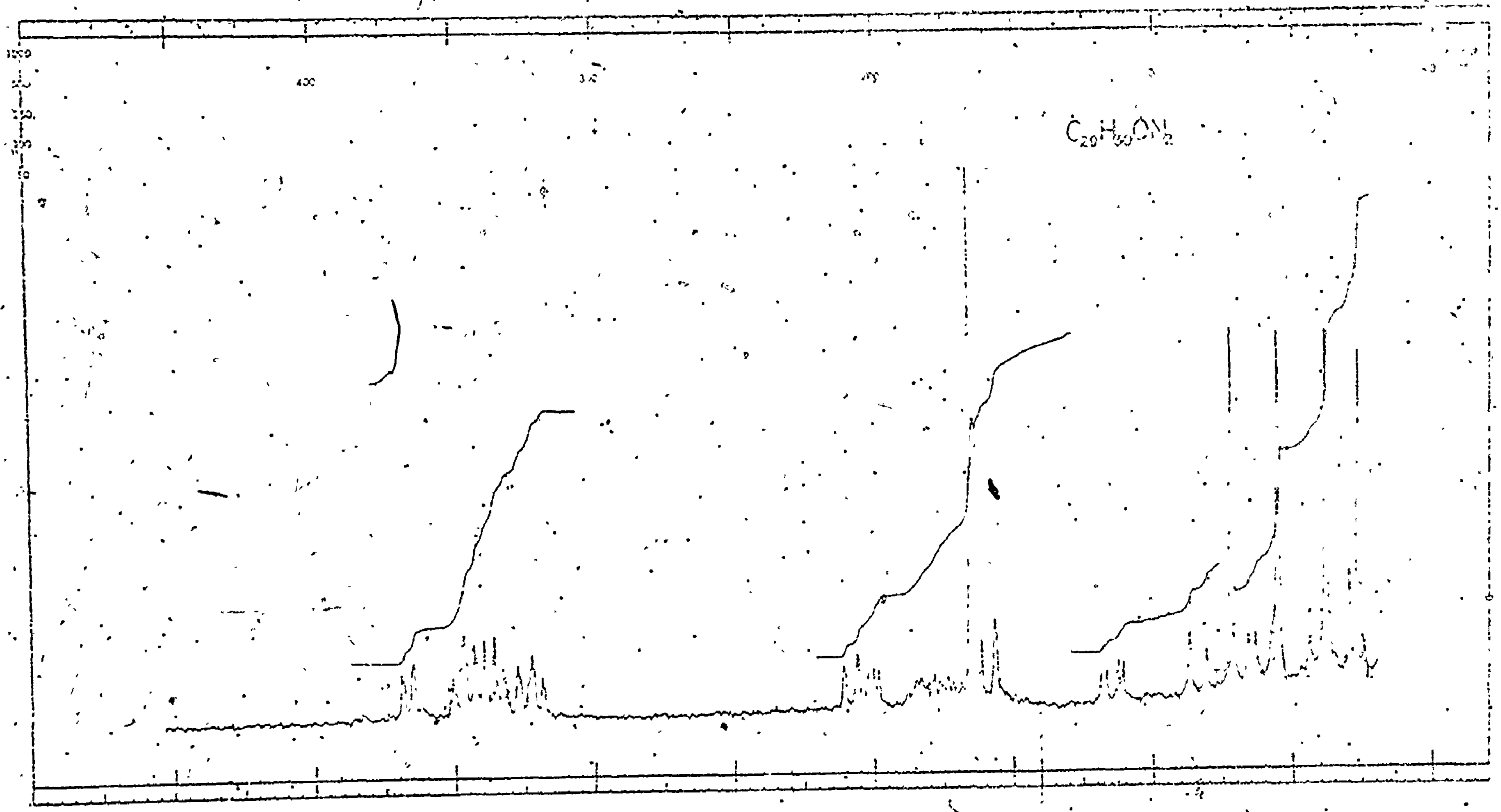
NMR Spectrum of Compound 46



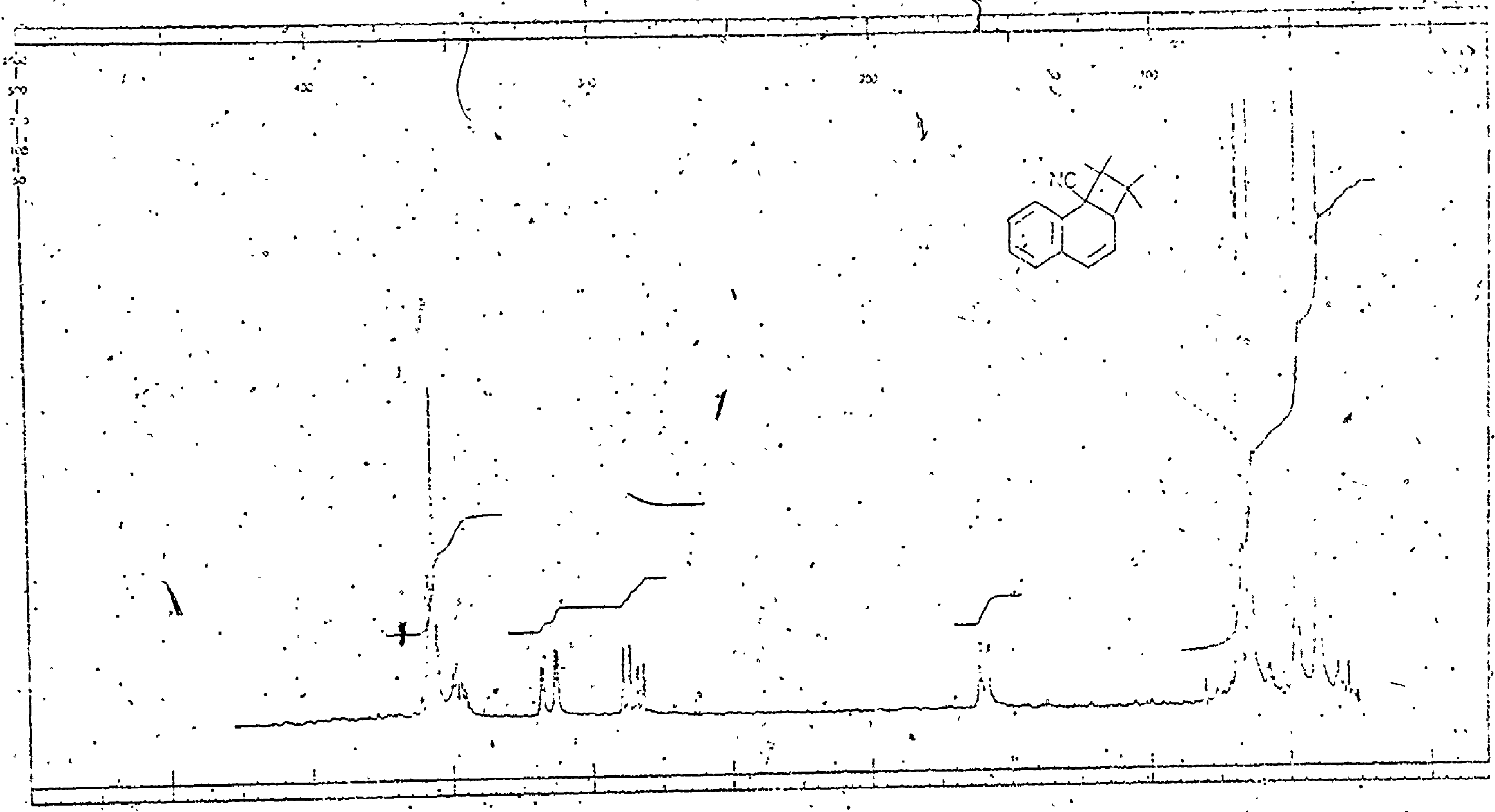
