Steric Factors in 1-Naphthonitrile-Olefin Exciplex Formation

by

© William Keith MacInnis, B.Sc.

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University
September 1981

Steric Factors in
1-Naphthonitrile-Olefin Exciplex Formation

DOCTOR OF PHILOSOPHY (1981)
(Chemistry)

McMaster University
Hamilton, Ontario

TITLE: Steric Factors in 1-Naphthonitrile-Olefin Exciplex Formation

AUTHOR: William Keith MacInnis, B.Sc. (Acadia University)

SUPERVISOR: Professor J.J. McCullough

NUMBER OF PAGES: xi, 167

Dedicated

to the loving memory of

my mother

Mrs. Margaret Ina MacInnis

ABSTRACT

The fluorescence quenching and photochemistry of 2-methyl-, 4-methyl- and 6-methyl-1-naphthonitrile with tetramethylethylene have been studied in benzene and ethyl acetate. Stern-Volmer constants (benzene solvent) are 10.1, 15.7 and 9.0 M^{-1}, respectively, showing that quenching is insensitive to position of the methyl group. Exciplex emission was observed in each case, and exciplex lifetimes were measured by the technique of time-correlated single photon counting. The methyl-1-naphthonitriles react with tetramethylethylene to give 1-cyano-7,7,8,8-tetramethyl-2,3-benzobicyclo[4.2.0]octa-2,4-diene derivatives, and limiting quantum yields were determined. Quenching with biacetyl showed that the exciplex is an intermediate in the cycloaddition reaction involving 4-methyl-1-naphthonitrile. Also, no triplets were formed from the decay of the exciplex. The decay rate constants for deactivation of the exciplex were measured. The bichromophoric molecules 2,3-dimethyl-2-butenyl-1-cyano-2-methylnaphthyl ether, 2,3-dimethyl-2-butenyl 1-cyano-4-methylnaphthyl ether and 2,3-dimethyl-2-butenyl 1-cyano-6-methylnaphthyl ether, in which the chromophores are linked by a three atom chain, were synthesized. All three show strong quenching of the monomer (naphthonitrile) fluorescence and weak exciplex emission. The three bichromophoric compounds also react on irradiation giving internal cycloaddition products.

The structures of the latter were determined, and the structure work is described. Comparison of quantum yields for intramolecular cycloaddition with limiting quantum yields for the bimolecular cases, indicate that the three-atom chain greatly expedites collapse of the exciplexes to products in these systems. The results are discussed within the context of the model for exciplex formation and decay introduced by Michl.

ACKNOWLEDGEMENTS

The author offers special thanks to his research director, Dr. J.J. McCullough, for his guidance, encouragement and optimism which made this work possible. Thanks to Dave Evans and Professor A.J. Yarwood for their invaluable assistance with the time correlated single photon counting experiments.

Thanks to all the Chemical Shifts past and present for affording the author the thrills of competitive softball. Thanks also to the memorable people who inhabited laboratory 467: S. Yeroushalmi, G. Timmins, R. Miller, C. Manning, K. DeFonseca, S. Vaitekunas and I. Akhtar.

Special thanks to Jan Gallo and Fajar Ramelan for their help in preparing this thesis.

Thanks to my family (Dad, Bob and Joan) for their love and steadfast support through the difficult times.

The author also wishes to thank Professor C.J.L. Lock, R. Faggiani and Dr. M. Zvagulis for their help in the X-ray crystallographic structure determination.

Table of Contents

TABLES AND FIGURES

TABLES AND FIGURES (Continued)

INTRODUCTION

Part 1: FORMATION AND DEACTIVATION OF EXCITED STATES

Organic photochemistry may be defined as the study of physical and chemical processes of carbon containing compounds induced by the absorption of photons.[1] The absorptive act, which involves the interaction of a photon and a molecule, results in absorption of the photon and formation of an electronically excited molecule. The energy of the molecule is increased by an amount equal to that of the absorbed photon, as given by the Einstein relationship where, h, $\bar{\nu}$, c and λ are Planck's constant,

$$E = h\bar{\nu} = hc/\lambda$$

the frequency of the radiation, the velocity of light and the wavelength of the radiation, respectively.

The absorption of electromagnetic radiation (visible or ultraviolet light) promotes an electron from an occupied bonding orbital to an unoccupied antibonding orbital. The process is faster (10^{-15} sec) than nuclear movement and as a result, spin multiplicity is conserved.* Since most organic

---

* Ground state singlet (S_0) to excited state triplet (T_1) transitions are known to occur when spin orbit perturbations are possible. For example, heavy atom rare gases such as xenon have been employed to enhance the S_0-T_1 absorption of aromatic hydrocarbons.

molecules are in a singlet state (all electron spins paired) in their electronic state of lowest energy, an excited singlet, S_N, is formed. The excitation may occur into any one of the upper vibrational or rotational energy sublevels in the S_N state. The S_N state can dissipate the excess energy by collision with neighbouring molecules to give S_1, the first excited singlet state. This rapid process (10^{-12} sec), as well as radiationless transitions between any two states of the same multiplicity ($S_N \rightarrow S_1$, $S_1 \rightarrow S_0$, $T_N \rightarrow T_1$) is termed internal conversion).

The S_1 of a molecule can be deactivated in several ways. Radiationless internal conversion (described above) to the ground state, S_0, is one route. Intersystem crossing to a triplet state, usually the lowest triplet state, T_1, is another deactivation pathway. The deactivation of T_1 can occur by emission of a photon (phosphorescence) or by nonradiative intersystem crossing to S_0. Both processes are "forbidden" because of the necessity for spin inversion. Thus, the molecule can remain in the triplet state for reasonably long time intervals (as long as several seconds). A third possible decay route from S_1 is by a radiative transition to S_0 (fluorescence). Fluorescence conserves spin multiplicity and as a result is a fast process (10^{-9} sec).

Another mode for deactivation of an electronically excited molecule is bimolecular quenching, i.e., an interaction of an excited molecule, D^*, with a ground state molecule, Q. Three distinctive mechanisms for bimolecular quenching can be observed:

1. Direct energy transfer[2]

$$D^* + Q \rightarrow D + Q^*$$

2. Enhancement of intersystem crossing (heavy atom effect).[3,4]

3. Charge[5] or electron transfer[6]

$$D^* + Q \rightarrow D^{\delta+}\text{-}Q^{\delta-}$$

The charge or electron transfer mechanism can lead to the formation of stable excited complexes, known as excimers and exciplexes. The study of excited-state dimers (excimers) and complexes (exciplexes) has been a fertile area of investigation and the results as they pertain to aromatic compounds will be discussed in the next section.

Part II: EXCIMERS AND EXCIPLEXES

(a) Introduction

Excimers and Exciplexes have been defined by Birks in the following manner:

"A molecular dimer or stoichiometric complex which is associated in an excited electronic state and which is dissociative (i.e., would dissociate in the absence of external restraints) in its ground electronic state."[7]

The first reported example of such an excited dimer was that of Kasper and Förster.[8] They reported that the concentration quenching of pyrene fluorescence was accompanied by a new, structureless emission at long wavelength, which they assigned to emission from a pyrene excimer. Subsequently, many examples of excimer formation have been reported, and a useful review of the field has been provided by Förster.[9]

In 1963, Weller and Leonhardt[10] reported the first example of emission from a "heteroexcimer" or exciplex, in the perylene-N,N-dimethylaniline system. This was followed by a lengthy series of papers by Weller,[11] Mataga[12] and their coworkers, investigating exciplexes of the amine-aromatic hydrocarbon type.

The excimers and exciplexes were shown to be formed reversibly but with essentially diffusion controlled rate constants and, as evidenced by temperature-dependence studies,[13] had exothermic heats of association of several (5-10) kilocalories/mole. The red shift of the structureless emission of the exciplex or excimer relative to excited monomers was due both to the enthalpy of association and to ground-state repulsion of the closely held chromophores as depicted in Figure 1.

The stabilization in excimer association is attributed to some combination of both charge transfer interactions and exciton resonance.[9] This can be described as

$$A^+A^- \leftrightarrow A^-A^+ \leftrightarrow A^*A \leftrightarrow AA^*$$

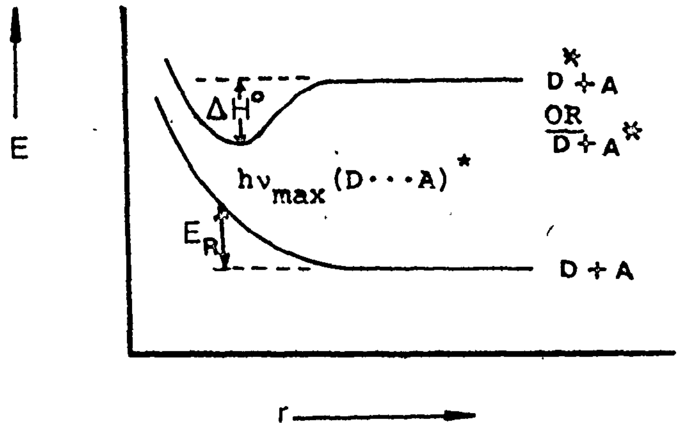


Figure 1. Potential energy vs. intermolecular separation for ground- and excited-state association of D (donor molecule) and A (acceptor molecule). ΔH^o is the exciplex association enthalpy, $h\nu_{max}$ is the energy corresponding to the exciplex emission maximum and E_R is the ground state repulsion energy.

with the corresponding wavefunction

$$\psi_{excimer} = C_1[\psi(A^+A^-) + \psi(A^-A^+)] + C_2[\psi(A^*A) + \psi(AA^*)]$$

Obviously, the stability of exciplexes such as the one from the perylene-N,N-dimethylaniline system does not arise from an excitation resonance interaction. The emitting species was interpreted as an excited charge-transfer complex A^-D^+, which is stabilized by charge transfer from the donor D (N,N-dimethylaniline) to the acceptor A (perylene).[10]

The polar nature of exciplexes was displayed by the red shifts of their emission maxima in solvents of increasing polarity as well as by the proneness of exciplex-forming systems to give radical ions or radical ion-related chemistry instead of emission.[14,15] Exciplex dipole moments can be estimated from the solvent dependence of the exciplex fluorescence emission maximum using equation (1),[16] where

$$\tilde{\nu} = \tilde{\nu}_0 - \frac{2\mu^2}{hca^3}\left[\frac{\varepsilon-1}{2\varepsilon+1} - \frac{N^2-1}{4N^2+2}\right] \qquad (1)$$

$\tilde{\nu}$ is the observed emission frequency (cm^{-1}), $\tilde{\nu}_0$ is the emission frequency in the gas phase, μ is the exciplex dipole moment, a is the interaction distance (assumed to be ∿ 4-5 Å), h is Planck's constant, c is the velocity of light, and ε and N are the solvent dielectric constant and index of refraction. Values obtained for several aromatic hydrocarbon-amine exciplexes using equation (1) vary from 12-15 D. The energy of the exciplex association has been estimated empirically by Weller and coworkers,[17] in terms of excitation energies and redox properties of the donor (D) and acceptor (A) (equation (2)). In this model, a one-electron transfer from excited

$$\Delta H^0 = \Delta E_{00} - [E_{1/2}^{ox}(D) - E_{1/2}^{red}(A) + 0.13\ V] \qquad (2)$$

donor to acceptor (or from donor to excited acceptor) quantitatively accounts for the stabilization of the exciplex.

Polar exciplexes are known to dissociate into non-fluorescent radical ions in polar solvents.[18] The solvent dependence of the pyrene-N,N-dimethylaniline exciplex fluorescence[19] and radical ion formation[18] is shown in Figure 2. As can be seen from Figure 2, exciplex fluorescence may not be observed when efficient non-radiative decay pathways are operative. It has been pointed out by Lewis[15] that since fluorescence rate constants for aromatic hydrocarbon exciplexes are generally 10^6-10^7 s^{-1},[13] an exciplex lifetime of 1 ns or longer may be required for the observation of exciplex fluorescence.

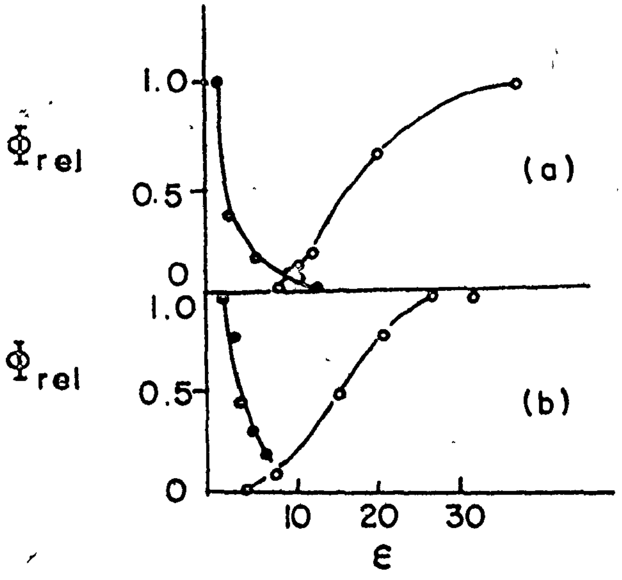


Figure 2. (a) Relative yields of radical ions (O) and fluorescence (•) from the pyrene-N,N-dimethylaniline exciplex and (b) relative yields of addition (O) and fluorescence (•) from the stilbene-triethylamine exciplex versus solvent dielectric constant.

(b) Amine-Aromatic Hydrocarbon Exciplexes

Various groups have been interested in the product of aromatic hydrocarbon-amine photoreactions.[20-23] The gross mechanistic features for a variety of these systems are similar and a discussion of the study of Lewis and coworkers[15] on the chemical reactions of singlet trans-stilbene (TS) with simple alkylamines provides an illustration of several important aspects of exciplex chemistry.

In nonpolar solvents stilbene does not form products with simple tertiary amines. In polar solvents, addition of the amine αC-H bond occurs, accompanied by the formation of diphenylethane and tetraphenylbutane (equation (3)). For a constant amine concentration, it was found that quantum yields increased with increasing size of the alkyl group (Me < Et < i-Pr).

$$TS^{*} + Et_3N \rightarrow PhCH_2CHPhCH(CH_3)NEt_2 + PhCH_2CH_2Ph + (PhCH_2CHPh-)_2 \tag{3}$$

With secondary amines, addition of the N-bond to trans-stilbene was found to occur. As well, 1,2-diphenylethane and 1,2,3,4-tetraphenylbutane were formed (equation (4)). These

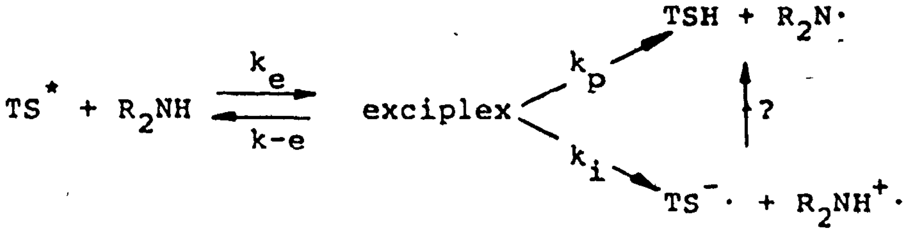
$$TS^{*} + R_2NH \rightarrow R_2N\cdot + Ph\dot{C}HCH_2Ph \rightarrow PhCH_2CHPhNR_2 + PhCH_2CH_2Ph + (PhCH_2CHPh-)_2 \tag{4}$$

products suggested the existence of intermediates arising from N-H abstraction by singlet stilbene. In contrast to the tertiary amine-stilbene systems, product quantum yields for secondary amines decrease with increasing size of the alkyl group and with increasing solvent polarity. The chemical behaviour of primary amines to singlet stilbene was reported to be similar to that of secondary amines although they are much less reactive.

Exciplex fluorescence was observed from singlet stilbene with triethylamine in nonpolar aprotic solvents such as hexane. As was the case with the previously studied perylene-N,N-dimethylaniline system,[19] the exciplex emission maximum was red shifted as the polarity of the solvent was increased. The emission intensity of the exciplex decreased as the polarity of the solvent was changed from hexane to ethyl acetate. A comparison of the exciplex fluorescence frequency and lifetime in hexane for the stilbene-triethylamine and diisopropylethyl amine exciplexes indicated, as expected, that the latter exciplex, which contained the better electron donor, formed a more polar, longer-lived exciplex. In Figure (2b), relative exciplex fluorescence yields and amine addition yields were plotted as a function of solvent dielectric constant. Since Figure (2b) is strikingly similar to that of Figure (2a), Lewis and Hoyle[24] inferred that electron transfer to form a pair of radical ions (k_i) occurred prior to free radical formation (equation (5)).

$$TS^{*} + R_3N \underset{k\text{-}e}{\overset{k_e}{\rightleftharpoons}} \text{exciplex} \xrightarrow{k_i} TS^{-}\cdot + R_3N^{+}\cdot \rightarrow \text{radicals} \qquad (5)$$

Although exciplex fluorescence was not observed for stilbene-secondary amine solutions, negative temperature dependence of the fluorescence quenching rate constant provided evidence for reversible exciplex formation.[24] Mataga and coworkers[15] had shown very rapid hydrogen transfer (equation (6), $k_p > 10^{10}\ s^{-1}$) in the aromatic hydrocarbon-secondary amine exciplexes precludes the observation of exciplex fluorescence. The decrease in yield of addition products with increasing



(6)

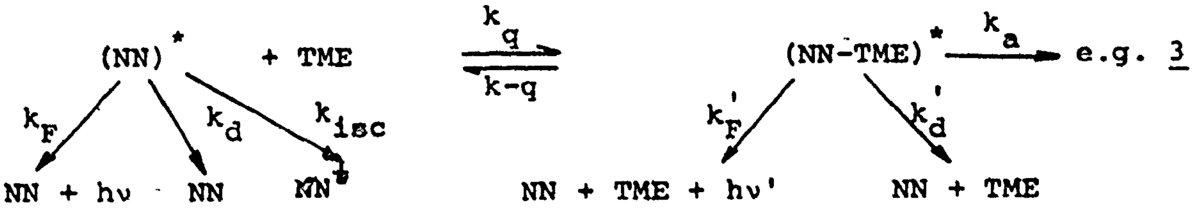
solvent polarity may result from radical ion formation which is known to compete with hydrogen transfer in polar solvents.[18]

The reactivity of secondary amines was found to decrease with a decrease in ionization potentials. This is consistent with the mechanism shown in equation (6) since electron-releasing alkyl groups should stabilize the electron deficient amine nitrogen in the exciplex resulting in a decrease in its acidity and the rate of hydrogen transfer (k_p). The low reactivity of stilbene with primary alkylamines was concluded to be a consequence of their high ionization potentials which hinder charge-transfer stabilization of the exciplex.

(c) Exciplexes from Aromatic Hydrocarbons and Substituted Ethylenes

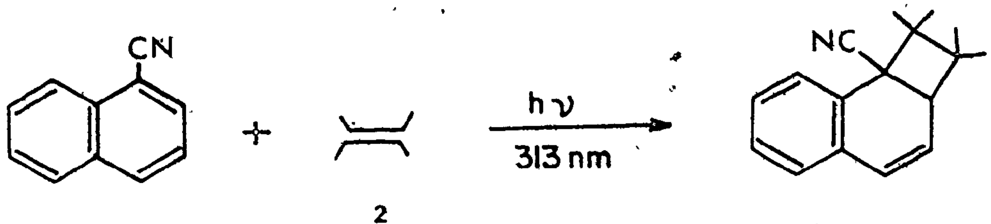
The first report of exciplex emission from aromatic hydrocarbon-olefin and diene systems was by Taylor in 1971.[25] Quenching of 1-naphthonitrile fluorescence was accompanied by the appearance of a structureless red-shifted emission, similar to that previously observed in excimer formation[9] and in amine exciplexes.[10] The physical observation of the excited 1-naphthonitrile-olefin and diene complexes supported the earlier hypothesis of Srinivasan and others that exciplexes could be key intermediates in the photochemical cycloadditions of olefins and dienes to benzene.[26]

The presence of both naphthonitrile emission and exciplex emission allowed Ware and coworkers to study the photokinetics of this system.[27] They showed that the exciplex was reversibly formed at ambient temperatures and that Scheme 1 was consistent with their results.



Scheme 1

McCullough and coworkers investigated the photoreaction of 1-naphthonitrile (1) and tetramethylethylene (TME) (2).[28] The cyclobutane (3) was the major product formed in benzene (equation (7)).



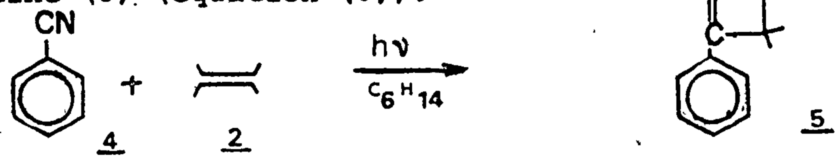
(7)

1 2 3

There is a dramatic dependence of the reactivity of cyano aromatic compounds with olefins, such as tetramethylethylene, upon the nature of the reactants and the solvents. As pointed out by Arnold,[29] seven distinct types of reactivity have now been observed:

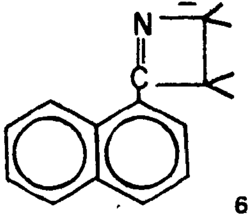
1. cycloaddition of the olefin to the cyano substituted aromatic ring (equation (7));[28]

2. cycloaddition of the olefin to the cyano group to give an azetine (5) (equation (8)).[30]



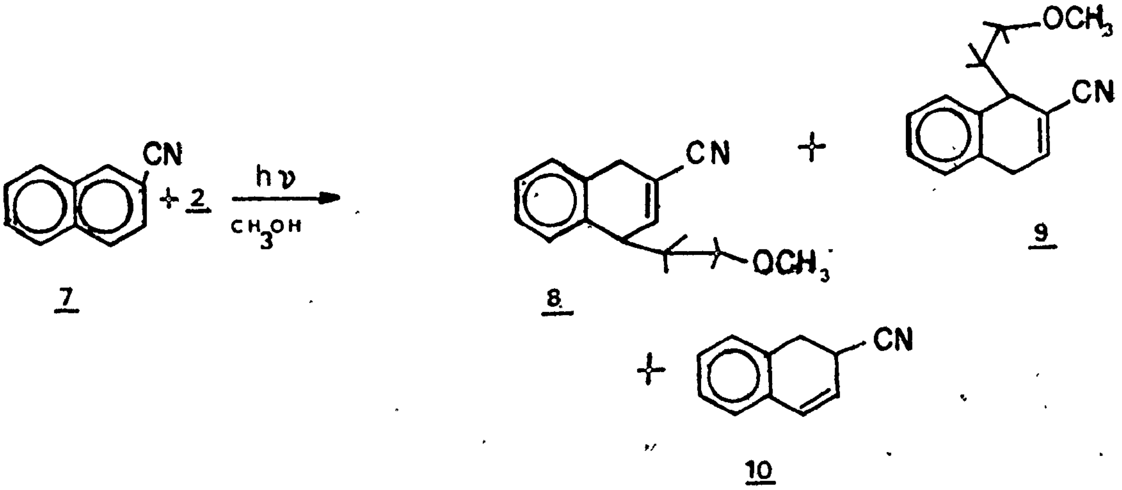
(8)

An azetine (6) has also been reported from the prolonged irradiation of 1-naphthonitrile (1) with TME in hexane;[31]



6

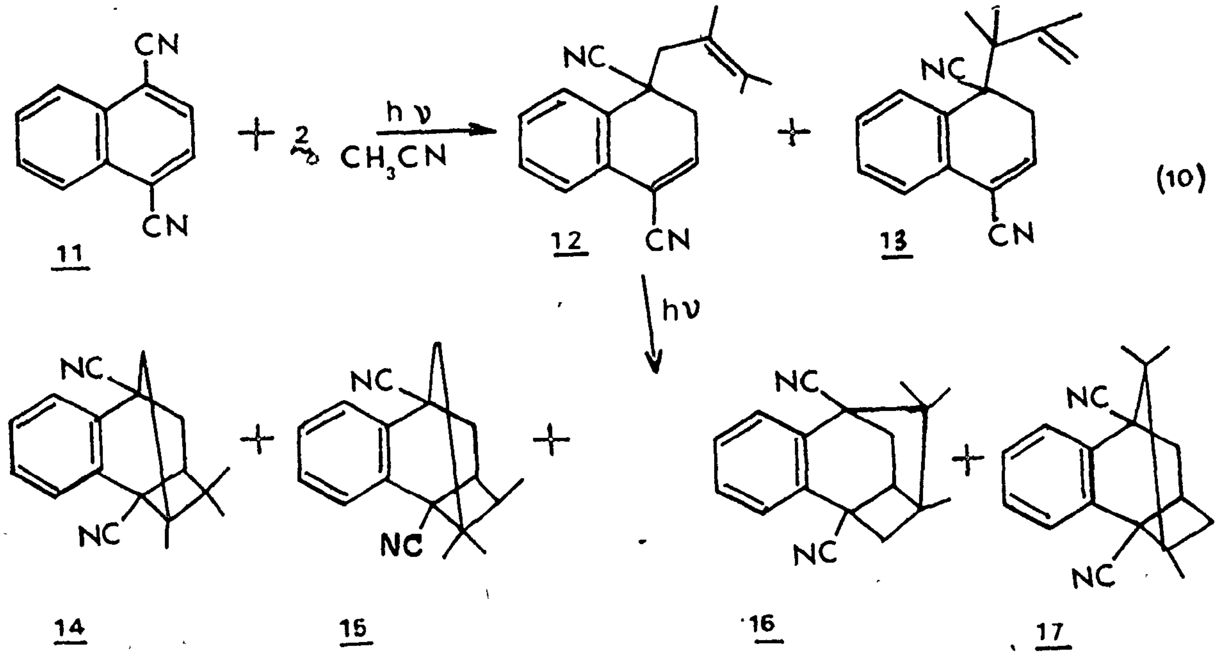
3. formation of 1:1:1 adducts incorporating alcohol solvents (compounds 8 and 9, equation (9));[32]



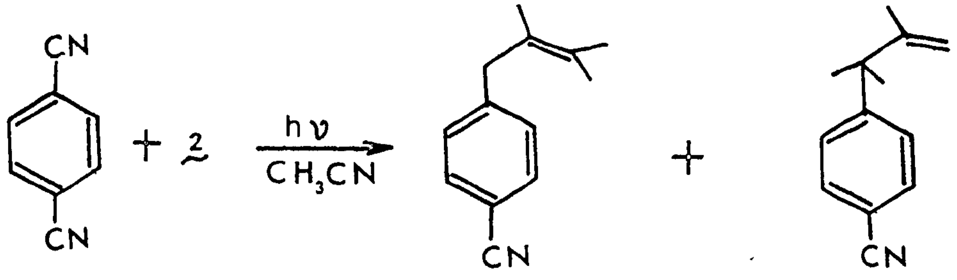
(9)

4. the ring of the cyano aromatic is sometimes reduced upon irradiation in the presence of olefins (e.g., formation of 10 in equation (9));[32]

5. substitution of the olefin, at the ambient sites of the allylic radical, to the aromatic ring.[29] It was believed that intermediates (12) and (13), which were not identified, underwent an efficient intramolecular cycloaddition to give the products (14), (15), (16) and (17) (equation (10));



6. substitution of the aromatic ring by the olefin at the ambient sites of the allylic radical with loss of the cyano group (equation (11));[33a]

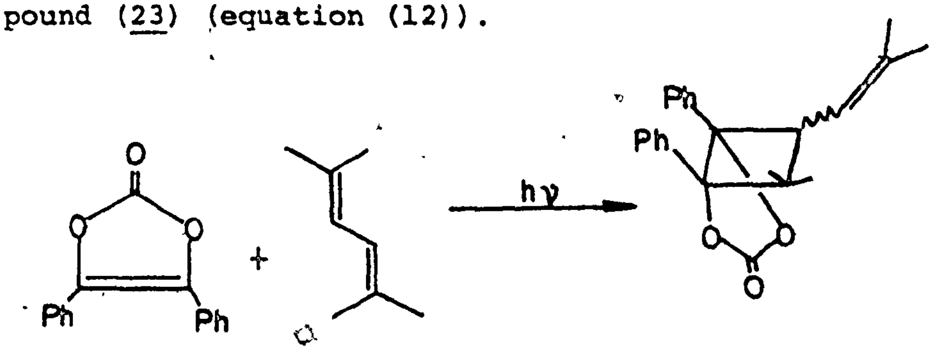


(11)

18 19 20

7. the use of 1,4-dicyanobenzene (18) and 1,4-dicyanonaphthalene (11) as photosensitizers (electron acceptors for the formation of radical cations).[33]

As can be seen, the solvent used for the irradiation can have a profound effect on the photochemistry of aromatic hydrocarbon-olefin systems. Studies concerning the photophysical and photochemical effects of the solvent have been carried out by McCullough and Miller[34] using the naphthonitrile-TME system and by Lewis and Hoyle[35] with the diphenylvinylene-carbonate-2,5-dimethyl-2,4-hexadiene system. In the former case, it was found that cycloaddition of the olefin to the cyano substituted aromatic ring occurred in low polarity solvents (equation (7)). In polar solvents, the photochemistry takes on entirely different course; consistent with the involvement of radical ion intermediates (equation (9)). In the latter case, cycloaddition of the diene (22) to diphenylvinylenecarbonate (21) occurs in low polarity solvents to give compound (23) (equation (12)).



(12)

21 22 23

In very polar solvents (23) is still formed but the quantum yields of product formation is very low. This was attributed to the competitive formation of an unreactive solvated ion pair.

The effect of solvent on exciplex lifetime, radiative decay and cycloaddition was investigated by both groups. In moderately polar solvents, cycloaddition reactivities decreased rapidly with increasing solvent polarity leading to an increase in exciplex lifetime and fluorescence quantum yield. The decrease in cycloaddition reactivity was attributed to greater solvent stabilization of the polar exciplex intermediate than the transition state leading to nonpolar cycloadduct. This behaviour is in agreement with Michl's qualitative description of exciplex cycloaddition processes based upon calculations involving biradicaloid species.[36a] These calculations indicate the possibility of two excited species; one (S) of an ionic or charge separated nature with a minimum corresponding to exciplex formation and the other (D) possessing a pericyclic minimum that correlates with a doubly excited state of isolated molecules (Figure 3).

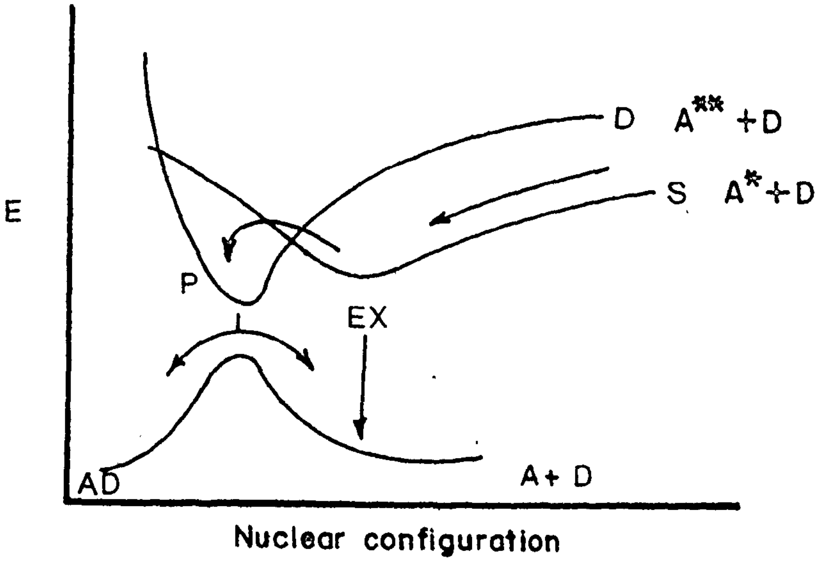


Figure 3. Schematic representation of energy surfaces found in exciplex formation and cycloaddition. D: doubly excited non-polar state; S: singly excited, polar state; EX: exciplex minimum; P: pericyclic, biradicaloid minimum.

The D state is expected to be non-polar. It was reasoned that singlet photocycloaddition may involve up to two intermediates; a "loose complex" (EX), and a "tighter complex" (P) at the pericyclic geometry with old bonds half-broken and new ones half-formed. The rate determining step in cycloaddition can be visualized as the surface crossing from the exciplex (EX) minimum. Solvation of the exciplex state would tend to increase the barrier for the surface crossing.

Caldwell[36b] has developed a paradigm of reactivity in allowed [2+2] singlet state photodimerizations and photocycloadditions based on the Michl model. Favourable features for high reactivity are high singlet energy, low triplet energy and high frontier orbital density at reacting positions.

The two groups found that both exciplex cycloaddition and fluorescence rate constants decrease in highly polar solvents such as methanol. It was reasoned that a solvated ion-pair of lower energy than the exciplex was formed. Michl[36a] pointed out that complications can result from formations of ion pairs in polar solvents. The presence of ion pairs in polar solvents leads to other decay pathways not easily visualized by Michl's model.

Another model which can be used to interpret solvent-induced changes in exciplex behaviour was developed by Weller[14,37,38] and Mataga.[16,39-41] In non-polar solvents an encounter of an excited acceptor with a ground state donor forms a moderately polar exciplex. This excited complex can be regarded as a resonance hybrid of locally excited and charge transfer configurations ($A^{*}D \leftrightarrow A^{-}\cdot D^{+}\cdot$). As the solvent polarity increases, the energy of the solvated ion-pair configuration ($A^{-}\cdot \cdots D^{+}\cdot$) will, at some point, fall below that of the exciplex. Under these conditions, ion-pair formation may occur either directly or via the exciplex. In highly polar solvents, the free radical ions ($A\cdot^{-} + D\cdot^{+}$) may exist. These energies of these various states as a function of solvent polarity are depicted in Figure 4.

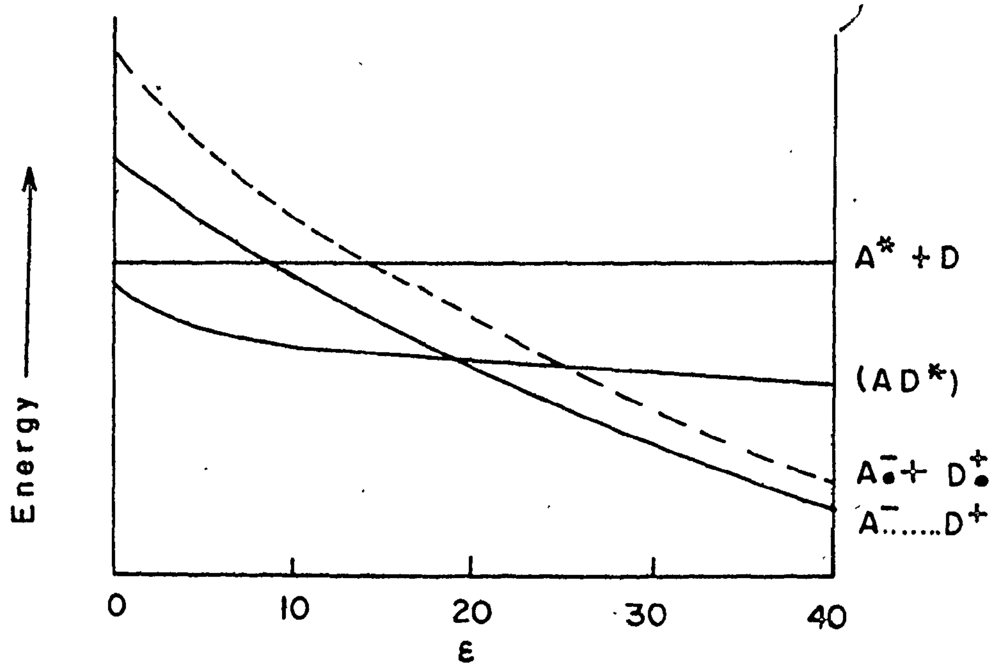
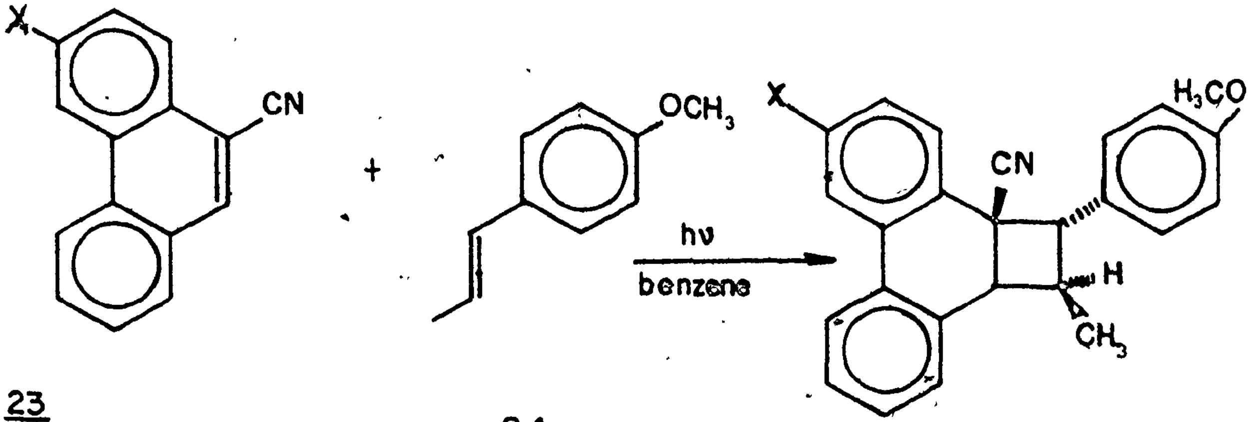


Figure 4. Influence of solvent polarity on the energy of the isolated molecules, $^{1}A^{*} + D$; the exciplex, (AD^{*}); the solvent ion-pair, $A^{-}\cdot \ldots, D^{+}\cdot$; and the free radical ions, $A^{-}\cdot + D^{+}\cdot$.

The results of both the fluorescence quenching experiments and the product studies are consistent with this qualitative picture. The pronounced solvent dependence on fluorescence quenching rate found by both groups was accounted for by a transition from exciplex to ion-pair formation. McCullough and Miller found a distinct change in the nature of the products formed as the solvent polarity was increased. They attributed this change to the presence of ion-pairs in solvents of high polarity, like ethanol and methanol ($\varepsilon > 20$).

The role of substituent dependence of photocycloadditions involving exciplexes has been studied by Caldwell and Creed.[42] They systematically varied the substituent in a series of substituted 9-cyanophenanthrenes (23a-c) with anethole (24) (equation (13)). They found that as the remote phenanthrene



23

a, X = CN
b, X = H
c, X = OCH_3

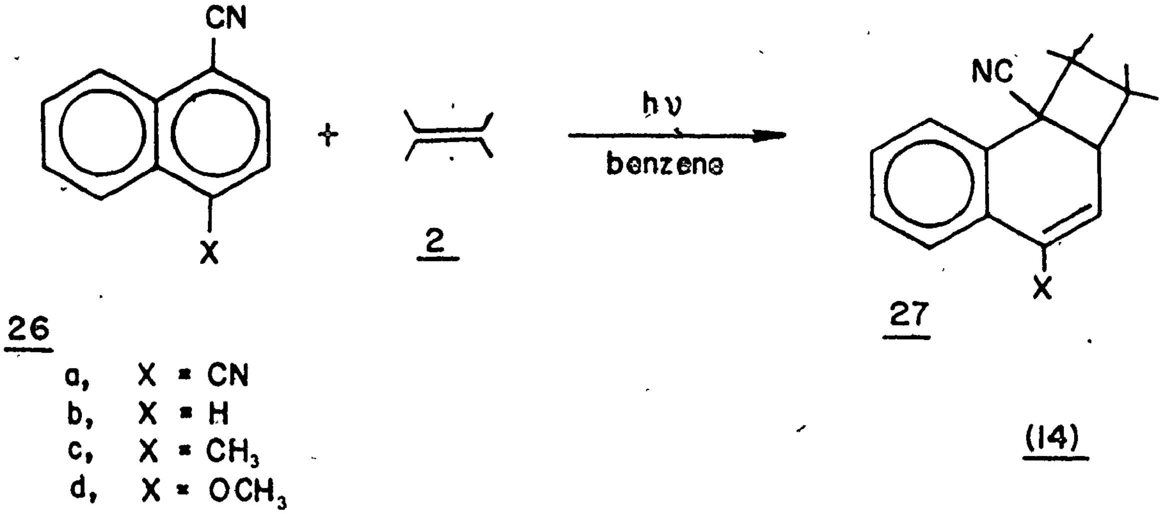
24

25

(13)

substituent was varied from -CN to -H to $-OCH_3$, i.e., the order of decreasing charge transfer stabilization expected for the exciplex, the rate of formation of the cycloadduct (25) increased sharply. This is consistent with the model proposed by Michl (Figure 3) in that it suggests the presence of a transition state for cycloadduct formation markedly less polar than the exciplex.

A similar study was carried out in our laboratory. The substituent was varied in a series of substituted 1-naphthonitriles (26a-d) with tetramethylethylene[43] (equation (14)). The results paralleled those described above and are shown in Table 1. The 1,4-dicyanonaphthalene-TME exciplex fluoresces but no cycloaddition occurred under normal photochemical conditions. On the other hand, 4-methoxy-1-naphthonitrile was not quenched efficiently by tetramethylethylene and an emissive exciplex was not detected. Presumably, the addition of the



(14)

Table 1. Substituent Effects on the Formation and Collapse of 1-Naphthonitrile-TME Exciplexes in Benzene

System	Existence of Emissive Exciplex	Exciplex Emission Maximum (nm)	Limiting Quantum Yield of Cycloaddition (Φ)
26a-2	yes	444[c]	~ 0
26b-2	yes	403[a]	0.14[a]
26c-2	yes	392[c]	0.51[b]
26d-2	no	--	--

[a] R.C. Miller, Ph.D. Thesis, McMaster University, 1978.

[b] J.J. McCullough, W.K. MacInnis, C.J.L. Lock, R. Faggiani, J. Am. Chem. Soc., 102, 7780 (1980).

[c] W.K. MacInnis, unpublished results.

methoxy group increases the electron affinity of the naphthonitrile to the point where charge transfer stabilization of the exciplex is hindered.

The exciplex emission maximum decreases and the efficiency of cycloaddition increases as the substituent is varied from -CN to -H to -CH_3. These observations are consistent with a decrease in charge transfer stabilization of the exciplex which, according to Michl's model, should favour the cycloaddition process.

Presumably cycloadducts such as (25) arose from collapse of the exciplex. However, caution has to be exercised in making such an interpretation. Förster said:

"Although the participation of excimers and exciplexes as intermediates in photoreactions ... seems likely, it cannot yet be considered as proven ... only quantitative spectral and photochemical data under varying conditions and the representation of both by a common reaction mechanism may be considered as proof."[9b]

Recently, such proof has been provided by Caldwell and Smith.[44] They investigated the 9-cyanophenanthrene-transanethole system (equation (13), X = H) in benzene. Both cycloadduct formation and exciplex emission was observed with this system. Exciplex formation and cycloaddition could be parallel and unrelated pathways for singlet hydrocarbon quenching. Caldwell and Smith found that the exciplex emission was sharply attenuated by dimethyl acetylenedicarboxylate ($k_q\tau$ in benzene = 64 ± 5 M^{-1}), while the singlet 9-cyanophenanthrene was quenched only to a small extent ($k_q\tau = 2.2\ m^{-1}$). This result indicated that the quenching observed in the former case must have been due to an interaction of the dimethyl acetylenedicarboxylate with the exciplex. An identical Stern-Volmer slope (62 ± 5 m^{-1}) was obtained for the quenching of product formation. This experiment demonstrated conclusively that exciplex formation directly precedes cycloaddition in the 9-cyanophenanthrene-anethole system.

The type of experiment described above has been used by other workers to prove the intermediacy of exciplexes in cycloaddition reactions. For example, Sakurai and Pac[45] used pyridine to quench the 9-cyanophenanthrene-tetramethylethylene exciplex. Further studies by Caldwell and coworkers[46] concerning exciplex quenching have indicated that exciplex substitution may be an important photochemical process (equation (15)).

$$(MQ_1)^* + Q_2 \rightarrow (MQ_2)^* + Q_1 \qquad (15)$$

Several studies on the role of steric factors in exciplex formation have been reported. For example, Morrison and Froehlich[47] investigated the quenching of the fluorescence of benzene and 22 mono- and polyalkylated benzenes by cis-piperylene. The quenching of fluorescence of the compounds by dienes was believed to occur via a non-emissive exciplex.[48] It was found that the quenching rate constant was relatively independent of the number and size of the alkyl substituents, changing only significantly when two or three tert-butyl groups were appended to the ring. Based on this data, they proposed a "loose" exciplex where the interplanar distance between quencher and quenchee is 4.0 to 5.5 Å.

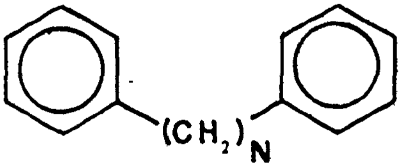
De Schryver and coworkers[49] studied structural effects in exciplex formation of 2-methylnaphthalene (2-MN) with tertiary amines by using triethylamine (TEA) and N-methylpiperidine (NMP). They found that NMP was a poorer quencher than TEA in the polar solvent, ethanol. In the nonpolar solvent, isooctane, the entropy of exciplex formation was more negative for TEA than NMP. Also, the enthalpy of formation for the 2-MN-TEA complex was found to be more negative than for the 2-MN-NMP complex, indicating a tighter bound complex for the former system than for the latter complex. These observations were interpreted as arising from geometric restrictions in the approach of the amine to the excited 2-methylnaphthalene.

Part III: INTRAMOLECULAR EXCIMERS AND EXCIPLEXES

G.S. Hammond, in Advances in Photochemistry, 7, 389 (1969), wrote:

> "Much information can probably be obtained from bichromophoric molecules in which the two chromophores interact more strongly in the excited state than in the ground state of the molecules."

This technique has been applied with considerable success to the study of excimers and exciplexes.[50] One of the first studies was undertaken by Hirayama.[51] He examined the fluorescence spectra of a series of α,ω-diphenylalkanes (29) where the number of methylene groups was varied from 1 to 6.

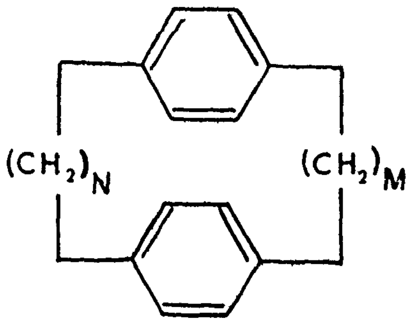


N = 1 to 6

29

Excimer fluorescence was only observed when N = 3. Based on these findings, Hirayama postulated the so-called N = 3 rule, which states that excimers can only be formed when the two chromophores are separated by four saturated bonds (3 methylene groups). This rule assumed that a sandwich configuration had to be reached for excimer formation. Only the trimethylethylene chain can take this rather favourable conformation in an excimer-like structure. The longer chains did not show excimer fluorescence because the probability to reach a favourable spatial arrangement within the lifetime of the excited state was severely diminished.

Further evidence for the necessity of the symmetric sandwich configuration was provided by Chandross and Dempster.[52] They found that strong intramolecular excimer formation only occurred in the two symmetrical 1,3-dinaphthylpropanes. On the other hand, 1-(α-naphthyl)-3-(β-naphthyl)-propane did not show excimer fluorescence. Additional proof for the requirement of the symmetric sandwich configuration was obtained in the paracyclophane series;[53] 4,4'-paracyclophane (30a) showed excimer fluorescence while the 4,5'-paracyclophane (30b) did not.

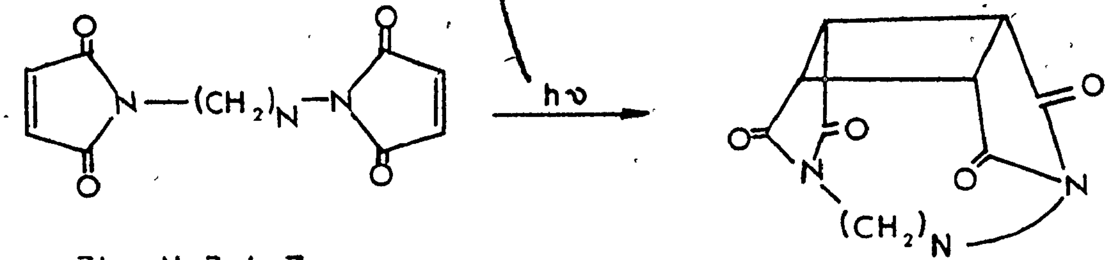


30

a, N=4, M=4

b, N=4, M=5

Recently, De Schryver and coworkers proposed the intermediacy of non-emitting excimers in photochemical reactions of bichromophoric systems in which the two chromophores were linked by a chain with more than three units. For example, they found N,N'-alkylenebismaleimide [31] cyclomerizes on direct irradiation to give the tetracyclomer (32) for N = 3 to 7 (equation (16)).[54] Mechanistic studies showed that the reaction occurred from the excited singlet while spectroscopic studies gave no indication of important ground state interactions.[55] The lack of emission from the excited state complex was attributed to its efficient collapse to photoproduct.



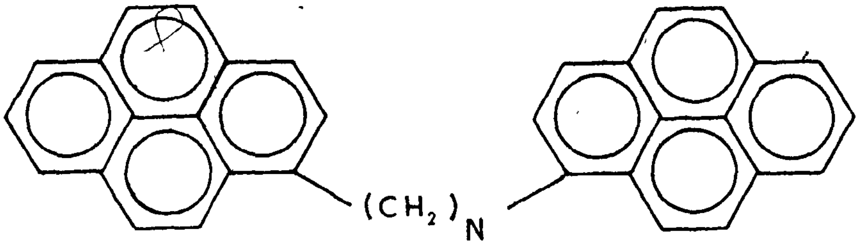
31 N=3 to 7

32

(16)

On the basis of these results, De Schryver and coworkers[55] reformulated Hirayama's rule as follows: the possibility of intramolecular complex formation is limited by the probability to reach, within the lifetime of the excited state involved, a favourable conformation and by the extent of stabilization in the complex, covalent bond formations being the extreme.

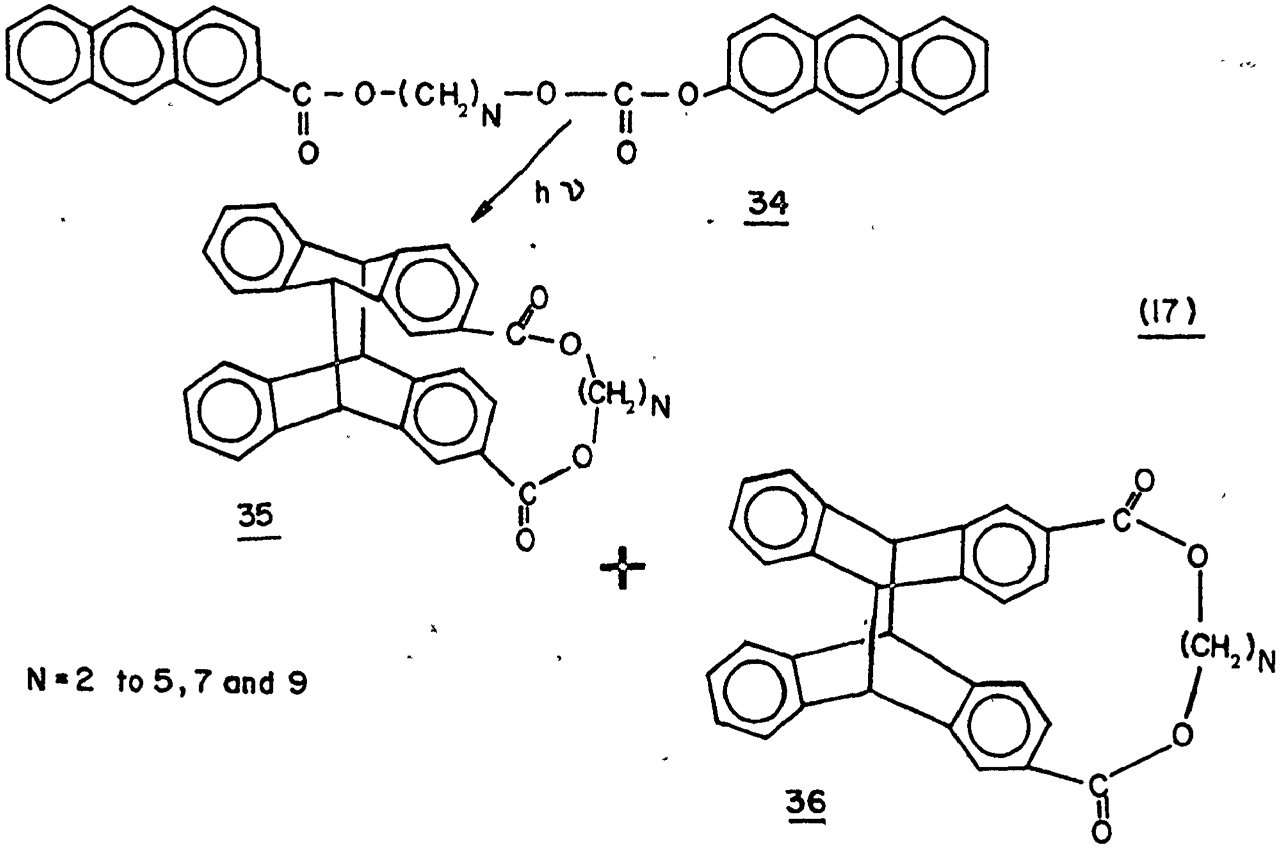
Confirmation for this proposal was provided by Zachariasse and Kühnle[56] in their study of a series of α,ω-di(1-pyrenyl)-alkanes, $Py(CH_2)_N$-Py (33).