NMR Spectrum of Compound 48



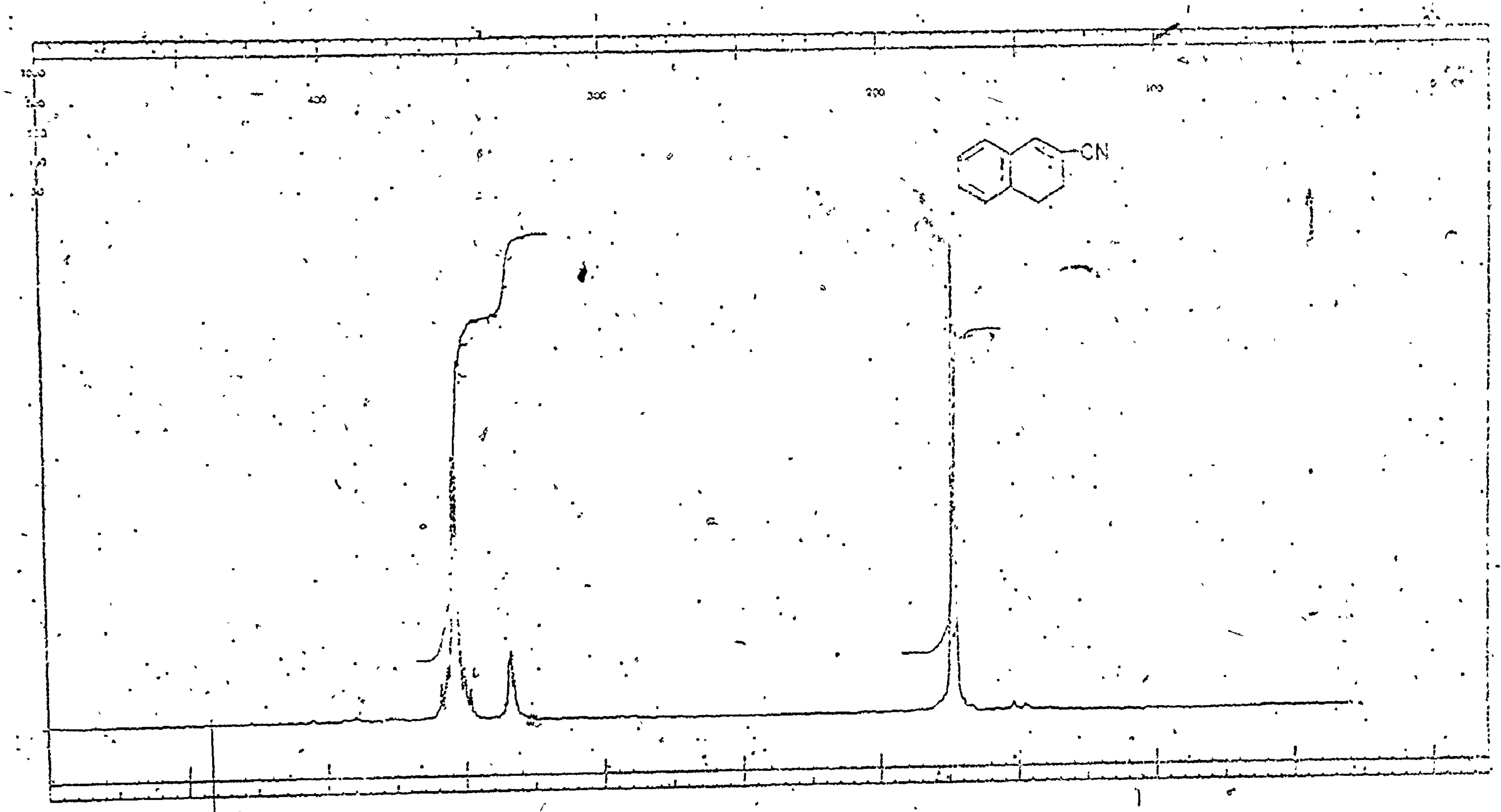
NMR Spectrum of Compound 49



NMR Spectrum of Compound 50



NMR Spectrum of Compound 51



NMR Spectrum of Compound 52

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