33 N=2 to 16 and 22

Excimer fluorescence in these compounds was observed for compounds with up to 22 methylene units in the linking chain. It was concluded that intramolecular excimer formation was possible in this system, due to the large excimer stabilization energy of pyrene, which would compensate the steric and statistical effects. The maximum of the excimer emission band varied with chain length indicating the excimer geometry changed as a function of the chain length. The most stable excimer was observed for N = 3. This molecule can adopt an intramolecular sandwich configuration of the pyrene moieties.

De Schryver and coworkers[50a,57] have studied the intramolecular cycloaddition of bisanthracenes linked at the 2,2'-position (equation (17)). Both cycloaddition and excimer fluorescence was detected in this system. Kinetic analysis by quenching of the reaction and quenching of fluorescence indicated that the excimer formation lies on the pathway leading to product. The observation of excimer emission in a photo-



34

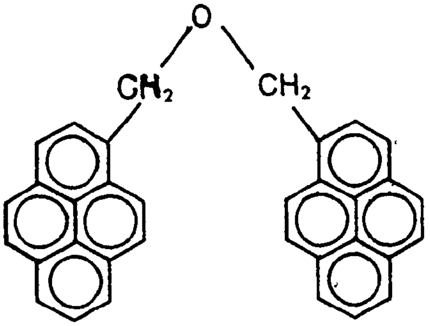
35

36

(17)

chemical reactive system in which the chain contains more than four saturated bonds provides a link between the non-emissive bismaleimides[54] and the emissive but photochemically unreactive bispyrenes studied by Zachariasse and Kühnle.[57]

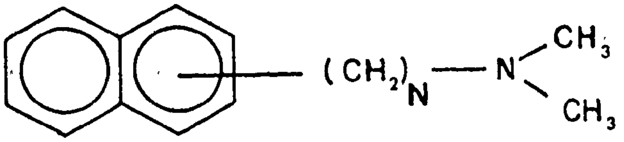
Intermolecular excimer formation has been used as a molecular marker for the study of membrane systems. For example, Georgescauld and Duclohier[58] have used pyrene excimer formation as a probe to study phase transitions in membranes. One difficulty encountered using pyrene as a molecular marker is the relatively high concentrations required to detect excimer fluorescence. This problem can be alleviated by using bichromophoric molecules such as (1,1'-dipyrenyl)-methyl ether (37).



37

Georgescauld and Winnik[59] have shown that phase transition studies of synthetic phospholipid membranes can be carried out at a mole ratio of probe-to-lipid 10^2-10^3 smaller than that required to observe bimolecular pyrene excimer formation.

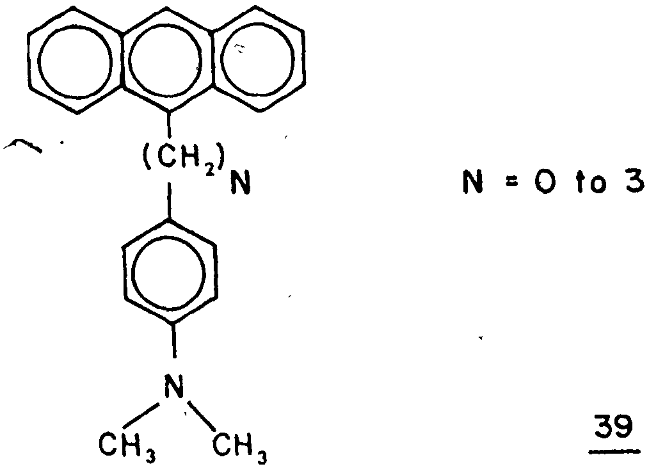
The geometrical requirements in amine-aromatic hydrocarbon exciplex formation have been investigated using bichromophoric probes. Chandross and Thomas[60] studied intramolecular exciplex formation in naphthylalkylamines (38) in which N varied from 1 to 4. No emission due to the exciplex was found for N = 1.



38 N = 1 to 4

Exciplex emission was detected for N = 2 to 4. A maximal interaction for (38) was observed when N = 3 and the exciplexes with the chain α were found to be more stable than those with the chain β. It was concluded that the nitrogen atom of the amine probably occupies a position of the periphery on the naphthalene near C_1.

Mataga and coworkers[61] have also shown that the geometrical requirements for intramolecular interaction in amine-aromatic hydrocarbon systems are not very strict. They studied the (9-anthryl)-$(CH_2)_N$-(P-N,N-dimethylaminophenyl) system (39), where N = 0,1,2,3. The absorption spectra showed only for (39)(N = 0) an interaction in the ground state. In all cases, exciplex emission was observable. This indicated that the two rings do not have to cover each other completely or do not have to be parallel.

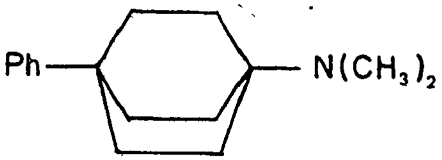


39

Davidson and coworkers[62] examined the fluorescence spectra of N,N-diethyl-4-phenyl-butylamine (40, N = 4) and 1,1-dimethylamino-4-phenylbicyclo[2,2,2]octane (41) in order to see the effects of substituting a rigid insulating spacer

$Ph(CH_2)_N-N-Et_2$

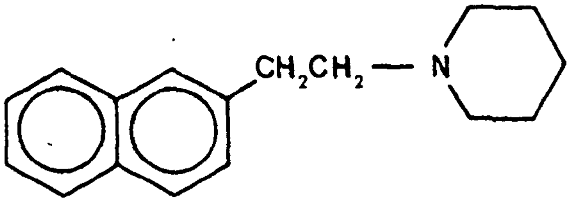
40, N=2 to 4



41

group to that of a flexible chain on exciplex formation. As previously reported,[63] (40) formed a fluorescent exciplex. Since in (41) the amino group cannot come near the phenyl group, it did not show fluorescent exciplex formation.

Recently, De Schryver and coworkers[64,65] have investigated the influence of starting conformations on intramolecular exciplex formation in aromatic hydrocarbon-amine bichromophoric systems. The intramolecular complex formation of ω-phenyl-α-N,N-dimethylaminoalkanes (40, N = 2 to 4) in isopentane was investigated[64] and a complete kinetic analysis of the system indicated exciplex formation was occurring with a different rate from two different assemblies of starting conformations, related to the relative orientation of the dimethylamino group and the aryl group. 1-β-Naphthyl-2-N-piperidinoethane (42) was also used to elucidate the role of internal geometrical limitations in the exciplex formation process.[65] The results of a kinetic analysis were explained by assuming the existence of two assemblies of ground-state conformations in equilibrium

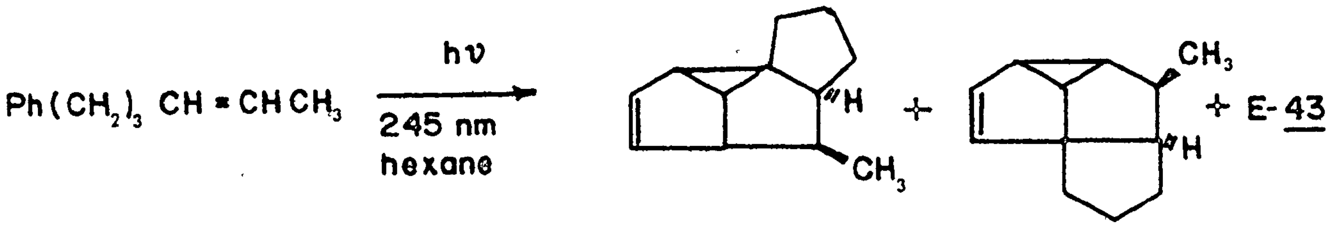


42

through a high energy barrier, only one of the assemblies leading to the exciplex within the excited state lifetime. The barrier were said to be related to N-inversion and C-N rotation.

The use of bichromophoric molecules to probe exciplexes formed from aromatic hydrocarbon-olefin systems has not been as extensive as that for the amine-aromatic hydrocarbon systems. Morrison and coworkers[66,67] found that a change in the number of methylene groups separating the aryl and vinyl groups, from one in 1-phenyl-2-butene to three in 6-phenyl-2-hexene greatly reduced the efficiency of triplet sensitized E/Z isomerization. This change was attributed to the emergence of a new aryl/olefin interaction which all but completely eliminates intersystem crossing in 6-phenyl-2-hexene (equation (18)). Although no new emission was detected, this new interaction was ascribed to the formation of an exciplex which collapsed to 1,3-cycloadducts in high efficiency ($\Phi_{44+45} = 0.25$).

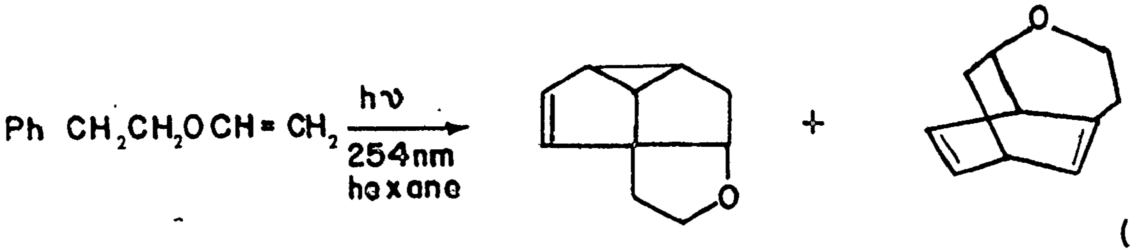
In a closely related study, Gilbert and Taylor[68] found that irradiation of phenethyl vinyl ether (46) gave intra-



Z - 43 44 45

(18)

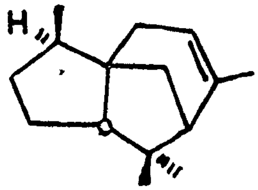
molecular 1,3- and 1,4-cycloadducts in a 1:15 ratio (equation (19)). As with 6-phenyl-2-hexene, efficient internal fluorescence quenching was reported.



46 47 48

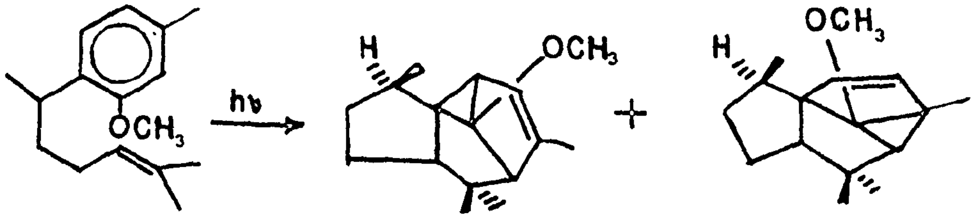
(19)

Morrison's elegant studies on bichromophoric molecules has recently been utilized by Wender[69] to design a cycloaddition methodology which was utilized in the total synthesis of (±)-α-cedrene (49) in four steps. The key step was the intra-



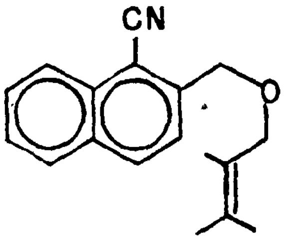
49

molecular photocycloaddition of (50) to give (51) and (52) (51:52 = 1:1) in an isolated yield of 64% (equation (20)).

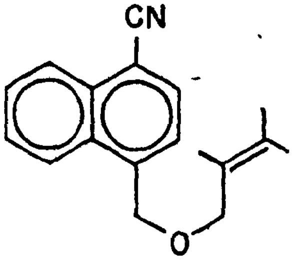


50 51 52 (20)

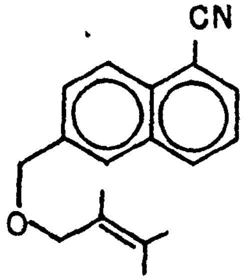
Geometric factors in arylnitrile-alkene exciplex chemistry have not been investigated previously. A study of this type was considered worthwhile since exciplex formation had been demonstrated to be important in this system. Since bichromophoric molecules have been successfully used to study the structural requirement of amine-aromatic hydrocarbon systems, we utilized tethered chromophores to probe the geometric factors in exciplex formation and decay. The bichromophoric compounds (53), (54) and (55) were used for the investigation.



53

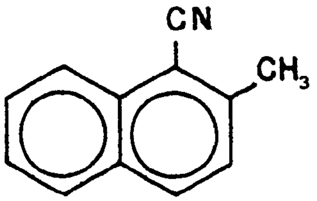


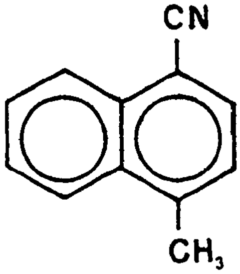
54

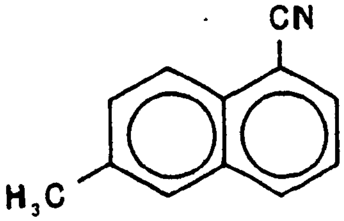


55

A substituent on the naphthonitrile aromatic ring plays a major role in determining whether an emissive exciplex is formed for the naphthonitrile-TME system.[38] Therefore, it was necessary to study the effect of methyl substitution on the aromatic ring on exciplex formation in the bimolecular naphthonitrile-TME system. The compounds chosen for this investigation were the three methylnaphthonitriles (56), (57) and (58).







56

57

58

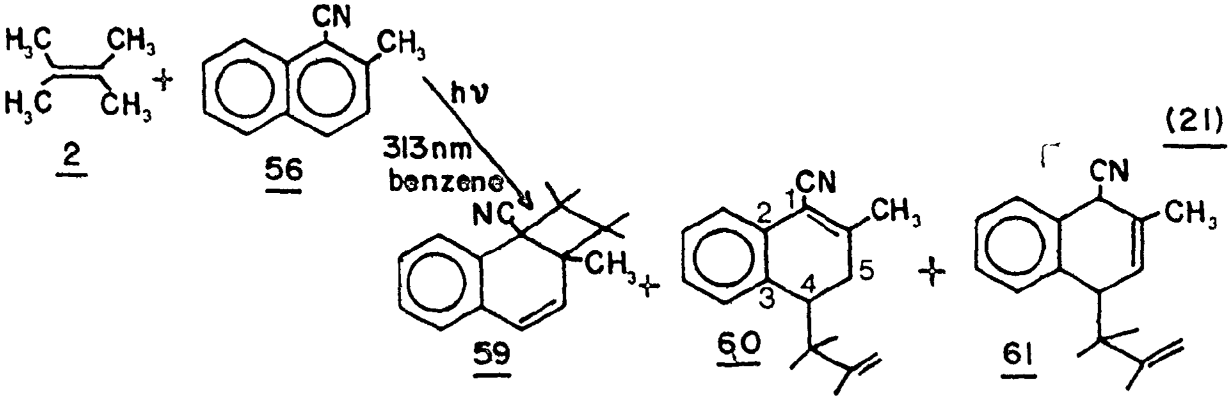
RESULTS

RESULTS

A) THE METHYL-1-NAPHTHONITRILE-TETRAMETHYLETHYLENE SYSTEMS

Products and Structural Assignments

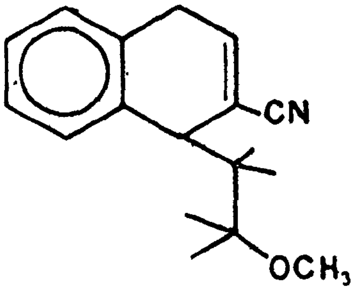
Irradiation of 2-methyl-1-naphthonitrile and tetramethylethylene in benzene with 313 nm light gave two major products which were isolated by preparative vpc (equation (21)). They were formed in equal amounts in a slow reaction, and (59) was an oil while (60) was a solid, m.p. 101-102°C.



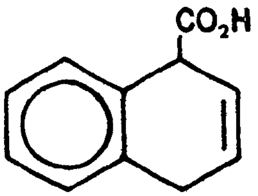
(21)

The nmr spectrum of (59) showed resonances as follows: five singlets at δ 0.79, 0.96, 1.20, 1.27 and 1.30 (3H each) were assigned to the methyl groups. An AB system at δ 5.71 and 6.29, J = 10.2 Hz, was attributed to the vinylic protons. Protons of the benzene ring gave two multiplets centred at δ 7.02 (1H) and δ 7.22 (3H). The infrared spectrum of (59) showed a band at 2225 cm^{-1} of medium intensity corresponding to the nitrile stretching frequency. On the basis of this data (59) is assigned the structure 1-cyano-6,7,7,8,8-pentamethyl-2,3-benzobicyclo[4.2.0]octa-2,4-diene.

Photoproduct (60) was also isolated from the reaction mixture by preparative vpc. It was found that the cyclobutane (59) was photolabile, and irradiation through corex afforded mainly (60). Under these conditions, (60) was isolated in a 30% yield by column chromatography. The nmr spectrum of (60) showed resonances at 0.78 and 0.97 δ (singlets, 3H each), gem-dimethyl group, at 1.80 δ (3H), doublet of doublets, J = 1.2 and 0.75 Hz, vinylic side-chain methyl group, and at 2.20 δ (3H), singlet, ring methyl group. A multiplet at 2.47 δ (2H), is assigned to the ring methylene group, and a resonance at 2.93 δ (1H), doublet of doublets, J = 6.0 and 2.4 Hz is assigned to the ring methine. The vinylic protons resonated at 4.80 and 4.90 δ (2H), multiplets. The protons of the aromatic ring resonated at 7.1-7.5 δ. The ring methyl group protons and those of the methylene group at C-5 exchanged on $NaOCH_3/CH_3OD$ treatment. The ir showed an intense nitrile band at 2220 cm^{-1}. As further confirmation of the structure, an attempt was made to dehydrogenate (60) with palladium on charcoal. The major product was 2-methyl-1-naphthonitrile which arose from the loss of the side chain. A similar reaction was reported for the attempted dehydrogenation of (62). The major product from the reaction was 2-naphthonitrile.[32] On the basis of this data, (60) is assigned the structure (1-(2',3'-dimethyl-3'-but-1-enyl)-3-methyl-4-cyano-1,2-dihydronaphthalene.

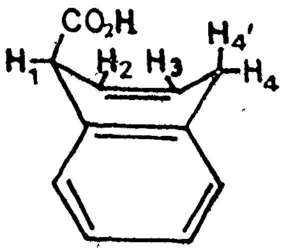


62

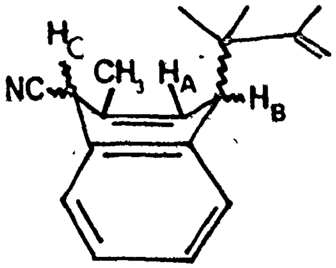


63

However, (60) was shown not to be a primary photoproduct. Aliquots from the reaction were evaporated in the cold, and the ir and nmr spectra were taken immediately. The infrared spectrum showed a nitrile band at 2242 cm^{-1}. Signals due to (60) were not observed in the nmr. Instead, resonances of equal intensity appeared at 3.50 and 5.84 δ which may correspond to protons from compound (61). Recently, Marshall and coworkers[70] have used nmr to investigate the conformation of 1,4-dihydro-1-naphthoic acid (63). They concluded that it had a flattened boat conformation. Table (2) gives some chemical shift data for (63)[70] as well as a partial chemical shift assignment for compound (61). H_C was observed as a shoulder on the resonance at 4.60 ppm.



63



61

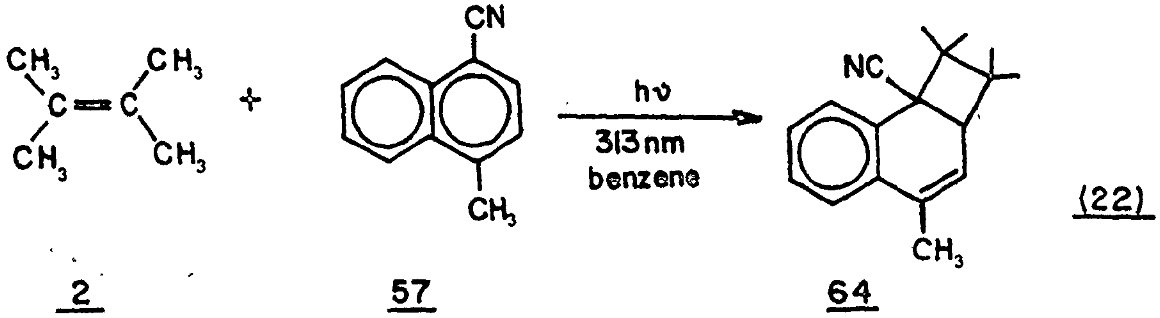
Proton	Chemical Shift (ppm) (δ)	Proton	Chemical Shift (ppm) (δ)
1	4.55	C	4.60
2	6.07		
3	6.25	A	5.84
4	3.47		
4'	3.67	B	3.50

Table 2. Chemical Shift Data for 1,4-Dihydro-1-naphthoic acid (63) and compound (61)

Both compounds (63) and (61) have the same basic carbon skeleton. H_B has a similar chemical shift to that found for protons H_4 and $H_{4'}$. Also, the chemical shifts of H_A and H_3 are similar. However, the splitting pattern observed for H_A and H_B is unlike that found for $H_{3'}$, H_4 and $H_{4'}$. Rabideau has pointed out that substitution can lead to wide variation in the geometry of the 1,4-cyclohexadiene ring system.[71] The dissimilarity of splitting patterns between (61) and (63) may arise from a difference in geometry of the carbon skeleton of the two compounds. The conversion of (61) to (60) was base catalysed. On the basis of this data, the unstable adduct (61) is tentatively assigned the structure (1-(2',3')-dimethyl-3'-but-1-enyl)-3-methyl-4-cyano-1,4-dihydronaphthalene.[72]

Irradiation of 2-methyl-1-naphthonitrile and tetramethylethylene in ethyl acetate with 313 nm light gave a complex mixture of products as shown by vpc analysis. The reaction was very inefficient and no attempt was made to isolate these compounds.

Irradiation of 4-methyl-1-naphthonitrile and tetramethylethylene in benzene gave a single 1:1 adduct (64), m.p. 93-94° (equation (22)). It was isolated from residual



(22)

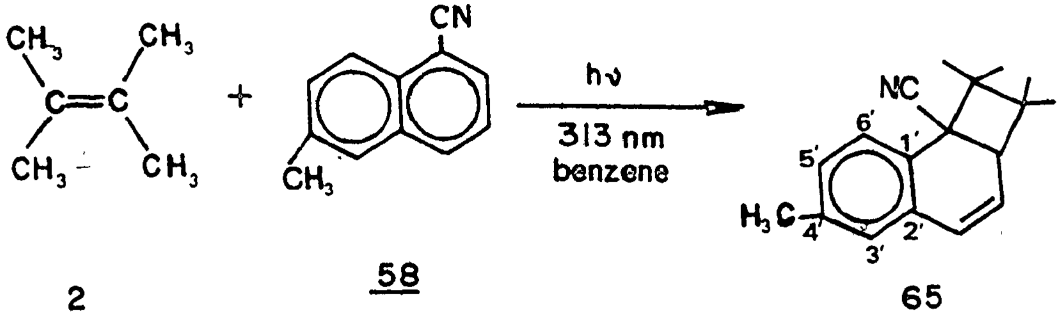
4-methyl-1-naphthonitrile in a 24% yield by silica gel chromatography.

The nmr spectrum of (64) showed resonances at 0.77 and 0.90 δ (s, 3H each) as well as 1.30 δ (s, 6H) which were assigned to the methyl groups. An AMX_3 system was observed at 2.03 δ (3H, J = 1.8 and 1.2 Hz (vinylic methyl group), 3.27 δ (1H), J = 4.8 Hz and 1.2 Hz (allylic proton), and 5.57 δ (1H), J = 4.8 Hz and 1.8 Hz (vinylic proton)). A multiplet at 7.23 δ (4H) was assigned to the protons of the aromatic ring. In a decoupling experiment, the protons at 2.03 δ were irradiated. The resonances at δ 3.27 and 5.57 collapsed to a doublet of doublets with J = 4.8 Hz. The infrared spectrum showed the nitrile band at 2221 cm^{-1}. On the basis of this data, adduct

(64) is assigned the structure 1-cyano-4,7,7,8,8-pentamethyl-2,3-benzobicyclo[4.2.0]octa-2,4-diene.

Irradiation of 4-methyl-1-naphthonitrile and tetramethylethylene in ethyl acetate with 313 nm light gave compound (64) as the major product.

Irradiation of 6-methyl-1-naphthonitrile and tetramethylethylene in benzene gave, as the major product, a 1:1 adduct (65), m.p. 89-90° (equation (23)). Isolation from residual 6-methyl-1-naphthonitrile was achieved by the chromatography technique of Still and coworkers.[73]



2 58 65

(23)

The nmr spectrum of (65) showed resonances at 0.77, 0.90, 1.27, 1.30 and 2.26 δ (3H) each due to the methyl groups. An AMX system was observed at δ 3.09 (J = 4.8 Hz and 1.8 Hz), 5.67 (J = 10.2 and 4.8 Hz) and 6.27 (J = 10.2 and 1.8 Hz) due to the ring methines. Broad singlets at 6.80 δ (1H) and 7.00 δ (2H) were attributed to the protons of the aromatic ring. The infrared spectrum showed the nitrile band at 2221 cm^{-1}. On the basis of this data, adduct (65) is assigned the structure 1-cyano-7,7,8,8-tetramethyl-2,3-(4-methylbenzo)-

bicyclo[4.2.0]-octa-2,4-diene.

Irradiation of 6-methyl-1-naphthonitrile and tetramethylethylene in ethyl acetate gave (65) as the major product.

Fluorescence Quenching

It was found that tetramethylethylene (TME) quenched the fluorescence emissions of 1-naphthonitrile, 2-methyl-1-naphthonitrile (56), 4-methyl-1-naphthonitrile (57) and 6-methyl-1-naphthonitrile (58). Quenching of the naphthonitrile fluorescence was accompanied by the appearance of a structureless red-shifted emission due to naphthonitrile-TME exciplex formation. Scheme 1, which involves an exciplex complex intermediate,[74] will be used to interpret the photochemistry. As expected, the Stern-Volmer plots for the quenching of the naphthonitrile fluorescence by TME were found to be linear (Fig. 5). It is clear from these linear plots that the fluorescent state (s_1) of these aromatic compounds is being quenched in a bimolecular process by TME in accord with the well known equation (24). I and I_o are the quenched and unquenched fluorescence intensities, Φ and Φ_o are the corresponding quantum yields of fluorescence. By application of steady state approximation

$$I_o/I = \Phi_o/\Phi = 1 + KSV[TME] \qquad (24)$$

to Scheme 1 (see Appendix A), it is shown that

$$KSV = k_q\tau(k_a + k_{d'} + k_{f'})/k_{-q} + k_a + k_{d'} + k_{f'} \qquad (25a)$$

where

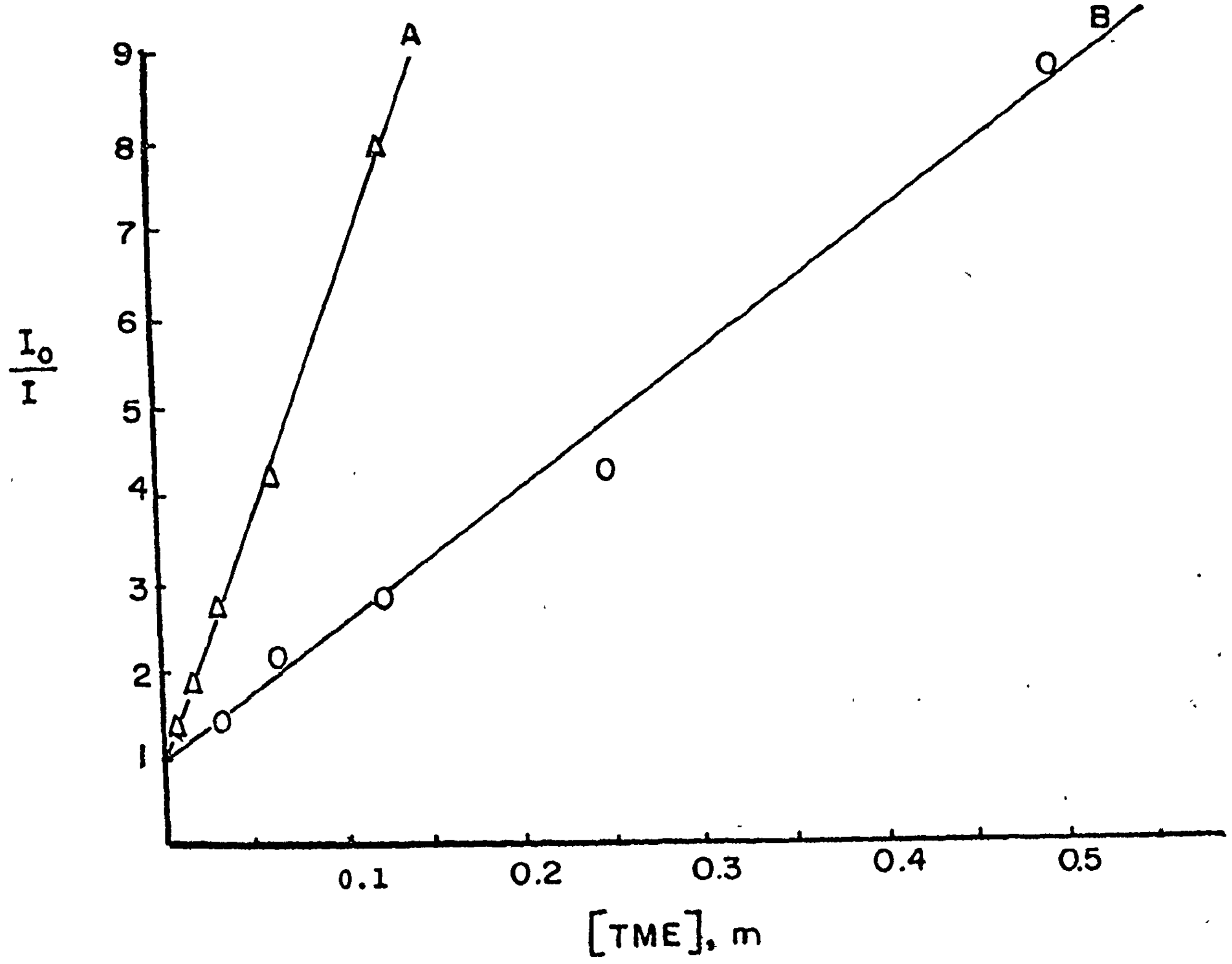


Figure 5. Stern-Volmer plots for the fluorescence quenching of 4-methyl-1-naphthonitrile by 2,3-dimethyl-but-2-ene in ethyl acetate (A) and benzene (B).

$$\tau = (k_f + k_d + k_{isc})^{-1} \qquad (25b)$$

The lifetimes of these methylnaphthonitriles were measured. As a result, K_{SV}/τ can be calculated, providing a measure of the quenching effectiveness of tetramethylethylene. The naphthonitrile fluorescence lifetimes, Stern-Volmer slopes and values for K_{SV}/τ are given in Table 3.

Clearly, tetramethylethylene quenches the singlet s_1 of the four aromatic nitriles, and the rate for 4-methyl-1-naphthonitrile is close to the diffusion limit (k_{diff} for benzene = 1×10^{10} m^{-1} sec^{-1}).[75] The intersystem crossing rate for 1-naphthonitrile is low (1.7×10^7 sec^{-1}).[76] This suggests that the additions to TME proceed via the lowest excited singlet state, S_1. Further support for this conclusion comes from the fact that sensitization of 1-naphthonitrile and TME by acetophenone results in no addition.[34] In order to definitely assign the excited state multiplicity, the quantum yield for the formation of product (64) was measured as a function of olefin concentration, and compared with fluorescence quenching efficiency as described in the following section.

4-Methyl-1-Naphthonitrile-Tetramethylethylene Quantum Yields and Multiplicity

Using the assumption that naphthonitrile S_1 is the photochemically active state and that quenching occurs by exciplex formation, Scheme 1 may be used to derive a relation-

Table 3. Fluorescence Quenching of 1-Naphthonitriles by Tetramethylethylene

Fluorescer	Solvent[a]	Lifetime (τ) nsec[b]	Slope[c] (KSV,m^{-1})	$\frac{KSV}{\tau} \times 10^{-9}$ m^{-1} sec^{-1}
1-Naphthonitrile[d]	Benzene	9.8	41.7	4.3
2-Methyl-1-Naphthonitrile	Benzene	11.1	10.1	0.9
	Ethyl Acetate	11.6	48.4	4.1
4-Methyl-1-Naphthonitrile	Benzene	9.2	15.7	1.7
	Ethyl Acetate	10.0	53.0	5.3
6-Methyl-1-Naphthonitrile	Benzene	11.1	9.0	0.8
	Ethyl Acetate	9.8	37.4	3.8

[a] Solutions were deoxygenated by purging with argon. Spectra were measured at room temperature.

[b] Lifetimes were determined by the single photon counting technique.

[c] The values for the slope are the average of several runs. Individual values generally agreed to within 6%.

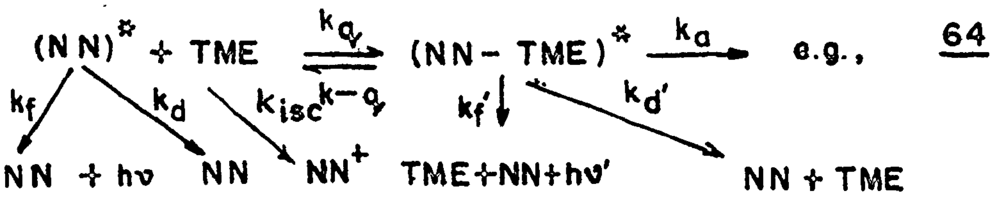
[d] Values are from R.C. Miller, Ph.D. Thesis, McMaster University, 1978.

ship between fluorescence, photoaddition quantum yields, and quencher concentration (see Appendix A). Steady state treatment gives the relationship

$$\Phi_a^{-1} = \Phi_{lim}^{-1}(1 + KSV^{-1}[TME]^{-1}) \qquad (\underline{26})$$

where Φ_a is the quantum yield of addition, Φ_{lim} is its value at infinite tetramethylethylene concentration, and KSV is defined in equations (25a) and (25b).

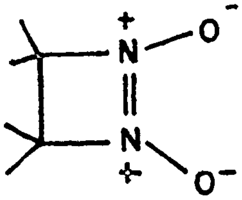
Scheme I



From equation (26), it can be seen that a plot of reciprocal quantum yield of adduct formation versus reciprocal quencher concentration should give a straight line whose intercept to slope ratio is equal to the Stern-Volmer quenching constant (KSV). KSV can also be determined by fluorescence quenching experiments through the relationship described by equation (24). If Scheme 1 is correct, the KSV's obtained by the two methods should be the same.

To make this comparison, quantum yields for formation of adduct (64) were measured as a function of TME concentration and the results are shown in Table 4 and Figure 6. In early experiments (measurements 1-5 in Table 4, Plot A in Figure 6), a considerable deviation from the expected linear relationship between Φ_a^{-1} and $[TME]^{-1}$ was observed, and the difference was greatest at low TME concentrations. It was originally believed that this deviation was due to triplet-sensitized decomposition of (64), since this cyclobutane decomposed when sensitized with 4-methyl-1-naphthonitrile to give 4-methyl-1-naphthonitrile. Similar behaviour has been reported for the cyclobutane formed in the photoreaction of naphthalene with acrylonitrile in ethanol.[77]

In an attempt to prevent the decomposition of (64), 0.01 m, 3,3,4,4-tetramethyl-1,2-diazetidine-1,2-dioxide (66) was added. This compound has been reported to be an effective triplet quencher of aromatic compounds such as trans-stilbene and anthracene.[78] On the other hand, it does not quench the fluorescence of naphthalene. As confirmation, a Stern-Volmer plot of 4-methyl-1-naphthonitrile and tetramethylethylene with 0.01 m (66) in benzene was obtained. The slope (KSV) was 14.0 m^{-1} which is in good agreement with the previously measured value of 15.7 m^{-1} (Table 3).



66

Plot B in Figure 6 shows the linear relationship which is obtained for Φ_a^{-1} vs $[TME]^{-1}$, when 0.01 m (66) is added in the quantum yield determinations. The derived KSV value from

Table 4

Quantum Yields of Adduct Formation in the Photoreaction of 4-Methyl-1-Naphthonitrile and Tetramethylethylene (TME)

Measurement[a]	TME Concn, m	TMDD[b] Concn, m	Light mEinstein	Total Product, mg	Quantum Yield, ϕ mmole/mEinstein	TME Concn^{-1}, m^{-1}	ϕ^{-1}, mEinstein mmole
1	0.35	0	0.3605	21.59	0.24	2.86	4.17
2	0.25	0	0.3525	15.33	0.17	4.00	5.88
3	0.15	0	0.0982	3.52	0.14	6.67	7.14
4	0.13	0	0.3631	9.25	0.10	7.70	10.00
5	0.10	0	0.3324	6.83	0.08	10.00	12.50
6	0.50	0.01	0.0986	6.63	0.27	2.00	3.70
7	0.26	0.01	0.1168	6.55	0.22	3.85	4.55
8	0.18	0.01	0.1912	9.11	0.19	5.56	5.26
9	0.14	0.01	0.0580	2.46	0.17	7.14	5.88
10	0.10	0.01	0.0903	3.66	0.16	10.00	6.25
11	0.50	0	0.0226	2.33	0.41	2.00	2.44
12	0.30	0	0.0136	1.33	0.39	3.33	2.56
13	0.20	0	0.0119	1.16	0.39	5.00	2.56
14	0.12	0	0.0135	0.92	0.27	8.33	3.70
15	0.10	0	0.0154	1.09	0.28	10.00	3.57

[a] The solvent was benzene at 23°C. 4-Methyl-1-naphthonitrile was 0.02M in 1-10 and 0.001M in 11-15.

[b] 3,3,4,4-Tetramethyldiazetidine-1,2-dioxide (0.02M) to suppress triplet decomposition of the cyclobutane.

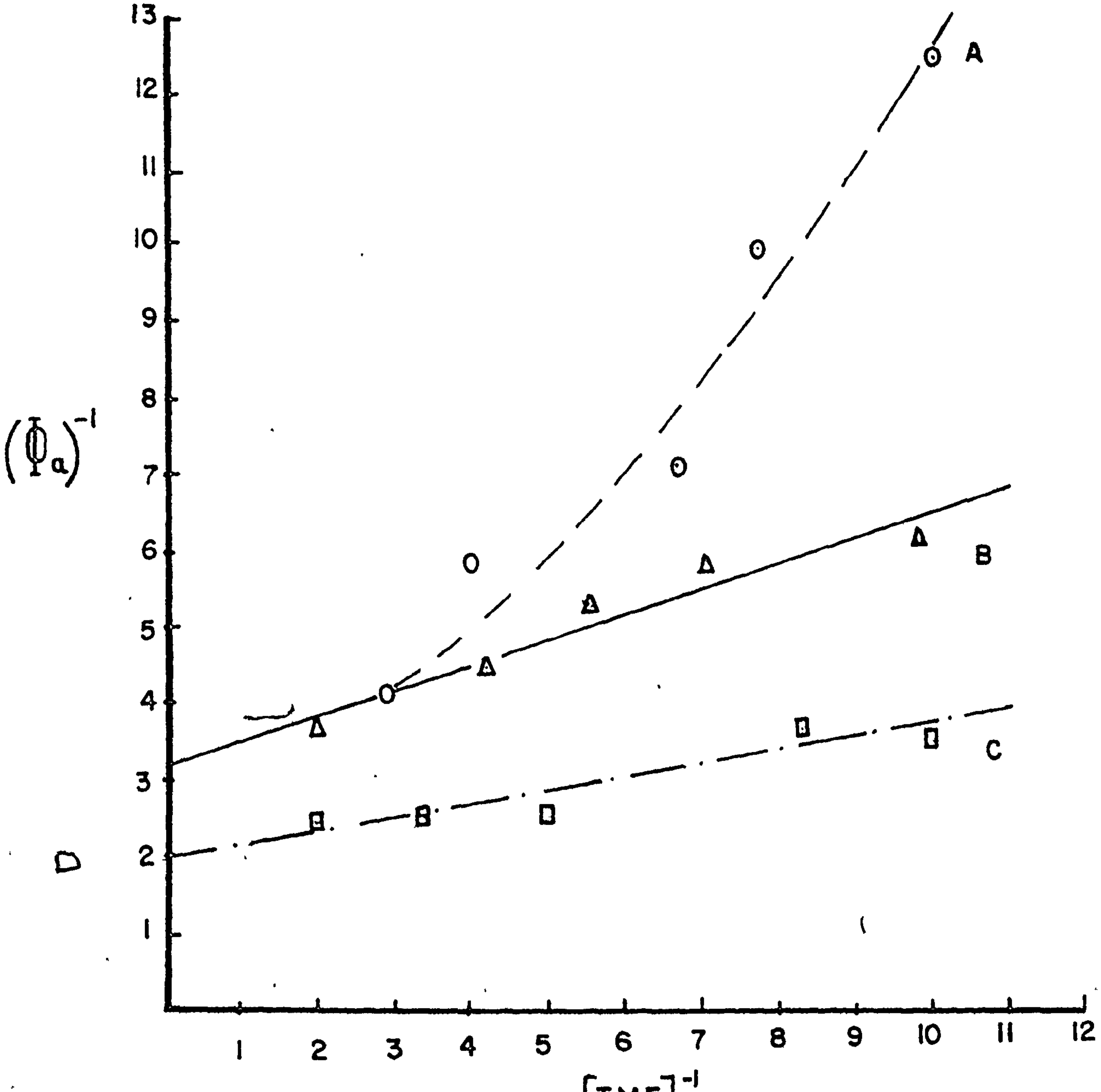


Figure 6. Dilution plots for quantum yields of 4-methyl-1-naphthonitrile-TME addition. In A, 0.02 M 4-methyl-1-naphthonitrile was used with no quencher; in B, 0.02 M 4-methyl-1-naphthonitrile was used with 0.01 M 3,3,4,4-tetramethyldiazetidine-1,2-dioxide added to quench decomposition of 64, in C, 0.001 M 4-Me-1-naphthonitrile was used with no quencher. Solvent was benzene.

dilution plot B was 10.1 m^{-1} as compared to 15.7 m^{-1} as determined by fluorescence quenching. The concentration of 4-methyl-1-naphthonitrile used in this study was 0.02 m, and at the excitation wavelength of 313 nm the solution had an OD of 114. This means that 99% of the light was being absorbed in the first 0.02 cm of the cell. Since the only mixing in the cell was provided by argon bubbling, it was possible that the naphthonitrile was being depleted at the front of the cell with a concomitant build-up of (64). A high local concentration of (64) could facilitate its sensitized decomposition.

As a check of this hypothesis, the concentration of 4-methyl-1-naphthonitrile was lowered to 0.001 m. The O.D. of the solution was 8 and as a result, 99% of the light was now being absorbed in the first 0.34 cm of the cell. It was thought that the cyclobutane build-up problem would not be as severe under these conditions. As a result, the quantum yields should be greater than those measured for Plots A and B.

Plot C in Figure 6 shows the linear relationship which is obtained for Φ_a^{-1} vs [TME] when the concentration of 4-methyl-1-naphthonitrile is reduced to 0.001 m. The quantum yields were found to be higher than those determined with a more concentrated 4-methyl-1-naphthonitrile solution. The derived KSV value from Plot C (Figure 6) was 11.6 m^{-1} which is in reasonable agreement with the value of 15.7 m^{-1} determined by fluorescence quenching. These results provide verification that naphthonitrile S_1 is the photoreactive state and evidence corroborating Scheme 1.

Exciplex Quenching

As indicated in Scheme 1, it is presumed that the products arise from the collapse of the naphthonitrile-olefin exciplex. Caution must be exercised in making such an interpretation since exciplex formation and cycloaddition may be parallel and unrelated paths for singlet hydrocarbon quenching. If a quencher can be found that deactivates an exciplex at a rate that differs from that of the initially excited monomer, experiments can be done that would unequivocally implicate the exciplex as an intermediate in product formation. In a series of papers, Caldwell and coworkers have discussed the successful application of this technique.[46] Their studies indicated that if the initially excited species was the acceptor, in the donor-acceptor pair, exciplex quenching was more facile using a second acceptor.[79] Using this criteria, a variety of acceptors were tested to see if the 1-naphthonitrile-TME exciplex could be successfully quenched.[34] Both fumaronitrile and dimethylacetylene dicarboxylate quenched the monomer at the same rate as the exciplex. Acrylonitrile and 2-chloroacrylonitrile did not appreciably quench either the monomer or the exciplex.

It was suggested[80] that a Förster quencher might serve as a selective quencher of the exciplex. Attenuation of the fluorescence of chloroanthracene by perylene has been shown to occur by the Förster quenching mechanism.[81] Addition of 0.007 m perylene to 4-methyl-1-naphthonitrile in benzene completely quenches the naphthonitrile fluorescence negating its use as a selective quencher of the exciplex. Coumarin 102 met the criteria required for a Förster quencher.[82] Unfortunately, Coumarin 102 quenched the exciplex by a radiative transfer mechanism. This conclusion was based on the low concentration of the quencher (2×10^{-5} m) required to completely quench the fluorescence of the exciplex.

It became obvious that locating a selective quencher of the exciplex would be very difficult. As a result, another approach was used. At room temperature, the 1-naphthonitrile-olefin system is in fast equilibrium as depicted in Scheme 1. It has been shown that as the temperature is decreased, k_q becomes increasingly larger than k-q until the reaction is essentially irreversible.[83] With such systems, it has been shown that the ratio of fluorescences intensity of (monomer)* and (exciplex)* varies with temperature. A plot of $\ln \frac{\Phi_{F_{EX}}}{\Phi_{F_m}}$ versus T^{-1} reveals the presence of two regions distinguished by the relative importance of dissociation versus deactivating processes in determining the lifetime of the exciplex.[84] In the high temperature region (the so-called α-region), $k_{-q} \gg k_{f'} + k_{d'} + k_a$ (Scheme 1) and an equilibrium is maintained. The slope of the linear section of the high temperature region is equal to $-\Delta H/R$. In the low temperature region, the condition is $k_{-q} << k_{f'} + k_{d'} + k_a$ and the exciplex is essentially irreversibly formed. A study of the temperature dependence of $\Phi_{F_{EX}}/\Phi_{F_m}$ for the 4-methyl-1-naphthonitrile-TME system (Figure 8, Table 5) and the 2-methyl-1-naphthonitrile-TME system (Figure 9) in ethyl acetate shows the behaviour described above. From Figure 8, it appears that exciplex formation becomes irreversible for the 4-methyl-1-naphthonitrile system below -10°C.

It was reasoned that by using a high TME concentration at -15°C, virtually all of the naphthonitrile S1 will be quenched to form the exciplex irreversibly. A quencher could then be used to quench the exciplex. Equivalent quenching of cycloaddition and exciplex fluorescence would prove the intermediacy of the exciplex and provide further verification for Scheme 1. The quencher chosen in this study was biacetyl. Using a concentration of 1 M TME, 98% of the 4-methyl-1-naphthonitrile S_1 was quenched. It was found that 4.3×10^{-3} m biacetyl quenched 69% of the exciplex fluorescence (Figure 7) and 48% of the cycloaddition thus providing strong evidence for the intermediacy of the exciplex.

Exciplex Decay

As shown by Figures 8 and 9, the 4-methyl-1-naphthonitrile-TME and 2-methyl-1-naphthonitrile-TME systems are in the rapid equilibrium limiting case at room temperature.[84]

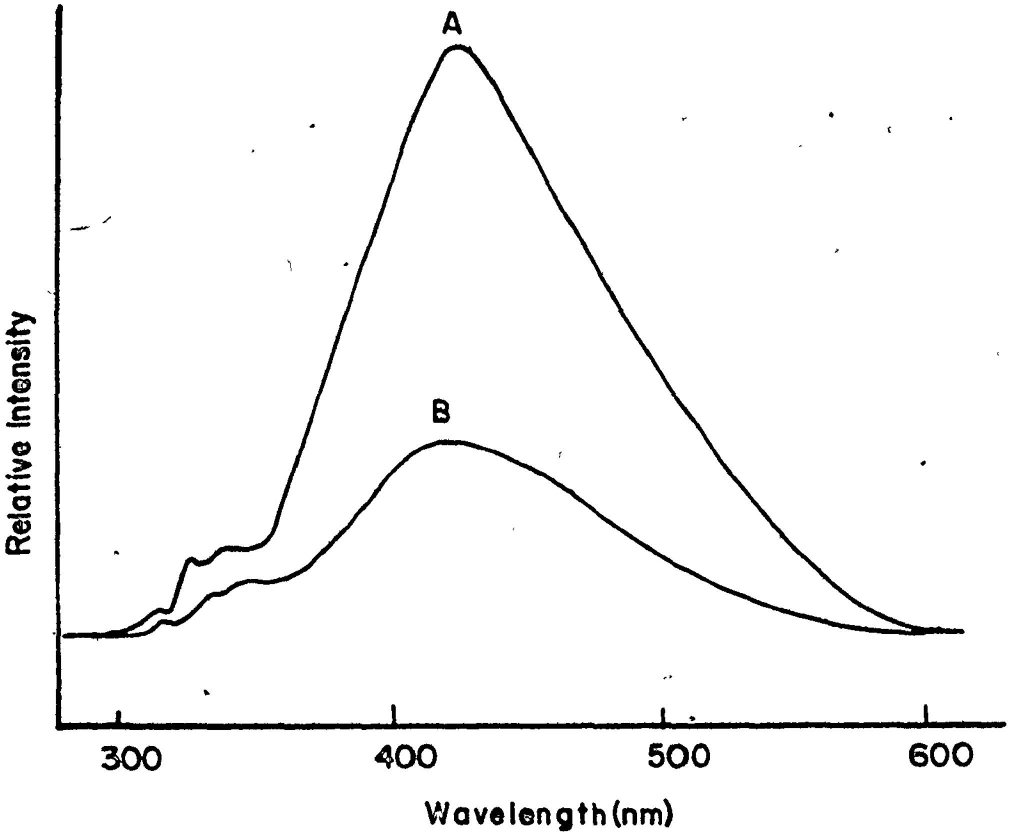


Figure 7. Fluorescence spectra of (a) 1.0×10^{-4} m 4-methyl-1-naphthonitrile and 1 m TME in ethyl acetate (A) and (b) 1.0×10^{-4} m 4-methyl-1-naphthonitrile, 1 m TME and 4.3×10^{-3} m biacetyl in ethyl acetate (B). Spectra were run at -14.5°.

In this case, the transient kinetics of a system involving reversible exciplex formation[83] are considerably simplified (Appendix A). Limiting values (high olefin concentrations) of the exciplex fluorescence quantum yield ($\Phi_{f'(lim)}$) and

Table 5. Data used in the plot[a] of $\ln(\Phi_{F_{EX}}/\Phi_{F_M})$ vs. T^{-1} for the system 4-Methyl-1-naphthonitrile-TME in ethyl acetate with [TME] = 0.063 M.

Measurement	T (^{o}K)	$T^{-1} \times 10^3$ (K^{-1})	$\frac{\Phi_{F_{EX}}}{\Phi_{F_M}}$	$\ln \frac{\Phi_{F_{EX}}}{\Phi_{F_M}}$
1	302.0	3.31	0.310	-1.171
2	296.5	3.37	0.346	-1.061
3	287.5	3.48	0.421	-0.865
4	279.5	3.58	0.487	-0.719
5	268.0	3.73	0.500	-0.693
6	263.0	3.80	0.462	-0.772
7	253.0	3.94	0.415	-0.879
8	239.5	4.18	0.315	-1.157

[a] 4-methyl-1-naphthonitrile was 1.6×10^{-4} M.

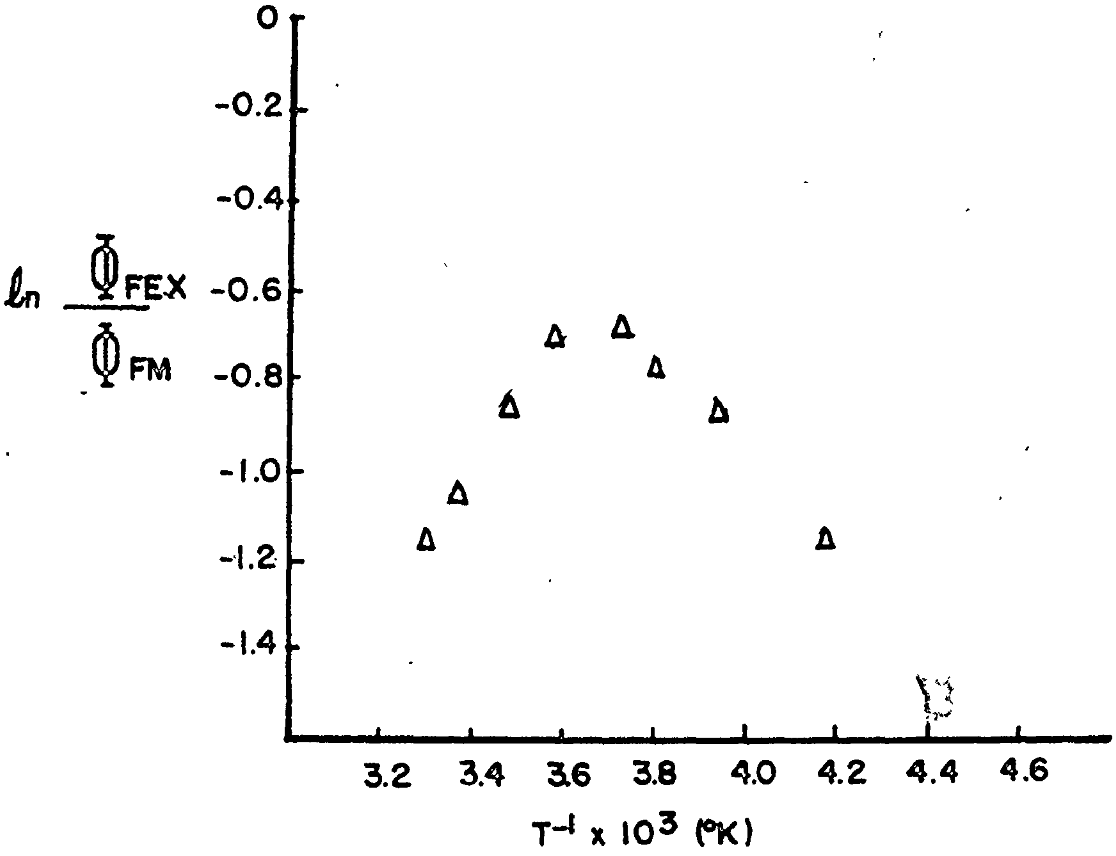


Figure 8. Plot of ℓn ($\Phi_{F_{EX}}/\Phi_{F_M}$) vs. T^{-1} for the system 4-methyl-1-naphthonitrile-TME in ethyl acetate with [TME] = 0.063 m.

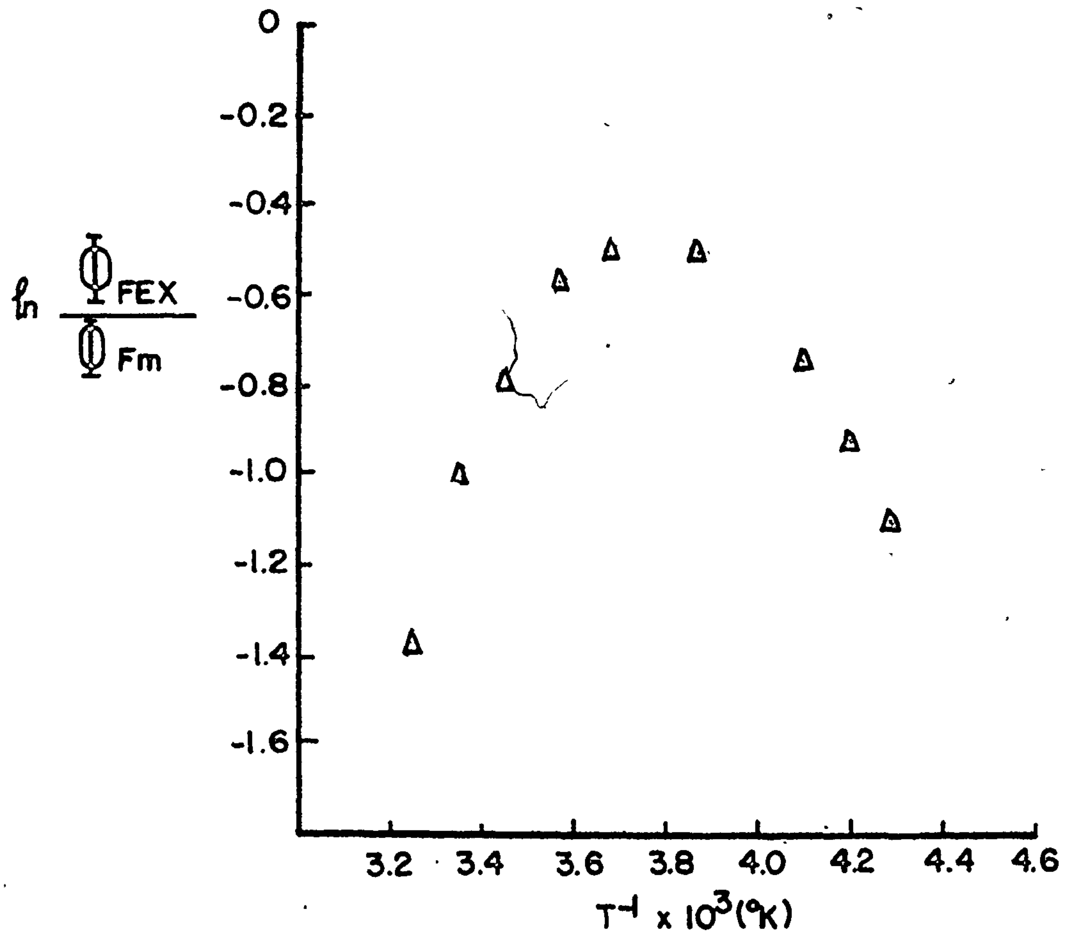
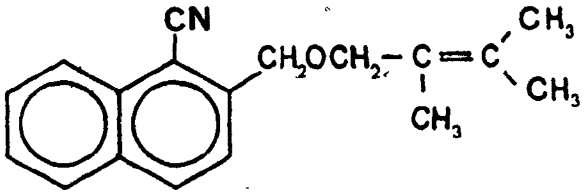


Figure 9. Plot of ℓn ($\Phi_{F_{EX}}/\Phi_{F_M}$) vs. T^{-1} for the system 2-methyl-1-naphthonitrile-TME in ethyl acetate with [TME] = 0.064 m.

the quantum yield of product formation ($\Phi_{a(lim)}$) were determined for the three methyl-1-naphthonitrile-TME systems (Table 6). When these values are used with exciplex lifetime measurements, individual values can be assigned to the exciplex unimolecular decay constants ($k_{f'}$, k_a, $k_{d'}$) shown in Scheme 1. These rate constants are tabulated in Table 7.

Exciplex Multiplicity

As can be seen from Table 6, the 2-methyl-1-naphthonitrile-TME exciplex collapses to products very inefficiently. One possible explanation involves the formation of exciplex triplets which do not form photoproducts. As a test of this hypothesis, an attempt was made to detect triplets from this system using biacetyl phosphorescence as monitor.[85] In an analogous experiment, a search was made for a triplet exciplex formed from the irradiation of 2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether (53). The synthesis and photochemistry of (53) will be described later.



53

At the concentration of biacetyl used in the experiment (1 x 10^{-4} m), it was calculated that approximately 1% of the

Table 6. Quantum Yields and Lifetimes for the Methyl-1-Naphthonitrile-TME Exciplexes

Fluorescer	Solvent	Exciplex Emission Maximum (NM)	Φ_a^a ± 15%	$\Phi_{F'}$ ± 20%	$\tau_{(NS)}^a$ ± 5%
2-Me-1-NN	Benzene	391	0.02	0.172	13.83
4-Me-1-NN	Benzene	392	0.51[b]	0.080	6.21
	Ethyl Acetate	424	0.19	---	11.18
6-Me-1-NN	Benzene	392	0.28	0.118	9.83

[a] TME concentrations adjusted to allow 96% quenching.

[b] Determined from intercept of Plot C, Figure 6. Realistic errors are as indicated.

Table 7. Decay constants for the Methyl-1-Naphthonitrile-Tetramethylethylene Exciplexes

Fluorescer	Solvent	k_a ($\times 10^{-7}$ sec^{-1})	$k_{F'}$ ($\times 10^{-7}$ sec^{-1})	$k_{d'}$ ($\times 10^{-7}$ sec^{-1})
2-Me-1-NN	Benzene	0.14 ± 0.02	1.2 ± 0.2	6 ± 2
4-Me-1-NN	Benzene	8.2 ± 1.3	1.3 ± 0.3	7 ± 2
	Ethyl Acetate	1.7 ± 0.3	---	---
6-Me-1-NN	Benzene	2.8 ± 0.4	1.2 ± 0.2	6 ± 2

2-methyl-1-naphthonitrile fluorescence would be quenched. The calculation assumed diffusion controlled quenching and used the fluorescence lifetime of the naphthonitrile monomer (11.1 nsec). Also, the naphthonitrile concentration (2.0×10^{-4} m) and the excitation wavelength (320 nm) were chosen to minimize the light absorbed by biacetyl. As a result of the above conditions, biacetyl phosphorescence would have to result from the sensitization of biacetyl to its triplet state by the 2-methyl-1-naphthonitrile triplet.

It was found that biacetyl phosphorescence was observed in the 2-methyl-1-naphthonitrile-biacetyl solution in benzene. Another experiment was performed using a benzene solution containing the same concentrations of 2-methyl-1-naphthonitrile and biacetyl. As well, the solution was 2.0 m in tetramethylethylene. At this concentration of the olefin, 95% of the emission of 2-methyl-1-naphthonitrile was quenched. No biacetyl phosphorescence was observed indicating the absence of exciplex triplet in this system.

In a similar experiment, biacetyl phosphorescence was found to be absent in a benzene solution which was 1.0×10^{-4} m in biacetyl and 2.2×10^{-4} m in 2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether (53). This indicated the absence of the exciplex triplet.

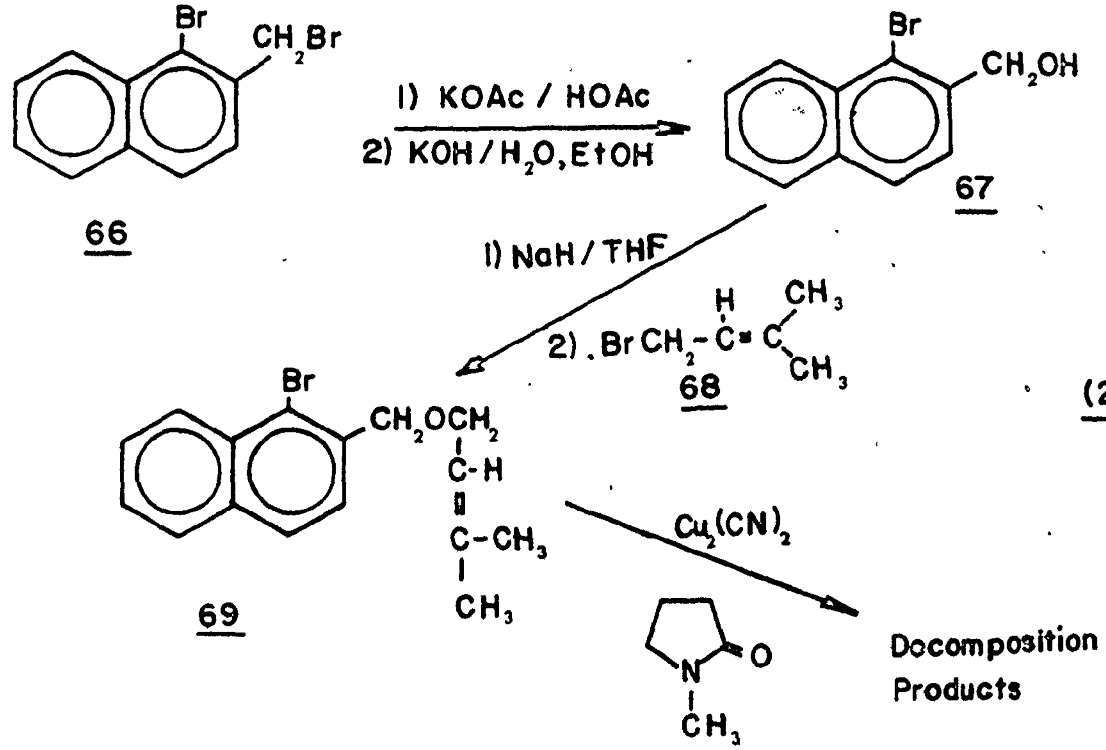
The above experiments assumed that the exciplex T_1, if present, would be of similar energy to the triplet state of

2-methyl-1-naphthonitrile.

(B) THE BICHROMOPHORIC SYSTEMS

i) Synthesis of Bichromophoric Molecules

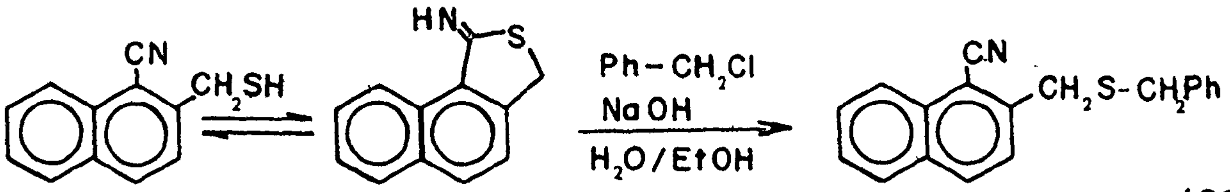
A general method for the synthesis of compounds containing both the naphthonitrile and the olefin moieties separated by a three-atom chain was sought. Bouas-Laurent and coworkers[86] have successfully used the sequence $-CH_2O-CH_2-$ to separate substituted anthryl groups. They also suggested that the ether linkage may be preferrable to the $-CH_2-CH_2-CH_2-$ sequence because of the expected lower rotational barrier about the C-O bonds which would facilitate cyclomerization.[87] Our initial effort involved the introduction of the side chain to a bromonaphthalene via a Williamson ether synthesis (equation (27)).



(27)

It was found that 2-methyl-2-butenyl 1-bromo-2-methylnaphthylether (69) was not stable to the conditions required for the cyanide displacement reaction.

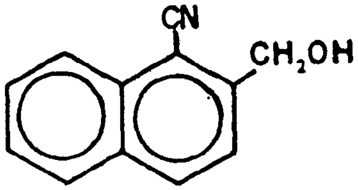
Stacy and coworkers[88] have reported that 2-mercaptomethyl-1-naphthonitrile (70a) exists in equilibrium with its ring chain tautomer naphtho[1,2-c]thiophen-1(3H)-mine (70b). It was shown that sulfide (71) could be synthesized in an 80% yield from (70) and benzylchloride in basic media (equation (28)).



(28)

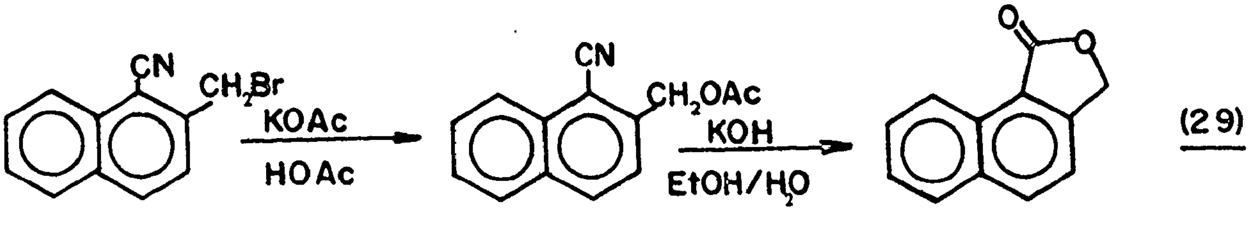
70a 70b 71

An analogous reaction with 1-cyano-2-naphthalenemethanol (72)



72

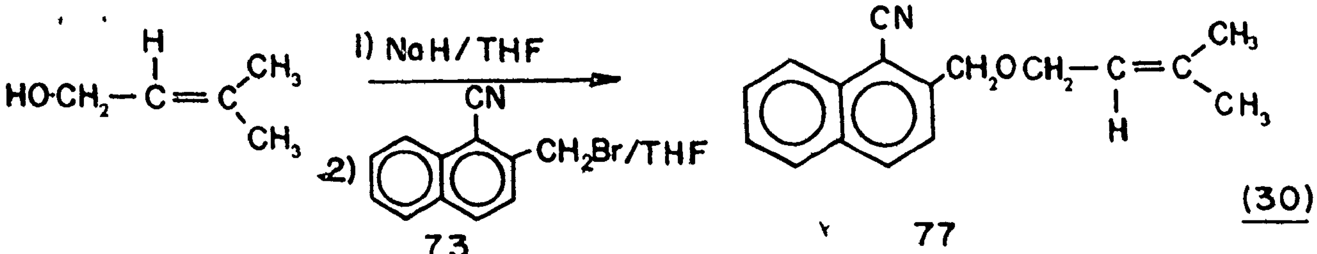
and the appropriate bromoolefin seemed a reasonable approach. Unfortunately, the aromatic alcohol (72) could not be synthesized from the acetate derivative (74) (equation (29)). The only product isolated from the reaction was 2-hydroxymethylnaphthalene-1-carboxylic lactone (75). Presumably, it is formed by hydrolysis of the intermediate iminolactone which



73 74 75

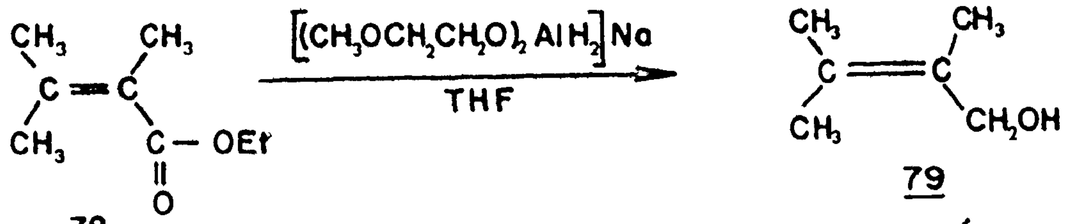
is the oxygen analogue of the iminothiolactone (70b).

The successful route utilized reaction of an unsaturated alkoxide (76) with 2-bromomethyl-1-naphthonitrile (73). As shown in equation (30), 2-methyl-2-butenyl 1-cyano-2-methylnaphthyl ether (77) was successfully synthesized using this



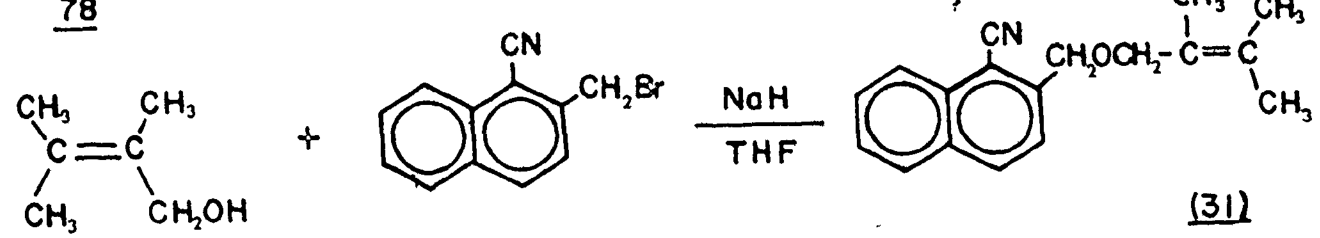
76 77

approach. Similarly, 2,3-dimethyl-but-2-enyl 1-cyano-2-methylnaphthyl ether (53) was formed by reaction of 2-bromomethyl-1-naphthonitrile (73) with the alkoxide from 2,3-dimethylbut-2-ene-1-ol (79) (equation (31)). This alcohol was made by reduction of ethyl-2,3-dimethyl-2-butenoate (78) with sodium bis(2-methoxyethoxy)-aluminum hydride (Red-Al).



78

79



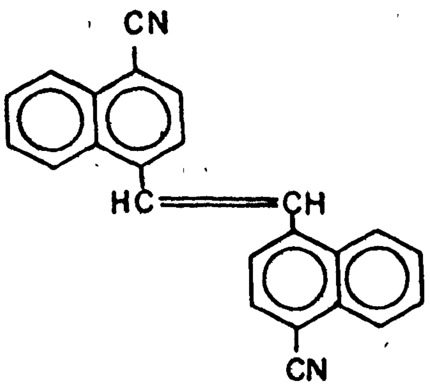
79

73

53

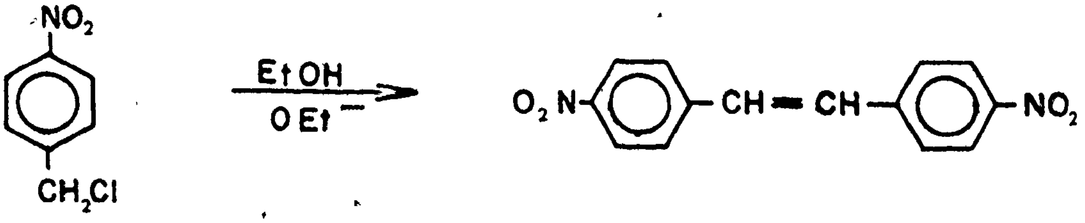
(31)

The next target molecule to be synthesized was one in which the side chain was attached to the "4" position of the aromatic ring of 1-naphthonitrile. The first route attempted involved the treatment of the alkoxide from 2,3-dimethyl-but-2-ene-1-ol (79) with 4-bromomethyl-1-naphthonitrile (83). On work-up, a yellow solid was isolated. NMR



80

analysis of the ether extracts showed the absence of aromatic products. The IR of the yellow solid showed an absorption at 2221 cm^{-1} (nitrile stretch). The mass spectrum showed the parent ion at m/e 330 and a peak at m/e 178 consistent with the molecular ion $C_{24}H_{14}N_2^+$ and loss of $C_{11}H_6N$, respectively. On the basis of this data, the product is tentatively assigned the structure 1,2-bis-(4-cyanonaphthyl)-ethene (80). Russell and Pecoraro[88] have reported a similar reaction in which p-nitrobenzyl chloride (81) reacts in the presence of ethoxide ion to give a 75% yield of 4,4'-dinitrostilbene (82) (equation (32)).



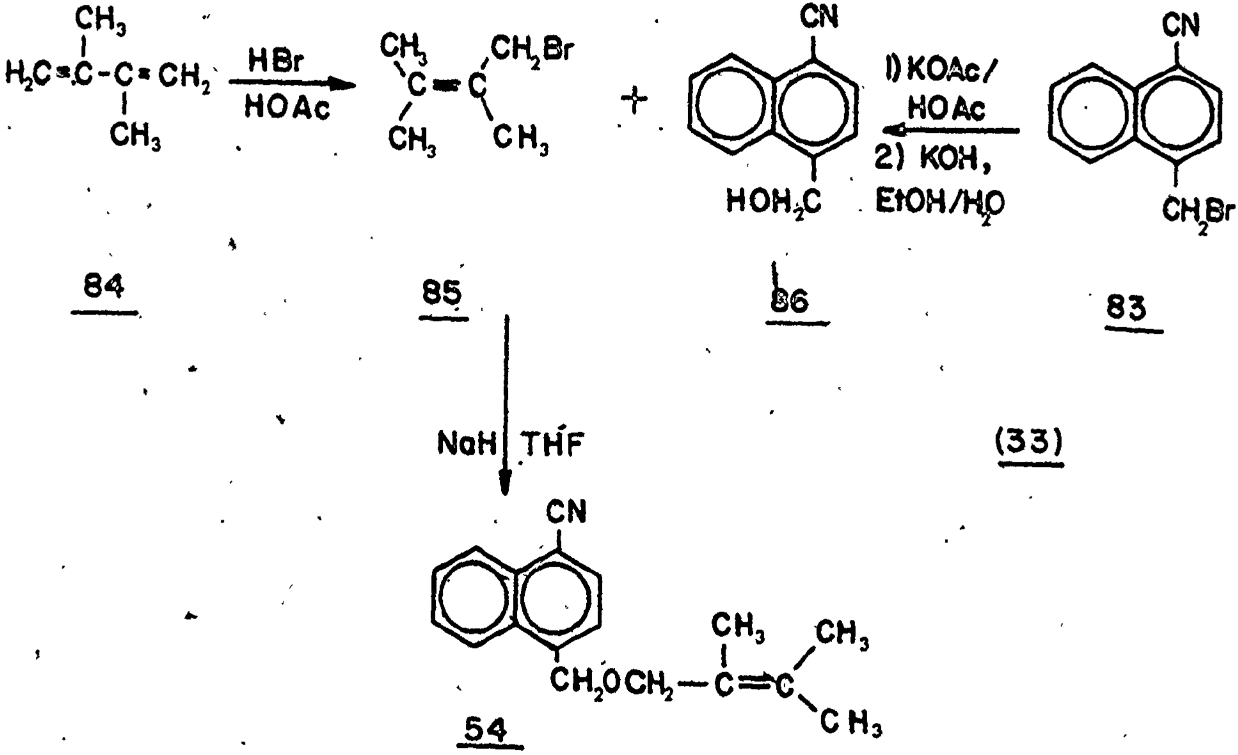
81

82

(32)

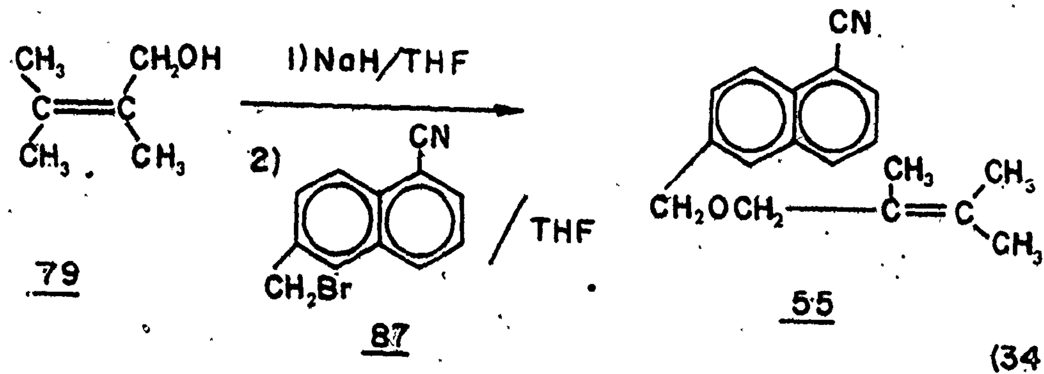
2,3-Dimethyl-2-butenyl 1-cyano-4-methylnaphthyl ether (54) was synthesized by reaction of the alkoxide from 1-cyano-4-hydroxymethylnaphthalene (86) with 1-bromo-2,3-dimethyl-2-butene (85) (equation (33)). The latter was prepared by reaction of 2,3-dimethyl-1,3-butadiene (84) with HBr in acetic acid.

The final bichromophoric molecule to be synthesized



(33)

was one in which the side chain was attached to the "6"-position of the aromatic ring of the 1-naphthonitrile. This compound was readily prepared from the alkoxide of (79) and 6-bromomethyl-1-naphthonitrile (87) to give 2,3-dimethyl-2-butenyl 1-cyano-6-methylnaphthyl ether (55) (equation (34)).

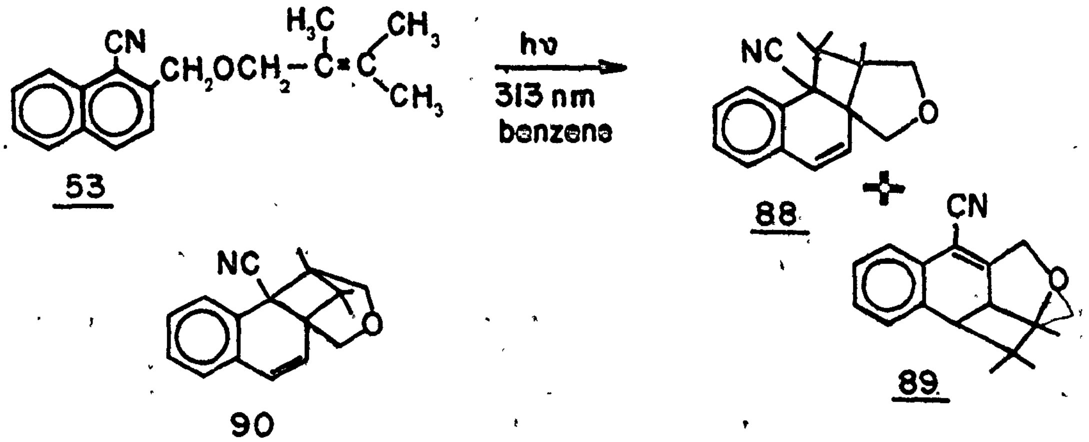


(34)

ii) Photochemistry of Bichromophoric Molecules

Products and Structural Assignments

Irradiation of 2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether (53) in benzene with 313 nm light gave two products which were separated by silica gel chromatography and were identified as 7-cyano-5,6,6-trimethyl-8,9-benzo-3-oxatricyclo[5.4.0.0^{1,5}]undeca-8,10-diene (88) and 6-cyano-1,10,10-trimethyl-7,8-benzo-3-oxatricyclo[5.3.1.1^{5,9}]-deca-5,7-diene (89) (equation (35)). The ratio of the products varied with time. In the early stages of the irradiation, (88) predominated, but upon continued irradiation, a build-up of (89) was observed.



53 88 89 90 (35)

The structure of photoproduct (88), m.p. 141.5-142.5°, was established by single-crystal X-ray diffraction[89] (Figure 10). The crystal structure was necessary to differentiate (88) from the "crossed addition product" (90). Crystal data (kindly provided by Professor C.J.L. Lock and R. Faggiani):[89]

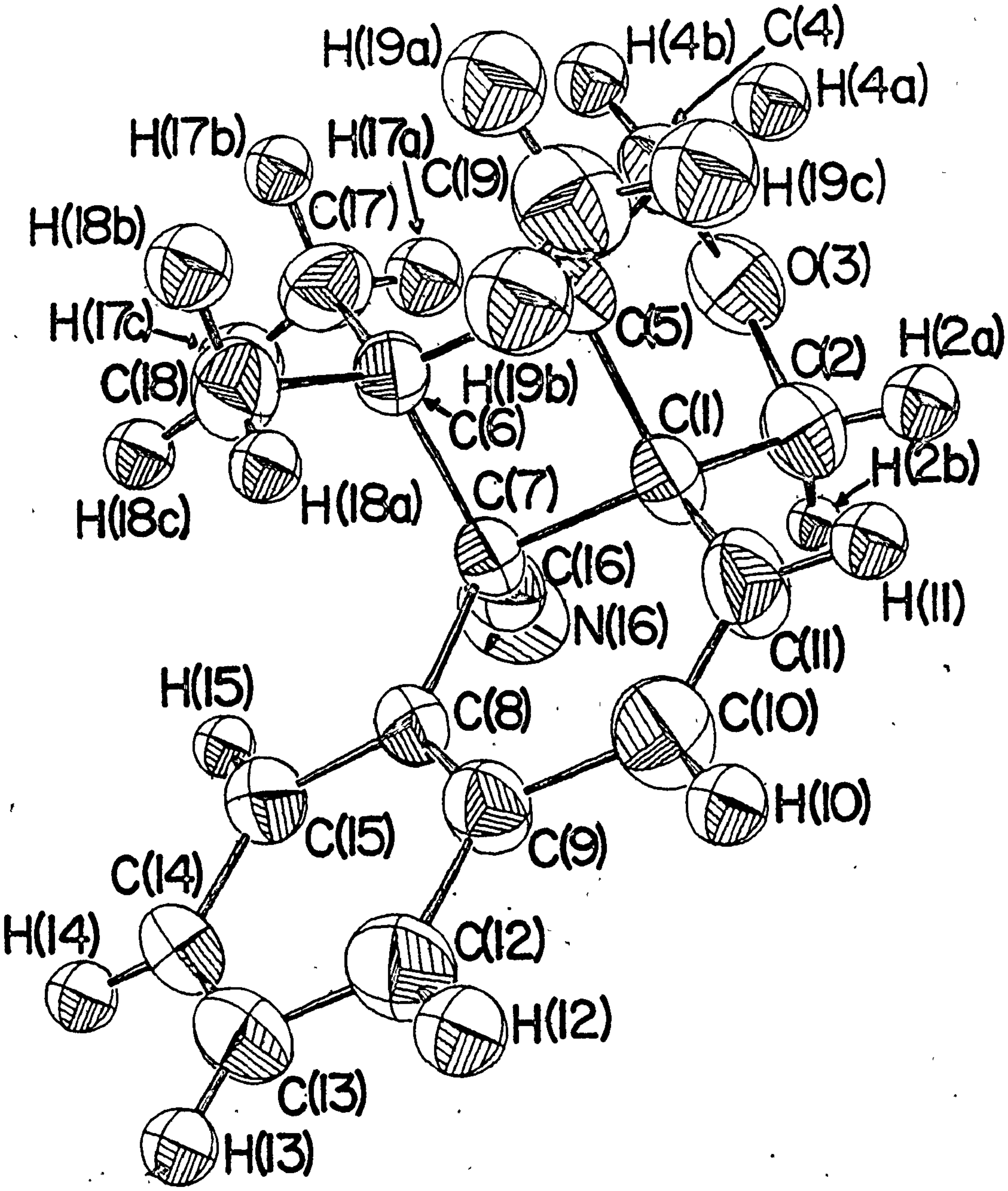


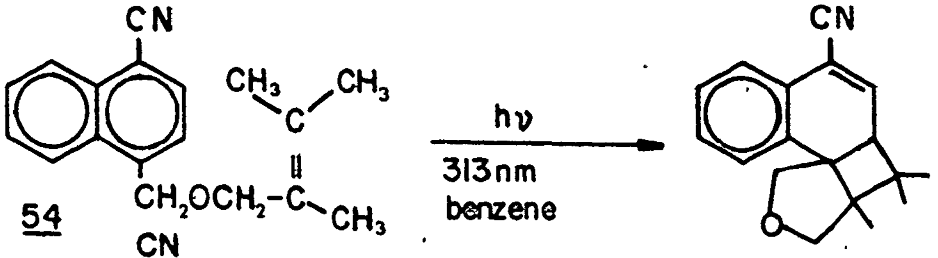
Figure 10. Structure of 7-cyano-5,6,6-trimethyl-8,9-benzo-3-oxatricyclo[5.4.0.$0^{1,5}$]undeca-8,10-diene, 88.

$C_{18}H_{19}NO$, monoclinic space group $P2_1/c$, C_{2h}, (No. 14), a = 12.088(3), b = 8.162(2), c = 15.152(3) Å, z = 4. A total of 2378 independent reflections in $2\theta_{M_oK_\alpha} \leq 55^\circ$ was collected on a Syntex $P2_1$ automated diffractometer using the θ-2θ scan mode and graphite monochromated M_o radiation. Initial coordinates for the non-hydrogen atoms were obtained by direct methods (MULTAN). Full-matrix least-squares refinement of the structural parameters and a scale factor, using anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms led to $R_1 = 0.064$, $R_2 = 0.060$. Bond lengths and angles within the structure are normal.

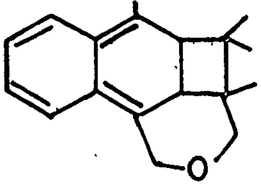
The nmr spectrum of (88) showed the methyl groups at δ 0.73, 1.03 and 1.37 (s, 3H each). Two AB quartets (δ 3.30, 4.43, J = 10.2 Hz, 2H and δ 3.36, 4.28, J = 10.2 Hz, 2H) were attributed to the methylene groups. The vinylic protons showed as an AB quartet (δ 5.40, 6.36, J = 10.0 Hz, 2H). The protons of the aromatic ring resonated at δ 7.0-7.3.

The structure of (89), m.p. 119-120°, was assigned from its spectra. Important features are as follows: IR 2217 cm^{-1} (conjugated CN); ^1H NMR (FT, 80 MHz, $CDCl_3$): δ 6.9-7.1 (m, aromatics), 3.85, 2.95 (AB quartets, J = 9.8 Hz, 2H, bridgehead methines), at δ 3.73 (J = 10.0 Hz, 2H, allylic CH_2), centred at δ 3.15 (J = 5.0 Hz, 2H, CH_2). Methyl groups appeared at δ 0.0, 0.059, and 1.1 (s, each 3H).

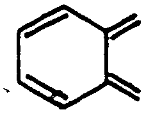
Irradiation of 2,3-dimethyl-2-butenyl 1-cyano-4-methylnaphthyl ether (54) in benzene with 313 nm light gave a dark yellow solution. Vpc analysis indicated the presence of two products in the ratio of 4.8:1. The major product, isolated by silica gel chromatography, was shown to be 9-cyano-5,6,6-trimethyl-10,11-benzo-3-oxatricyclo[5.4.0.$0^{1,5}$]undeca-8,10-diene (91), m.p. 138.5-139.5° (equation (36)). The structure of (91) was assigned from its spectra and the regiochemistry was assigned by analogy with the photoproduct (91) from irradiation of (53). The IR showed the conjugated nitrile stretch at 2220 cm^{-1}. The NMR of (91) showed resonances at δ 0.77, 1.04, and 1.48 (s, 3H each) due to the methyl groups. A doublet of doublets (δ 2.97, 6.53, J = 5.4 Hz, 2H) was assigned to the ring methines. Two AB quartets (δ 3.40, 3.95, J = 9.6 Hz, 2H and δ 3.50, 4.28, J = 9.3 Hz, 2H) were attributed to the methylene groups. The protons of the aromatic ring resonated at δ 6.9-7.5 (4H).



(36)



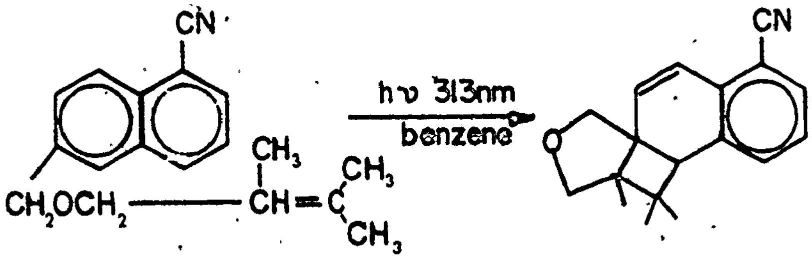
92



93

The minor product could not be isolated by chromatography.

Fractions 40-47 from the chromatographic separation showed a carbonyl stretch (1710 cm^{-1}) in the IR indicating that oxidation product had been formed. The UV of the irradiated mixture showed a maximum at 372 nm consistent with the formation of a compound such as (92). Flynn and Michl have reported that o-xylylene (93) has an absorption maximum at 375 nm.[90] Photoaddition to the 2,3-bond of 2-naphthonitrile by methyl vinyl ether to give a reactive intermediate has been proposed by McCullough and Chamberlain.[91] Attempts to trap (92) with dimethylacetylenedicarboxylate were unsuccessful. The irradiation of (54) in a sealed NMR tube in benzene-d_6 was performed in an attempt to see NMR signals due to the bridgehead methines of (92). Unfortunately, these protons could not be detected by NMR.



55 94 (37)

Irradiation of 2,3-dimethyl-2-butenyl 1-cyano-6-methylnaphthyl ether (55) in benzene gave one product which was isolated by silica gel chromatography. It was identified as 1,11,11-trimethyl-8,9-(6'-cyanobenzo)-3-oxatricyclo[6.3.0.$0^{5,10}$]-undeca-6,8-diene (94) (equation (37)).

The structure of photoproduct (94) was established by inspection of its spectra and the regiochemistry was assigned by analogy with the major photoproduct (88) formed in the irradiation of 2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether (53). The IR showed the conjugated nitrile band at 2219 cm^{-1}. NMR showed the methyl groups at δ 0.87, 1.20 and 1.33 (singlets, 3H each). Two AB quartets (δ 3.37, 3.98, J = 9.3 Hz, 2H and δ 3.43, 4.37, J = 10.0 Hz, 2H) were assigned to the methylene groups. The ring methine (δ 3.47, singlet, 1H) was observed when the AB quartet (δ 3.43, 4.37) was irradiated at δ 4.37. The aromatic protons resonated at δ 7.2-7.5 (3H).

The three 2,3-dimethyl-2-butenyl 1-cyanomethylnaphthyl ethers (53), (54) and (55) were purified by reverse phase H.P.L.C. and as depicted in Figure 11, all formed internal exciplexes which fluoresce in ethyl acetate. The fluorescence spectra of (53) and (54) in benzene show a tailing of the monomer fluorescence attributable to exciplex emission. In the case of (55), an exciplex with a maximum at 402 formed in benzene. Bimolecular complex formation is precluded because exciplex emission persists at 10^{-5} M. With ethyl acetate and benzene as the solvents, it was shown, by using the parent methylnaphthonitriles as standards, that 95% of the naphthonitrile monomer fluorescence was quenched by interaction with the olefinic side chain. The fluorescence quantum yields of the three methylnaphthonitriles have been determined in both benzene and ethyl acetate (Table 8). The fluorescence quantum yields of the three 2,3-dimethyl-2-butenyl 1-cyanomethylnaphthyl ethers are all 0.01 in both ethyl acetate and benzene. From intermolecular quenching experiments involving a methylnaphthonitrile and tetramethylethylene in ethyl

Table 8. Monomer Emission Quantum Yields for Methyl-1-Naphthonitriles in Benzene and Ethyl Acetate.

Fluorescer	Fluorescence Quantum Yield (± 20%)	
	Benzene	Ethyl Acetate
2-Methyl-1-naphthonitrile	0.21	0.26
4-Methyl-1-naphthonitrile	0.22	0.28
6-Methyl-1-naphthonitrile	0.16	0.25

acetate, 95% quenching of the monomer fluorescence was achieved, when the quencher concentration was 0.5 M.

The product **quantum** yields for (88), (91) and (94) in benzene are given in Table 9. The products from the irradiation of (53), (54) and (55) arise from collapse of the singlet exciplex. No triplets were detected from 2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether (53) using biacetyl as monitor.[85]

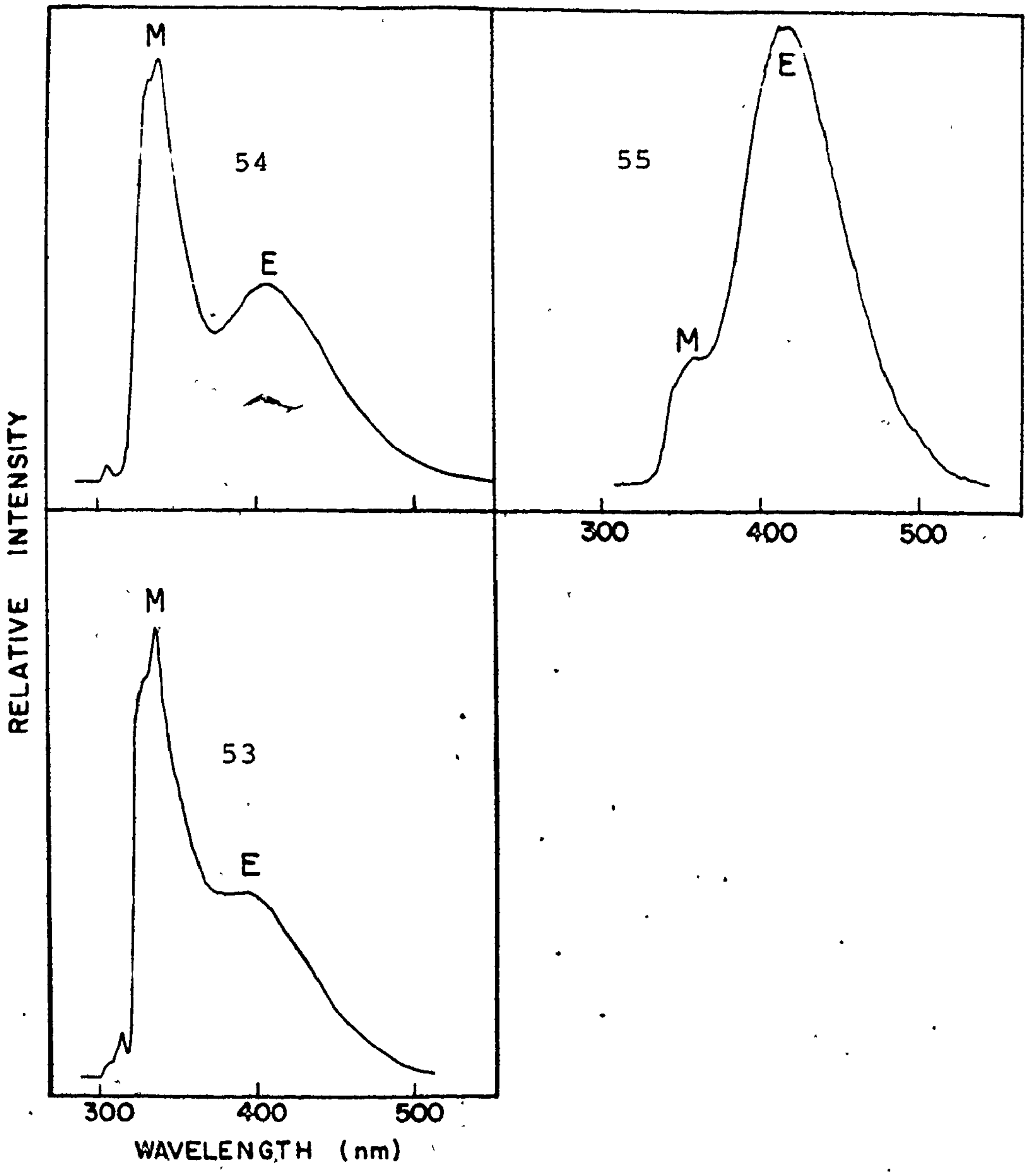


Figure 11. Fluorescence spectra of 53, 54 and 55 in ethylacetate at 10^{-4} M. Monomer (M) and exciplex emission (E) are visible with the latter at 418 nm (53), 428 nm (54) and 420 nm (55).

Table 9. Quantum Yields of Product Formation in the Irradiation of Bichromophoric Compounds (53), (54) and (55)[a]

Reactant[b]	Adduct	Quantum Yield, Φ_a^c mmole/meinstein
2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether (53)	(88)	0.68
2,3-dimethyl-2-butenyl 1-cyano 4-methylnaphthyl ether (54)	(91)	0.44
2,3-dimethyl-2-butenyl 1-cyano 6-methylnaphthyl ether (55)	(94)	0.54

[a] The solvent was benzene at 23°C.

[b] The reactant concentration was 0.001 M.

[c] Average of several runs. Individual values generally agreed to within 5%.

DISCUSSION

DISCUSSION

Formation of cyclobutanes (64) and (65) was predictable from previous results reported for the photoadditions of naphthonitriles[28,30b] and other substituted naphthalenes.[45,91] As expected, the limiting quantum yields for these additions are high, in the range 0.2-0.5 (Table 6, Results section). The photoaddition of 2-methyl-1-naphthonitrile (56) and tetramethylethylene was distinctive in that simultaneous formation of different products occurred (equation (21)) and the reaction was less efficient (ϕ^{a}_{lim} = 0.02). The inefficiency in formation of cyclobutane (59) is not surprising since four quaternary centres are formed at once.[92] Product (61) is interesting[72] and may be formed in a concerted reaction, via electron transfer[72] or by hydrogen abstraction from the TME.[93]

The intramolecular reactions of bichromophoric compounds (53)-(55) serve as useful comparisons with the bimolecular cases. Reaction of (53) involves addition of the alkene chromophore chiefly to the 1,2-bond of the naphthonitrile, as had been observed with the 2-methyl-1-naphthonitrile-TME system. Irradiation of (53) gives mainly (88) in a regiospecific manner consistent with the "rule of five".[94]

(91) and (94) are formed by addition of the TME chromophore at the naphthonitrile 3,4- and 5,6-bond respectively.

These reactions are not observed in the bimolecular systems.

Linking with a saturated chain can facilitate excimer fluorescence[50a] and intramolecular reactions.[86,95] Since exciplexes are evidently intermediates in these reactions, the chain could affect the addition reaction at two points (a) in exciplex formation and/or (b) in collapse of the exciplex to products. In the rest of the discussion, the effect of linking, and of methyl substitution, on these two steps in the reaction will be considered.

Exciplex Formation

The studies of Ware and coworkers[27,83] have demonstrated that for non-polar and medium polarity solvents, the processes summarized in Scheme 1 (Results section) are sufficient to describe the photokinetics of 1-naphthonitrile and TME. Our results are in agreement. In the case of the three methyl-1-naphthonitriles, exciplex formation is also rapidly reversible above +5°C (Figures 8 and 9); the exciplex does not decay to triplet naphthonitrile and the exciplex is evidently an intermediate in the cycloaddition. Also, quenching of the exciplex by TME is unimportant in the 1-3 M TME range as shown by lifetime measurements with 2-methyl-1-naphthonitrile and an isoemissive point is observed in the fluorescence quenching of the methyl-1-naphthonitriles by TME. This evidence indicates the exciplex possesses a 1:1 stoichiometry.

Using steady state data and lifetimes, the decay rate constants $k_{F'}$, $k_{d'}$ and k_a for 2-methyl- and 4-methyl-1-naphthonitrile-TME systems in benzene were determined. The equations (24), (25a), (38-40) were used (see Appendix).

$$\frac{\phi_0}{\phi} = 1 + KSV(TME) \tag{24}$$

where

$$KSV = \frac{k_q(k_{F'} + k_{d'} + k_a)\tau_0}{k_{-q} + k_{F'} + k_{d'} + k_a} \tag{25a}$$

$$\phi^F_{lim} = \frac{k_{F'}}{k_{F'} + k_{d'} + k_a} = k_{F'} \cdot \tau_{lim} \tag{38}$$

$$\phi^a_{lim} = \frac{k_a}{k_{F'} + k_{d'} + k_a} = k_a \cdot \tau_{lim} \tag{39}$$

$$\phi^f_0 = \frac{k_F}{k_F + k_{isc} + k_f} = k_F \tau_0 \tag{40}$$

Note that $(k_{F'} + k_{d'} + k_a)$ is the single exponential decay constant for exciplex fluorescence at infinite [TME]. In practice, τ_{lim} was determined at > 95% monomer quenching. Thus, rate constants derived using equations (38) and (39) are approximate. However, τ_{lim} for the 1-naphthonitrile-TME system in hexane (3.75 nsec)[34] is close to the value determined in the complete kinetic analysis of the 1-naphthonitrile-TME exciplex (3.31 nsec).[27] The exciplex decay rate constants are given in Table 7 (Results section). The ratio, KSV/τ was determined from equation (24) and the ratios are listed in Table 3.

The ratios KSV/τ, appear to be reasonable measures of exciplex **stability** (Table 3, Results section). As expected, methyl substitution **destabilizes** the exciplex and an increase in solvent polarity causes an increase in exciplex stability. Also, the position of methyl substitution was found to be unimportant indicating there is little steric interference with exciplex formation. A similar conclusion was reached by Morrison and Froehlich[47] based on their quenching studies of alkylbenzenes with piperylene. A non-fluorescent exciplex is formed with this system.

The fluorescence spectra of (53), (54) and (55) in ethyl acetate has been shown in Figure 11 (Results section). The monomer emission is approximately 95% quenched by the olefinic side chain. Consequently, although the intramolecular exciplexes are formed efficiently, their emission is weak[96] except for (55), where exciplex fluorescence intensity is similar to the bimolecular exciplexes. These spectra demonstrate that formation of the fluorescent exciplex is not dependent upon bonding of the TME unit at a particular ring position of the naphthonitrile. This is consistent with the absence of a steric affect on methyl substitution.

Exciplex Decay

According to Scheme 1, three decay rate constants (k_a, $k_{F'}$, $k_{d'}$) account for the deactivation of the exciplex. The radiative rate constant $k_{F'}$ is virtually independent of the position of the methyl substituent, which is consistent with the notion that a "loose" exciplex is the fluorescent species.

The sum of $k_a + k_{d'}$ is also insensitive to the site of the methyl group. Thus, the passage from the exciplex to the pericyclic minimum as envisioned by Michl's model (Figure 3, Introduction) is essentially the same for the three methyl-1-naphthonitrile systems. The rate of product formation (k_a), however, is highly sensitive to the position of the methyl group. (64) is formed 59 times faster than is the case for (59) where the methyl substituent is alpha to the cyano group. Thus, much of the organization preceding cycloadduct formation appears to occur at the pericyclic minimum. Also, it is tempting to conclude that the preferred geometry at the pericyclic minimum is a localized one in which the TME is situated over the 1,2-bond of the naphthonitrile.

It should be noted that crossing from the pericyclic minimum to the ground state is highly dependent upon the position of the methyl group as indicated by the $k_{d'}/k_a$ ratios. For the 4-methyl-1-naphthonitrile and 6-methyl-1-naphthonitrile systems, the ratios are 0.85 and 2.1, respectively. The near unity of these ratios appears to show that the processes themselves are similar. Michl[36a] has previously suggested this similarity on theoretical grounds and Caldwell[42] has reported that $k_{d'}$ and k_a are nearly identical for the photocycloadditions involving substituted 9-cyanophenanthrenes with anethole. The 2-methyl-1-naphthonitrile system is distinctive in that the $k_{d'}/k_a$ ratio is 42.9. The crossing from the pericyclic minimum to the ground state is being perturbed in such a way that k_a

is much slower than was the case for the other two methyl-1-naphthonitrile systems. However, k_d, was found to be the same for all three cases.

Although individual rate constants for the decay of the intramolecular exciplexes were not determined some comments can be made about these systems based on the products formed in the photoreactions. The quantum yield for formation of (88) was 0.68 (Table 9, Results section), while the limiting quantum yield for (59) was 0.020. Since (53) is a 2-alkyl-1-naphthonitrile, the much higher quantum yield of (88) versus (59) indicates that the order introduced in the reactant by the three atom chain significantly favours exciplex collapse to product. Also, the ability of (54) and (55) to form products efficiently at sites of the naphthonitrile ring not seen in the bimolecular reactions suggests that various geometries with similar energies are possible at the pericyclic minimum.

CONCLUSIONS

Bichromophoric compounds, when coupled with their bimolecular analogues, have been shown to be useful probes of the steric requirements of naphthonitrile-alkene exciplexes. The results of this study can be qualitatively rationalized within the context of existing theories of exciplex formation and behaviour. The demonstrated success of tethered chromophores encourages their further use in the investigation of the chemistry of exciplexes. For example, the bichromophoric molecules synthesized in this study could be used to probe the behaviour of naphthonitrile-alkene systems in polar solvents, such as methanol. Also, it would be of interest to synthesize molecules in which the olefin moiety is held at fixed distances from the naphthonitrile ring in order to determine the threshold distance required for exciplex formation. Finally, the reactivities of various positions of the naphthonitrile ring to cycloaddition could be investigated by synthesizing a bichromophoric molecule in which the chain length is greater than three.

EXPERIMENTAL

EXPERIMENTAL

Materials

All solvents were reagent grade and were distilled before use. Benzene was carefully fractionated to remove water. Tetrahydrofuran was freshly distilled from sodium and benzophenone before use.

Tetramethylethylene was obtained either from the Aldrich Chemical Company as Gold Label 99^+% grade or from the Fairfield Chemical Company. It was distilled through a short vigreux column prior to use, b.p. 73°. For quantitative work, tetramethylethylene was chromatographed on a column of basic alumina (I.C.N. Pharmaceuticals, activity 1) immediately before use.

1-Bromo-2-methylnaphthalene, 1-bromo-4-methylnaphthalene, N-methylpyrrolidinone, 2-furoic acid, isoprene, 2,3-dimethyl-1,3-butadiene, ethyl-2-bromopropionate and 3-methylbut-2-ene-1-ol were obtained from the Aldrich Chemical Company.

CH_3OD was prepared by the method of Streitweiser and coworkers.[97] Dimethyl carbonate was obtained from BDH Ltd.

Photochemical and Analytical Methods

All irradiations were done under argon (Canadian Liquid Air, certified grade) in either a Srinivasan-Griffin Photochemical Reactor (Rayonet) using RPR 3000 Å type lamps or with a Hanovia Type L 450 W mercury vapour lamp in a quartz water-cooled immersion well.

Column chromatography was on silica gel (Baker Analysed Reagent grade (60-200 mesh), Fisher grade 923 (100-200 mesh), or Macherey, Nagel and Co. MN Kiesel gel G). The chromatographic technique of Still and coworkers[73] required the use of Merck silica gel 60 (30-230 mesh). All columns were dry-packed and the length of each column was 6 inches. The diameter of the column to be used depended upon the weight of the material to be chromatographed.

Analytical vapour phase chromatography (vpc) was performed on a Varian-Aerograph series 200 or a Tracor 560 dual column instrument with flame ionization detectors. The column used on the Varian instrument was 5' x 1/8" of 5% SE-30 on 60/80 Chromosorb W. The Tracor instrument was used with
(a) 6' x 1/4" column of 3% OV-1 on Chromosorb WHP, and
(b) 4' x 1/4" column of 3% OV-1 on Chromosorb WHP. The flow rate of the carrier gas (helium) was 45-55 ml/min. Integration of vpc peak areas was carried out using a Varian Aerograph model 485 Electronic Digital Integrator.

Preparative vpc was on an Aerograph Model 200 dual column instrument with thermal conductivity detectors. A helium flow rate of ca. 50 ml/min was used with a 7' x 1/4" column of 15% SE-30 on Chromosorb W.

For high pressure liquid chromatography, a system with a single 2000 psi pump was used. The detection system was a fixed wavelength (254 nm) ultraviolet monitor. "Reverse phase" chromatography was used with 95% methanol/water on a Whatman Magnum-9ODS-2 9.0 x 500 mm column with 10 μm packing and a guard column.

The nuclear magnetic resonance (NMR) spectra were obtained with a Varian EM-390 or a Bruker WH-90 FT spectrometer. Chemical shifts (δ) are reported as ppm downfield from tetramethylsilane as internal standard. Mass spectra were recorded on a Perkin-Elmer 283 infrared spectrophotometer using spectral grade chloroform as solvent. Ultraviolet spectra were run on a Cary 14 spectrophotometer.

Fluorescence spectra were taken using an Aminco Bowman spectrofluorimeter utilizing a Hanovia 200 w mercury-zenon lamp. Melting points were measured using a Kofler hot stage and are reported uncorrected. Microanalyses were determined by Galbraith Laboratories, Inc., Knoxville, Tennessee.

A. Methyl-1-naphthonitrile-tetramethylethylene Systems

2-Methyl-1-naphthonitrile and 4-methyl-1-naphthonitrile were synthesized from the corresponding bromomethylnaphthalenes. 6-Methyl-1-naphthonitrile was made by dehydrating 6-methyl-1-naphthamide. The amide was prepared by treating 6-methyl-1-naphthoic acid with thionyl chloride followed by aqueous ammonia. 3,3,4,4-Tetramethyl-1,2-diazetidine-1,2-dioxide (11) was synthesized according to the procedure of Ullman and coworkers.[98]

2-Methyl-1-naphthonitrile (56)

1-Bromo-2-methylnaphthalene (38.4 gm, 0.174 moles) and cuprous cyanide (18.6 gm, 0.209 moles) were added to 90 ml N-methylpyrrolidinone. The solution was stirred and refluxed under nitrogen for 3 hours, cooled slightly, and carefully poured into 400 ml benzene and 200 ml of 20% aqueous sodium cyanide. The resulting mixture was filtered through celite and the aqueous layer was washed with 100 ml benzene. The combined benzene extracts were washed with 200 ml 10% aqueous sodium cyanide, 200 ml water, dried (Na_2SO_4) and concentrated to give a dark brown solid. Chromatography on Baker 60-200 mesh silica gel (9 x 9 cm) with ether as eluant was used to purify the crude naphthonitrile. The first 1900 ml of eluant was concentrated to give a light brown solid. Recrystallization from 60-110° petroleum ether with charcoal treatment yielded white needles, 16.2 gm (55%), m.p. 87-88° (lit.[99] 87-88°). NMR ($CDCl_3$): δ 2.68 (s, 3H), 7.2-8.2 (m, 6H). IR ($CHCl_3$): 2220 cm^{-1} (CN).

4-Methyl-1-naphthonitrile (57)

1-Bromo-4-methylnaphthalene (7.3 gm, 0.033 moles) and cuprous cyanide (5.4 gm, 0.06 moles) were added to 30 ml N-methyl-pyrrolidinone. The reaction mixture was stirred and refluxed under nitrogen for 4 hours, cooled slightly and poured into 200 ml of 4% aqueous sodium cyanide. 500 Ml benzene was added and the mixture was filtered through celite.

The aqueous fraction was washed with 50 ml benzene. The combined benzene fractions were washed with 200 ml 10% aq. NaCN, 200 ml water, dried (Na_2SO_4) and concentrated to give a brown solid. Chromatography on Brockman 80-200 mesh neutral alumina (2.5 x 1 in.) gave, upon concentration of the ether fraction, a yellow solid. Recrystallization from 60-110° petroleum ether yielded 2.55 gm (46%) of white needles, m.p. 53-54° (lit.[100] 53-54°). NMR ($CDCl_3$): δ 2.73 (s, 3H), 7.2-8.3 (m, 6H). IR ($CHCl_3$): 2220 cm^{-1} (CN).

6-Methyl-1-naphthoic acid

The title compound was synthesized according to the method of Price and coworkers.[101] A mixture of 2-furoic acid (146 gm, 0.77 moles) and 1200 ml of toluene was mechanically stirred in an ice bath while 360 gm (2.7 moles) of aluminum trichloride was added in portions. The mixture was then stirred for 21 hours at 55°C. The dark red viscous mixture was cooled, carefully poured into 1200 ml cold 25% aqueous HCl and stirred vigorously for 2.5 hours, at which time the tan cake, formed on first contact with water, was completely dissolved. The toluene layer was separated, washed with water (200 ml) and thoroughly extracted with 10% aqueous $NaHCO_3$ (2 x 450 ml). Acidification of the aqueous fraction with conc. HCl yielded a greenish-yellow solid. Recrystallization from benzene gave green crystals, 11.3 gm (9%), m.p. 175-177° (lit.[101] 176.5-177°). NMR (acetone-d_6): δ 2.47 (s, 3H), 7.3-

8.3 (m, 5H), and 8.95 (broad doublet, 1H).

6-Methyl-1-naphthamide

6-Methyl-1-naphthoic acid (13 gm, 0.07 moles) was stirred and refluxed in 52 ml thionyl chloride for 5 hours. The thionyl chloride was distilled and the remaining liquid was cooled in ice. 200 Ml of conc. NH_4OH was added and the mixture was warmed to room temperature. After 40 min, the resulting brown solid was collected and washed with 200 ml water. Initial purification by vacuum sublimation at 170° gave 7.7 gm of a pale yellow solid. Recrystallization from 40 ml benzene and 200 ml absolute ethanol gave white needles, 4.75 gm (37%), m.p. 212-214°. NMR (acetone-d_6): δ 2.47 (s, 3H), 2.76 (broad s, 2H), 7.3-7.9 (m, 5H) and 8.12 (broad doublet, 1H). IR (KBr disk): 3380, 3180, 1648 and 1618 cm^{-1}. Mass spectrum: m/e 185 (M^+). Anal. calcd. for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.60. Found: C, 77.81; H, 6.13; N, 7.39.

6-Methyl-1-naphthonitrile (58)

Tosyl chloride (4.7 gm, 0.025 moles) was added portionwise to a mixture of 6-methyl-1-naphthamide (4.5 gm, 0.024 moles) and dry pyridine (10 ml). The mixture was stirred and gently refluxed for 24 hours, cooled and 50 ml H_2O was added. The aqueous mixture was extracted with ether (2 x 50 ml). The combined etherextracts were washed with 10% aq. HCl (2 x 50 ml), saturated $NaHCO_3$ (2 x 50 ml), dried (Na_2SO_4) and concentrated to give 3.9 gm of crude (9). Recrystallization from 60-110° petroleum ether gave colourless needles, m.p. 67.5-68.0°, yield 2.8 gm (69%). NMR ($CDCl_3$): δ 2.52 (3H), 7.3-8.2 (m, 6H). IR ($CHCl_3$): 2220 cm^{-1} (CN). Mass spectrum: m/e 167 (M^+). Anal. calcd. for $C_{12}H_9N$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.38; H, 5.48; N, 8.24.

Photoaddition of 2-Methyl-1-Naphthonitrile and Tetramethylethylene in Benzene

a) Irradiation in the Rayonet Reactor: 2-Methyl-1-naphthonitrile (0.585 gm, 3.5 mmoles) and tetramethylethylene (6.318 gm, 0.075 moles) in benzene (50 ml) were degassed by three freeze-pump-thaw cycles and sealed in Pyrex. The sample was irradiated for 68 hr with 10 RPR-3000 lamps. Analysis on 5' x 1/4" in 5% SE-30 on Chromosorb W at 180° showed three peaks of retention times 9.0, 14.0 and 15.0 min. corresponding to (59), (61) and (60), respectively. Upon standing, the peak corresponding to (61), disappeared with a concomitant increase in the peak corresponding to (60). In this run, approximately 70% of 2-methyl-1-naphthonitrile was unreacted. Adducts (59) and (60) were isolated from the mixture by preparative vpc on 7' x 1/4" 15% SE-30 on chromosorb W at 177°C. The compound with lowest retention time was an oil which declined to crystallize. Analytical vpc showed one peak corresponding to the photoproduct (59). It showed a parent ion of m/e 251.1674, corresponding to $C_{18}H_{21}N$. Based on its NMR and IR spectra, the adduct was assigned the structure 6,7,7,8,8-pentamethyl-2,3-benzobicyclo[4.2.0]octa-2,4-diene (<u>59</u>).

(1-(2',3'-dimethyl-3'-but-1-enyl)-3-methyl-4-cyano-1,2-dihydronaphthalene (<u>60</u>) was isolated as an oil. Trituration (30-60° pet. ether) gave colourless crystals, m.p. 101-102°. Mass spectrum: m/e 251 (M^+). Anal. Calcd. for $C_{18}H_{21}N$: C, 86.02; H, 8.42; N, 5.57. Found: C, 85.86; H, 8.31; N, 5.77.

b) <u>Irradiation through Corex</u>

i) 2-Methyl-1-naphthonitrile (1.01 gm, 0.006 moles) and tetramethylethylene (8.0 gm, 0.095 moles) in benzene (400 ml) were irradiated under a blanket of argon with a Hanovia 450 w lamp through Corex for 15.5 hr. The benzene was removed and analysis of the residue on 5' x 1/8" 5% SE-30 on Chromosorb W at 180° showed one major peak corresponding to (<u>60</u>). In this run, approximately 25% of the 2-methyl-1-naphthonitrile was unreacted. Trituration of the residue with 30-60 petroleum ether at 0° gave a solid. Recrystallization from 60-110° petroleum ether gave 0.341 gm of colourless needles, m.p. 101-102°. The mother liquor was chromatographed on a 3 x 58 cm column of silica gel (Fisher grade 923, 100-200 mesh). Elution was with 20% 30-60° petroleum ether in CCl_4 and 25 ml portions were collected. Fractions 9-10 contained (<u>60</u>). Fractions 11-17 contained (<u>60</u>) and 2-methyl-1-naphthonitrile. The solid from fractions 9-10 was recrystallized from 60-110° petroleum ether to give 0.111 gm, m.p. 101-102°. The total yield of (<u>60</u>) was 0.452 gm (30%).

ii) Structural evidence for (1-(2',3'-dimethyl-3'-but-1-enyl)-3-methyl-4-cyano-1,4-dihydronaphthalene (61). 2-Methyl-1-naphthonitrile (0.996 gm, 6 mmoles) and tetramethylethylene (8.02 gm, 0.095 moles) in benzene (400 ml) were irradiated under argon with a Hanovia 450 W lamp (Corex filter) for 23 h. A 10 ml aliquot was removed and the benzene evaporated. The NMR and IR spectra were taken immediately. The NMR spectrum ($CDCl_3$) indicated that (60) was not present in appreciable quantity. Multiplets of equal area were detected at δ 3.50 and 5.80. The IR ($CHCl_3$) showed a band at 2242 cm^{-1}. After the spectra were obtained, vpc analysis of the product mixture on 6 ft x 1/4 in 3% OVI on chromosorb WHP at 180° showed that it was composed of 70% (61) and 21% (60).

Photoaddition of 4-methyl-1-naphthonitrile and tetramethylethylene in benzene. A solution of 4-methyl-1-naphthonitrile (0.589 gm, 3.5 mmoles) and tetramethylethylene (6.342 gm, 0.075 moles) in benzene (50 ml) was degassed by three freeze-pump-thaw cycles and was sealed in Pyrex. The sample was irradiated for 42 hr with 10 RPR 3000 lamps. Analysis on 5 ft x 1/8 in of 5% SE-30 on chromosorb W at 165°C showed one major peak of retention time 8.3 min. In this run, approximately 30% of 4-methyl-1-naphthonitrile was unreacted. The benzene was evaporated leaving a yellow solid. Recrystallization from 30-60° petroleum ether gave white needles of (64) (74 mg), m.p. 93-94°. The mother liquor was concentrated and chromatographed on a 1 x 51 cm column of Kreselgel G silica gel with 20% ether in CCl_4. 3 Ml fractions were collected. Fractions 1-35 contained the cyclobutane (64). Fractions 36-45 contained 4-methyl-1-naphthonitrile. The former fractions were concentrated and the solid was recrystallized twice from 30-60° petroleum ether to give white needles of 1-cyano-4,7,7,8,8-pentamethyl-2,3-benzobicyclo[4.2.0]octa-2,4-diene (64), 0.141 gm, m.p. 93-94°, mass spectrum: m/e 251 (M^+). Anal. Calcd. for $C_{18}H_{21}N$: C, 86.02; H, 8.42; N, 5.57. Found: C, 86.00; H, 8.44; N, 5.46.

Photoaddition of 6-methyl-1-naphthonitrile and tetramethylethylene in benzene. A solution of 6-methyl-1-naphthonitrile (0.522 gm, 3.1 mmoles) and tetramethylethylene (4.00 gm, 0.046 moles) in benzene (50 ml) was irradiated through Pyrex under argon with 14 RPR 3000 lamps for 6 hrs. Analysis on 4 ft x 4 mm 3% OV-1 on chromosorb WHP at 190° showed two product peaks of retention time 6.1 m and 10.0 min, in ratio 9:1, respectively. In this run, approximately 70% of the naphthonitrile was unreacted. The benzene was evaporated and the residue was chromatographed using the chromatography technique of Still and coworkers.[73] A 50 mm diameter column of silica gel was used with 10% ethylacetate in 30-60 petroleum ether as eluent. 50 Ml fractions were collected. Fractions 6-8 contained the major adduct. Fractions 9-13 contained 6-methyl-1-naphthonitrile. Concentration of fractions 6-8 gave an oil (0.18 gm). Upon standing at 0°C, the oil solidified. Recrystallization from 60-110 petroleum ether gave 1-cyano-7,7,8,8-tetramethyl-2,3-(4'-methylbenzo)bicyclo[4.2.0]octa-2,4-diene (10) (65) (0.051 gm), m.p. 79-80°C. Mass spectrum: m/e 251 (M^+). Anal. Calcd. for $C_{18}H_{21}N$: C, 86.02; H, 8.42; N, 5.57. Found: C, 86.15; H, 8.49; N, 5.60.

The product with retention time 10.0 min was not isolated. When the reaction is taken to low conversion, little of this compound is detected. It is speculated that this substance is an azetine. Yang[31] has reported azetine formation on prolonged irradiation of 1-naphthonitrile with tetramethylethylene.

Photoaddition of 2-methyl-1-naphthonitrile and tetramethylethylene in ethyl acetate. 2-Methyl-1-naphthonitrile (0.062 gm, 0.37 mmoles) and tetramethylethylene (0.654 gm, 7.8 mmoles) in ethyl acetate (5 ml) was degassed by three freeze-pump-thaw cycles and was sealed in Pyrex. The sample was irradiated for 4 hr. with 14 RPR-3000 lamps. Analysis on 6 ft x 1/4 in 3% OV-1 on chromosorb WHP at 190° indicated the formation of at least 6 products in an inefficient reaction. In this run, about 85% of the naphthonitrile was unreacted. Three of the products had the same retention times as (59), (60), and (61). The other products may be an azetine and its decomposition products. The mixture was not investigated further.

Photoaddition of 4-methyl-1-naphthonitrile and tetramethylethylene in ethyl acetate. 4-Methyl-1-naphthonitrile (0.241 gm, 1.4 mmoles) and tetramethylethylene (2.52 gm, 0.03 moles) in ethyl acetate (20 ml) was degassed by three freeze-pump-thaw cycles and was sealed in Pyrex. The sample was irradiated for 16.5 hr with 14 RPR 3000 lamps. Analysis on 6 ft x 1/4 in 3% OV-1 on chromosorb WHP at 180° showed the formation of one major adduct with retention time 13 min. In this run, approximately 25% of the naphthonitrile was unreacted. Three other minor products were detected which represented less than 5% of the material present. These products may be the azetine and its decomposition products. The benzene was removed and, upon standing, crystals formed which corresponded to the major photoadduct. Recrystallization from hexane gave colourless needles of 1-cyano-4,7,7,8,8-pentamethyl-2,3-benzobicyclo[4.2.0]-octa-2,4-diene (64), m.p. 92.5-93.5°. A mixture melting point with authentic (64) gave a m.p. 92-93.3°.

Photoaddition of 6-methyl-1-naphthonitrile and tetramethylethylene in ethyl acetate. 6-Methyl-1-naphthonitrile (0.195 gm, 1.2 mmoles) and tetramethylethylene (2.49 gm, 0.03 moles) in ethyl acetate (20 ml) was irradiated under argon through Pyrex for 4.5 hr with 14 RPR 3000 Å lamps. Analysis on 4 ft x 1/4 in 3% OV-1 on chromosorb WHP at 195°C showed one major adduct with retention time 4.7 min. In this run, 40% of the naphthonitrile was unreacted. Two other minor products were seen. They represented less than 5% of the reaction mixture. These products may be an azetine as a decomposition product. The chromatography technique of Still and coworkers[73] on a 35 mm diameter column with 10% ethyl acetate in 30-60 petroleum ether as eluent was used to isolate the major product. 20 Ml fractions were collected and fractions 6-8 upon evaporation gave a solid. Recrystallization from 60-110° petroleum ether gave colourless crystals of 1-cyano-7,7,8,8-tetramethyl-2,3-(4'-methylbenzo)-bicyclo[4.2.0]octa-2,4-diene (65), m.p. 79-80°. A mixture melting with authentic (65) gave a m.p. 78.5-79.5°.

Deuterium exchange of 1-(2',3'-dimethyl-3'-but-1-enyl)-3-methyl-4-cyano-1,2-dihydronaphthalene (60). 10 Ml of methanol-OD, 0.1 gm sodium and (60) (0.096 gm) were stirred under reflux for 17 hours. The methanol was removed and 5 ml D_2O was added. The aqueous fraction was extracted with ether (2 x 10 ml). The combined organic extracts were dried (Na_2SO_4) and concentrated to give a yellow oil. NMR ($CDCl_3$): δ 0.78 and 0.97 (singlets, 3H each), δ 1.80 (broad singlet, 3H), δ 2.93 (singlet, 1H), δ 4.80 and 4.90 (multiplets, 1H each), δ 7.1-7.5 (multiplets, 4H).

Dehydrogenation of 1-(2',3'-dimethyl-3'-but-1-enyl)-3-methyl-4-cyano-1,2-dihydronaphthalene (60). A mixture of (60) (0.17 gm) and 0.15 10% palladium-on-charcoal in 15 ml p-xylene was refluxed for 6 days. The catalyst was filtered and the solution was concentrated to give an oil. Vpc analysis on

6 ft x 1/4 in 3% OV-1 on chromosorb WHP at 180° indicated that 90% of (60) had reacted. Two major products were observed. The first had a retention time of 144 sec, which was identical to authentic 2-methyl-1-naphthonitrile. The second product had a retention time of 319 seconds. The ratio of the products was 2:1. Crystals formed on standing, and recrystallization from 60-110° pet. ether gave white needles of 2-methyl-1-naphthonitrile, m.p. 85.5-86.0° (Lit.[99] 87-88°). The NMR was identical to that of an authentic sample. The compound with longer retention time was not isolated.

B. Bichromophoric Molecules

i) Synthesis.

1-Bromo-2-bromomethylnaphthalene (66). (66) was synthesized according to the method of Newman and Kosak.[97]

N-Bromosuccinimide (65.3 gm, 0.37 moles) and 1-bromo-2-methylnaphthalene (81.1 gm, 0.37 moles) were added to 500 ml CCl_4 and the solutions were continuously irradiated with a 1000 watt tungsten lamp. The solution was stirred and refluxed for 4 hours. The warm mixture was filtered and concentrated to give a yellow solid. Recrystallization from 60-110° petroleum ether gave 64.1 gm (58% yield) of (66), m.p. 104-105.5° (Lit.[102] 103.5-105.5°). NMR ($CDCl_3$): δ 4.80 (s, 2H), 7.4-7.9 (m, 5H), 8.3-8.4 (m, 1H).

1-Bromo-2-hydroxymethylnaphthalene (67). (67) was prepared by the method of Hebbelynck and Martin.[103]

1-Bromo-2-bromomethylnaphthalene (5.0 gm, 0.017 moles), and potassium acetate (8.3 gm, 0.085 moles) in 42 ml glacial acetic acid was stirred and refluxed for 4 hours. After cooling, the mixture was poured into 100 ml water. Upon standing in the cold, the acetate solidified. It was collected and washed with water. The crude 1-bromo-2-acetoxymethylnaphthalene was added to 3.7 gm potassium hydroxide in 25 ml water and 5 ml 95% ethanol. The solution was stirred and refluxed for 4 hours. After cooling the resulting yellow solid was collected, washed with water and recrystallized from absolute ethanol to give 2.5 gm (57% yield) of 1-bromo-2-hydroxymethylnaphthalene (67), m.p. 102-103° (Lit.[103] 103-104°). NMR ($CDCl_3$): δ 2.10 (s, 1H), 4.93 (s, 2H), 7.5-7.9 (m, 5H), 8.3-8.4 (m, 1H).

1-Bromo-3-methyl-but-2-ene (68). (68) was synthesized by the procedure of Samokhvalov and coworkers.[104]

Isoprene (4.2 gm, 0.06 moles) was mixed with 13.2 ml of 45% HBr (w/v) in glacial acetic acid with ice cooling. After standing for 2.5 days in an ice bath, the solution was poured into 50 ml of ice water. The mixture was washed with ether (2 x 50 ml) and the combined organic fractions were extracted with saturated aqueous $NaHCO_3$ (50 ml), dried (Na_2SO_4) and the ether removed by distillation.

Distillation of the brown residue at 75 mm yielded a slightly yellow liquid, b.p. 80-84°. The yield of 1-bromo-3-methyl-but-2-ene was 3.8 gm (43%). NMR ($CDCl_3$): δ 1.55 (broad s, 3H), 1.60 (broad s, 3H), 3.83 (d, J = 7.5 Hz, 2H), 5.33 (broad t, J = 7.5 Hz, 1H).

3-Methyl-2-butenyl 1-bromo-2-methylnaphthyl ether (69). 1-Bromo-2-hydroxymethylnaphthalene (2.01 gm, 8.5 mmoles) in 20 ml dry THF was added to NaH (50% dispersion in oil, 0.62 gm, 12.9 mmoles) which had been previously washed with 30 ml dry THF. A blanket of argon was maintained over the solution during the course of the reaction. The mixture was refluxed with stirring for 8 hours after which 1-bromo-3-methyl-but-2-ene (1.99 gm, 13.4 mmoles) in 20 ml dry THF was added dropwise. The solution was refluxed for 2 hours, cooled, 50 ml H_2O was added and the resultant aqueous fraction was extracted with ether (2 x 30 ml). The combined organic extracts were dried (Na_2SO_4), filtered and evaporated to give an oil, which was chromatographed on Baker 60-200 mesh silica gel (74 cm x 3.5 cm) using 10% other in hexane as the eluent. 6 Ml fractions were collected. Fractions 105-142 were combined, and concentrated to give 1.13 gm of an oil. Kugel Rohr distillation (75°C, 0.1 mm) gave 0.97 gm of 3-methyl-2-butenyl 1-bromo-2-methylnaphthyl ether (25%) as a colourless oil. NMR ($CDCl_3$): δ 1.60 (broad s, 3H), 1.70 (broad s, 3H), 4.07 (d, J = 6.9 Hz, 2H), 4.74 (s, 2H), 5.43 (broad t, J = 6.9 Hz, 1H), 7.3-7.8 (m, 5H), 8.2-8.4 (m, 1H). Anal. Calcd. for $C_{16}H_{17}BrO$: C, 62.96;

H, 5.62; Br, 26.18. Found: C, 62.94; H, 5.72; Br, 26.06.

Attempted synthesis of 3-methyl-2-butenyl 1-cyano-2-methylnaphthyl ether (77). 3-Methyl-2-butenyl 1-bromo-2-methylnaphthyl ether (69) (0.70 gm, 2.3 mmoles) and cuprous cyanide (0.37 gm, 4.1 mmoles) were added to 20 ml N-methylpyrrolidinone. The mixture was stirred and refluxed under argon for 4.5 hours. It was cooled and poured into 200 ml of 2% aqueous sodium cyanide. 200 Ml benzene was added and the mixture was filtered through celite. The aqueous fraction was washed with 50 ml benzene. The combined benzene extracts were washed with 100 ml 10% aq. sodium cyanide, 100 ml water, dried (Na_2SO_4) and concentrated to give 0.61 gm of a dark red oil. Chromatography on Baker 60-120 mesh silica gel (28 cm x 3.5 cm) using 50% ether:hexane as eluent afforded 0.37 gm of oil. The NMR indicated the loss of the ether linkage from the aromatic compound. The IR showed a strong absorption at 1750 cm^{-1} (C=O) indicating that oxidation products were formed.

2-Bromomethyl-1-naphthonitrile (73). (73) was synthesized according to the method of Stacy and coworkers.[105]

N-Bromosuccinimide (17.21 gm, 0.097 moles) and 2-methyl-1-naphthonitrile (16.15 gm, 0.097 moles) were added to 100 ml CCl_4 and the solution was continuously irradiated with a 1000 watt tungsten lamp. The mixture was stirred and refluxed for 3 hours. The warm mixture was filtered and the filtrate concentrated to give a yellow solid. Two recrystallizations from CCl_4 yielded 15.73 gm of light yellow needles, m.p. 99.5-101.5° (Lit.[105] 101-102.5°). NMR, however, indicated that the crystals were a mixture of 81% 2-bromomethyl-1-naphthonitrile and 19% 2-methyl-1-naphthonitrile. Also, the elemental analysis was consistent with there being a two component mixture. Anal. calcd. for $C_{12}H_8BrN$: C, 58.56; H, 3.28; N, 5.69; Br, 32.47. Found: C, 60.32; H, 3.42; N, 6.07; Br, 29.96.

2.0 Gm of the mixture was chromatographed on Baker analyzed 60-200 mesh silica gel (29 cm x 3.5 cm) using 5% ether in hexane as eluent. 6 Ml fractions were collected. Fractions 65-130 yielded upon concentration 1.2 gm of 2-bromomethyl-1-naphthonitrile (<u>73</u>). Recrystallization from CCl_4 gave 0.95 gm of white needles, m.p. 110-110.5°. NMR ($CDCl_3$): δ 4.80 (s, 2H), 7.5-8.3 (m, 6H). IR ($CHCl_3$): 2220 cm^{-1} ($C{\equiv}N$ stretch) mass spectrum showed parent ions of m/e 245 and 247. Anal. calcd. for $C_{12}H_8BrN$: C, 58.56; H, 3.28; N, 5.69; Br, 32.47. Found: C, 58.40; H, 3.18; N, 5.60; Br, 32.30.

The mixture was also purified by the chromatographic technique of Still and coworkers.[73] A 50 mm diameter column was used with 20% ethyl acetate in 30-60 petroleum ether as the eluent. 50 Ml fractions were collected. 10.0 Gm of the mixture was chromatographed in 1.0 gm portions. The fractions were assayed by vpc (6 ft x 1/4 in, 3% OV-1 on 80/100 chromosorb WHP at 190°C). The appropriate fractions were collected and concentrated to give a white solid which, upon two recrystallizations from CCl_4, gave 3.1 gm of pure (73), m.p. 110-110.5°.

Attempted synthesis of 1-cyano-2-hydroxymethylnaphthalene (72).

4 Gm of crude 2-bromomethyl-1-naphthonitrile (m.p. 99.5-101.5°) and potassium acetate (8.6 gm) in 42 ml glacial acetic acid was stirred and refluxed for 3.5 hours. After cooling, the mixture was poured into 120 ml water. Upon further cooling, the acetate solidified. It was collected and washed with water. The crude mixture of 1-cyano-2-acetoxymethylnaphthalene (74) and 2-methyl-1-naphthonitrile was added to 1.2 gm of potassium hydroxide in 20 ml water and 4 ml ethanol. The solution was stirred and refluxed for 1.5 hours. After cooling, the yellow solid (2.27 g) was collected and washed with water. 1.0 Gm was chromatographed on 60-200 mesh Baker silica gel (31 cm x 3.5 cm) using 4% ether:hexane. 7 Ml fractions were collected. After fraction 105, the eluent was changed to ether and the next 500 ml were collected and concentrated to give 0.60 gm of a yellow solid. Recrystallization from absolute ethanol gave 0.42 gm of orange crystals, m.p. 152-156°. 0.17 Gm were sublimed (130°C, 0.02 mm) to give 0.13 gm of a white solid which upon recrystallization from absolute ethanol gave white needles (0.10 gm) of 2-hydroxymethylnaphthalene-1-carboxylic lactone (75), m.p. 156-157° (Lit.[106] 157°). NMR ($CDCl_3$): δ 5.22 (s, 2H), 7.4-8.2 (m, 5H), 8.9-9.1 (m, 1H). IR ($CHCl_3$): 1755 cm^{-1} (C=O). The mass spectrum showed

m/e 184 (M^+) and m/e 156 (M^+-CO).

3-Methyl-2-butenyl 1-cyano-2-methylnaphthyl ether (77). 3-Methylbut-2-ene-1-ol (0.638 gm, 7.4 mmoles) in 30 ml THF was added dropwise to sodium hydride (50% dispersion in oil, 0.40 gm, 8.3 mmoles) which had been washed with 30 ml THF, under argon. The mixture was stirred and refluxed for 2 hours at which time 2-bromomethyl-1-naphthonitrile (73) (0.841 gm, 3.4 mmoles) in 30 ml THF was added. The solution was stirred and refluxed for 5 hours. After cooling, 20 ml water was added. The aqueous layer was extracted with ether (2 x 30 ml). The combined organic extracts were dried (Na_2SO_4), concentrated and chromatographed on Baker 60-200 mesh silica gel (30 cm x 3.5 cm). Elution was with 5% ether in hexane and 7 ml fractions were collected. Concentration of fractions 25-57 gave 0.53 gm of a yellow solid, m.p. 44-49°. Recrystallization from 60-110 petroleum ether gave white needles of 3-methyl-2-butenyl 1-cyano-2-methyl naphthyl ether (77) (0.417 gm, 49% yield), m.p. 51-52°. NMR ($CDCl_3$): δ 1.67 (broad s, 3H), 1.75 (broad s, 3H), 4.10 (d, J = 6.9 Hz, 2H), 4.87 (s, 2H), 5.40 (broad t, J = 6.9 Hz, 1H), 7.5-8.3 (m, 6H). IR ($CHCl_3$): 2219 cm^{-1} (CN). Mass spectrum: m/e 251 (M^+). Anal. calcd. for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.22; H, 6.84; N, 5.58.

Ethyl 2,3-dimethyl-2-butenoate (78). The title compound was synthesized according to the method of Huston and Goerner.[107]

Ethyl 3-hydroxy-2,3-dimethylbutanoate was prepared by a Reformatsky reaction. 45 Gm of thirty mesh zinc was cleaned and dried by the method of Fieser and Johnson.[108] Initially, 4.8 gm acetone, 3.4 gm ethyl-2-bromopropionate and 1.5 ml BuLi (2M in hexane) in 15 ml benzene were added to the zinc. The mixture was heated to reflux and a solution of ethyl-2-bromopropionate (90 gm) and acetone (43 gm) in 125 ml benzene was added dropwise over a period of 30 minutes. After refluxing and stirring for two hours, the contents of the flask were cooled and poured, with vigorous stirring, into 500 ml of ice-cold 10% sulfuric acid and when hydrolysis was complete, the benzene layer was separated and the aqueous layer was washed with 50 ml benzene. The combined benzene extracts were washed with saturated Na_2CO_3 (50 ml), water (50 ml) and dried (Na_2SO_4). The benzene solution was distilled until the distillate became clear. Then 57 gm of phosphorus pentoxide was added to the benzene solution and the mixture was refluxed for 4 hours. After cooling, the benzene layer was decanted and the black solid was washed with 100 ml benzene. The benzene was removed by fractional distillation through a silver jacketed column packed with glass helices. The residue was then transferred to a spinning band still and distilled. The yield of ethyl 2,3-dimethyl-2-butenoate (<u>78</u>) (b.p. 93-94°/59 mm) was 15.1 gm (21%). NMR ($CDCl_3$): δ 1.33 (t, J = 7.0 Hz, 3H), 1.87 (broad s, 6H), 2.07 (broad s, 3H), 4.33 (q, J = 7.0 Hz, 2H).

Earlier fractions were enriched in ethyl 2,3-dimethyl-3-butenoate. 12 Gm of crude ethyl 2,3-dimethyl-3-butenoate was stirred with 1 ml benzyltrimethylammonium hydroxide (40% in methanol), at room temperature under nitrogen for 40 hours. The solution was then added to 10 ml 10% aq. HCl. The mixture was extracted with ether (2 x 20 ml) and the organic extracts were dried (Na_2SO_4). Distillation using a spinning band still yielded 7.4 gm of ethyl-2,3-dimethyl-2-butenoate. The total yield was 22.5 gm (31%).

2,3-Dimethyl-but-2-ene-1-ol (79). A solution of 25 ml Red Al (Aldrich, 70% solution of sodium bis (2-methoxyethoxy)-aluminumhydride in benzene) in 250 ml THF was added under argon over a period of 1.5 hours to a stirred ice-cooled solution of 2,3-dimethyl-2-butenoate (78) (10 gm, 0.065 moles) in 50 ml THF. The solution was then stirred with cooling for 4 hours at which time 75 ml of 5% aq. NaOH was added. The mixture was stirred until the white precipitate dissolved and the aqueous layer was extracted with ether (2 x 100 ml). The organic fractions were dried (Na_2SO_4) and the ether and THF were removed by fractional distillation through a silver jacketed column containing glass helices. The residue was transferred to a spinning band still and distillation yielded 6.12 gm (87% yield) of 2,3-dimethyl-but-2-ene-1-ol (79) (b.p. 82-83°/59 min). NMR ($CDCl_3$): δ 1.67 (broad s, 9H), 2.37 (s, 1H), 4.03 (s, 2H). (79) has also been synthesized in 83% yield by the reduction of α,β,β-trimethylacrylic acid with lithium aluminum hydride.[109]

2,3-Dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether (53). 2,3-Dimethyl-but-2-ene-1-ol (79) (0.872 gm, 8.7 mmoles) in 30 ml THF was added dropwise to sodium hydride (50% dispersion in oil, 0.469 gm, 9.8 mmoles) which had previously been washed with 20 ml THF. The reaction was carried out under an atmosphere of argon. The mixture was stirred and refluxed for 2 hours at which time 2-bromomethyl-1-naphthonitrile (73) (1.063 gm, 4.3 mmoles) in 30 ml THF was added dropwise. After stirring and refluxing for 4 hours, the mixture was cooled and 25 ml water was added. The aqueous layer was extracted with ether (3 x 25 ml). The organic fractions were dried (Na_2SO_4), concentrated and chromatographed on Baker 60-200 mesh silica gel (31 cm x 3.5 cm) using 5% ether in hexane as eluent. 7 Ml fractions were collected and concentration of fractions 38-74 yielded 0.70 gm of an oil which solidified upon cooling. Recrystallization from 60-110 petroleum ether gave white needles of 2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether (53) (0.307 gm, 27% yield), m.p. 55-56°. NMR ($CDCl_3$): δ 1.65 (broad s, 6H), 4.03 (s, 2H), 4.73 (s, 2H), 7.4-8.2 (m, 6H). IR ($CHCl_3$): 2220 cm^{-1} (CN). Mass spectrum: m/e 265 (M^+). Anal. calcd. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.39; N, 7.23; N, 5.28.

Further attempts to synthesize (53) using the same conditions as described above gave lower yields. As a result, the following procedure was adopted. Yields of (53) varied.

2,3-Dimethyl-but-2-ene-1-ol (0.310 gm, 3.1 mmoles) and 2-bromomethyl-1-naphthonitrile (0.502 gm, 2.0 mmoles) in 15 ml THF was added slowly under an atmosphere of argon to a rapidly stirred mixture of NaH (80% dispersion in oil, 0.116 gm, 3.9 mmoles) in 10 ml THF. The NaH was previously washed with 5 ml THF. The mixture was stirred and refluxed under argon for 8 hours. After cooling, 25 ml water was added and the aqueous extract was washed with ether (3 x 25 ml). The combined organic extracts were dried (Na_2SO_4) and concentrated. This procedure was repeated three more times and the resulting 1.92 gm of oil was divided into two equal batches which were individually chromatographed using the technique of Still and coworkers.[73] A 50 mm diameter column was used. The eluent was 5% ethyl acetate in 30-60 petroleum ether. In one run, fractions 19-30 were collected and in the second run using the same column, fractions 9-20 were collected. These fractions were combined and concentrated to give 0.772 gm of crude (53). Recrystallization from absolute ethanol gave 0.513 cm (24% yield) of pure 2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthylether, m.p. 55-56°.

4-Bromomethyl-1-naphthonitrile (83). (83) was synthesized according to the method of Stacy and coworkers.[105]

4-Methyl-1-naphthonitrile (4 gm, 0.024 moles) and

N-bromosuccinimide (4.3 gm, 0.024 moles) were added to 30 ml CCl_4 and the solution was irradiated continuously with a 1000 watt tungsten lamp. The mixture was stirred and refluxed for four hours. The warm solution was filtered, and the filtrate concentrated to give a yellow solid. Two recrystallizations from CCl_4 gave 4.0 gm of slightly yellow crystals, m.p. 135-137° (Lit.[105] 135.5°). NMR of the crystals indicated that they were composed of 88% 4-bromomethyl-1-naphthonitrile and 12% 4-methyl-1-naphthonitrile.

2.0 Gm of the mixture was chromatographed on Baker 60-200 mesh silica gel (30 cm x 3.5 cm) using 5% ether in hexane as eluent. 7 Ml fractions were collected. After fraction 70, the eluent was changed to ether. 550 Ml of ether was collected and concentrated to give 1.6 gm of a yellow solid. Recrystallization from CCl_4 gave 1.3 gm of colourless needles, m.p. 135-136°. NMR ($CDCl_3$): δ 4.92 (s, 2H), 7.5-8.4 (m, 6H). IR ($CHCl_3$): 2219 cm^{-1} (CN). Mass spectrum: m/e 245 and 247 (M^+). Anal. calcd. for $C_{12}H_8BrN$: C, 58.56; H, 3.28; N, 5.69; Br, 32.47. Found: C, 58.37; H, 3.48; N, 5.75; Br, 32.31.

Attempted synthesis of 2,3-dimethyl-2-butenyl 1-cyano-4-naphthylmethyl ether (54). 2,3-Dimethyl-but-2-ene-1-ol (79) (0.318 gm, 3.2 mmoles) in 20 ml THF was added dropwise to sodium hydride (50% dispersion in oil, 0.165 gm, 3.4 mmoles) which had been washed with 20 ml THF. The reaction was carried out under an atmosphere of argon. The mixture was stirred and refluxed for 1.5 h after which 4-bromomethyl-1-naphthonitrile (83) (0.380 gm, 1.5 mmoles) in 20 ml THF was added. The solution was stirred and refluxed for 5.5 hours. After cooling, 20 ml water was added.

A yellow precipitate was observed which was not soluble in organic solvents such as ether, acetone or dimethyl sulfoxide. After removal of this precipitate, the aqueous fraction was washed with ether (3 x 30 ml). The organic fractions were dried (Na_2SO_4) and concentrated to give a liquid. NMR of this liquid revealed the absence of aromatic protons. The mass spectrum of the yellow solid (1,3-bis-(4-cyanonaphthyl)ethene, 80) showed m/e 330 (M^+) and 178 consistent with the molecular ion $C_{24}H_{14}N_2^+$ and loss of $C_{11}H_6N$, respectively. IR (KBr disk): 2221 cm^{-1} (CN). The melting point of 80 was 330-334°.

1-Cyano-4-hydroxymethylnaphthalene (86). 3.0 Gm (0.012 moles) crude 4-bromomethyl-1-naphthonitrile (83) (m.p. 135-137°) and 6.6 gm potassium acetate were added to 32 ml glacial acetic acid. The solution was stirred and refluxed for 5 hours. It was then poured into 100 ml water. The solid which formed was collected and washed with water. The crude 1-cyano-4-acetoxymethylnaphthalene with 0.9 gm KOH was added to 24 ml of 17% aqueous ethanol. The mixture was stirred and refluxed for 3 hours. Upon cooling, a yellow solid separated which was collected, washed with water and chromatographed on Baker 60-200 mesh silica gel (29 cm x 3.5 cm) using 50% ether in hexane as eluent. 7 Ml fractions were collected and after fraction 75, the column was washed with 400 ml ether. Fractions 70-75 were combined with the ether fraction and were concentrated to give 1.3 gm of crude (86). Recrystallization from ethanol gave 1.1 gm (49% yield) of 1-cyano-4-hydroxymethylnaphthalene (86) as pale yellow needles, m.p. 118-119°. An analytical sample was prepared by treatment with charcoal, m.p. 118-119°. NMR ($CDCl_3$): δ 2.17 (t, J = 6.0 Hz, 1H), 5.12 (d, J = 6.0 Hz, 2H) and 7.5-8.3 (m, 6H). IR ($CHCl_3$): 3610 cm^{-1}, 3450 cm^{-1}, 2220 cm (CN). Mass spectrum: m/e 183 (M^+). Anal. calcd. for $C_{12}H_9NO$: C, 78.67; H, 4.95; N, 7.56. Found: C, 78.79; H, 5.20; N, 7.59.

1-Bromo-2,3-dimethylbut-2-ene (85). 2,3-Dimethyl-1,3-butadiene (5.0 gm, 0.038 moles) was added to 13.2 ml HBr (45% w/v) in glacial acetic acid with ice cooling. After standing for two days in the cold, the solution was poured into 60 ml cold water. The green liquid was separated, dried ($CaCl_2$) and distilled to give 4.2 gm (43% yield) of 1-bromo-2,3-dimethylbut-2-ene (85) as a pale yellow liquid (b.p. 68-72°/44 mm). NMR ($CDCl_3$): 1.79 (broad s, 9H), 4.07 (s, 2H). 1-Bromo-2,3-dimethylbut-2-ene has also been prepared by heating 2,4-dibromo-2,3-dimethylbutane in pyridine.[110]

2,3-Dimethyl-2-butenyl 1-cyano-4-naphthylmethyl ether (54). 1-Cyano-4-hydroxymethylnaphthalene (86) (0.50 gm, 2.7 mmoles) in 20 ml THF was added dropwise to sodium hydride (50% dispersion in oil, 0.146 gm, 3.0 mmoles) which had been washed with 25 ml THF. The reaction was run under an atmosphere of argon. The mixture was stirred and refluxed for 1 hour after which 1-bromo-2,3-dimethylbut-2-ene (85) (1.0 gm, 6.2 mmoles) in 20 ml THF was added. The solution was then stirred and refluxed for 3 hours. After cooling, 20 ml water was added and the aqueous fraction was extracted with ether (3 x 30 ml). The organic extracts were dried (Na_2SO_4), concentrated and chromatographed on Baker 60-200 mesh silica gel (30 cm x 3.5 cm) with 10% ether in hexane as eluent. 7 Ml fractions were collected and concentration of fractions 50-75 gave 0.4 gm of an oil which solidified upon cooling. Recrystallization from 30-60° petroleum other gave 0.31 gm (43% yield) of 2,3-dimethyl-2-butenyl 1-cyano-4-naphthylmethyl ether (54) as white crystals, m.p. 43-44°. NMR ($CHCl_3$): δ 1.70 (s, 9H), 4.07 (s, 2H), 4.85 (s, 2H), 7.4-8.3 (m, 6H). IR ($CHCl_3$): 2221 cm^{-1} (CN). Mass spectrum: m/e 265 (M^+). Anal. calcd. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.53; H, 7.23; N, 5.16.

6-Bromomethyl-1-naphthonitrile (87). 6-Methyl-1-naphthonitrile (1.50 gm, 9.0 mmoles) and N-bromosuccinimide (1.62 gm, 9.1 mmoles) were added to 15 ml CCl_4. The solution was continuously irradiated with a 1000 watt tungsten lamp. The mixture was stirred and refluxed for 3 hours. The warm solution was filtered and the filtrate concentrated to give a yellow solid. Recrystallization from CCl_4 gave 1.0 gm of (87), m.p. 106-114°C. A second recrystallization from CCl_4 gave 0.45 gm (20% yield) of 6-bromomethyl-1-naphthonitrile (87) as white needles, m.p. 114-115°. NMR ($CDCl_3$): δ 4.63 (s, 2H), 7.4-8.3 (m, 6H). IR ($CHCl_3$): 2221 cm^{-1} (CN). Mass spectrum: m/e 245 and 247 (M^+). Anal. calcd. for $C_{12}H_8BrN$: C, 58.56; H, 3.28; N, 5.69. Found: C, 58.56; H, 3.24; N, 5.72.

2,3-Dimethyl-2-butenyl 1-cyano-6-methylnaphthyl ether (55). 2,3-Dimethyl-but-2-ene-1-ol (79) (0.370 gm, 3.70 mmoles) in 15 ml THF was added dropwise to sodium hydride (50% dispersion in oil, 0.200 gm, 4.2 mmoles) which had been previously washed with 15 ml THF. The reaction was carried out under a blanket of argon. The mixture was stirred and refluxed for 1.5 hours, at which time, 6-bromomethyl-1-naphthonitrile (0.459 gm, 1.9 mmoles) in 15 ml THF was added. After stirring and refluxing for 3 hours, the mixture was cooled and 30 ml of water was added. The aqueous fraction was extracted with ether (3 x 20 ml). The organic fractions were dried (Na_2SO_4), concentrated, and chromatographed on Baker 60-120 mesh silica gel (31 cm x 3.5 cm) using 10% ether:hexane as eluent. 7 Ml fractions were collected and concentration of fractions 60-185 gave 0.42 gm of a colourless oil which solidified upon cooling, m.p. 68-71°. Two recrystallizations from 60-110° petroleum ether gave 0.194 gm (39% yield) of 2,3-dimethyl-2-butenyl 1-

cyano-6-methylnaphthyl ether (55) as white needles, m.p. 73-74°. NMR ($CDCl_3$): δ 1.63 (s, 3H), 4.03 (s, 2H), 4.45 (s, 2H), 7.3-8.3 (m, 6H). IR ($CHCl_3$): 2220 cm^{-1} (CN). Mass spectrum: m/e 265 (M^+). Anal. calcd. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.51; H, 7.30; N, 5.13.

ii) Photochemistry of Bichromophoric Molecules

Photoreaction of 2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether (53) in benzene. A solution of 2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether (53) (0.398, 1.5 mmoles) in benzene (50 ml) was deoxygenated by purging with argon, and irradiated through pyrex with 14 RPR-3000 lamps. The progress of the reaction was monitored by vpc (6 ft x 1/4 in 3% OV-1 on chromosorb WHP at 200°). After 45 minutes, two products with retention times of 7.1 and 9.6 minutes were formed in a ratio of 1:15, respectively. The starting material (53) had a retention time of 12.6 minutes and represented 59% of the mixture. The irradiation was terminated after 7 hours. 17% of (53) was present and the ratio of the major product (retention time 9.6 min.) to the minor product (retention time 7.1 min.) was 3:1. The mixture was chromatographed using the technique of Still and coworkers.[73] A 35 mm diameter column was used with 10% ethyl acetate in 30-60 petroleum ether as eluent. 25 Ml fractions were collected and the fractions were assayed by vpc (6 ft x 1/4 in 3% OV-1 on chromosorb WHP at 200°C). Fractions 2-9 (0.109 gm) contained (53) and the minor photoproduct (89). Fractions 10-18 (0.077 gm) were enriched in (89) with (88) as a minor component. Fractions 19-23 (0.053 gm) contained the major photoproduct (88) with (89) as an impurity. Fractions 24-36 (0.12 gm) were comprised of the major photoadduct (89). The recovery from the column was 90%. Concentration of fractions 24-36 gave a solid, m.p. 130-140°C. Two recrystallizations from 60-110° petroleum ether gave 7-cyano-5,6,6-trimethyl-8,9-benzo-3-oxatricyclo[5.4.0.0^{1,5}]-undeca-8,10-diene (88) as white needles (0.038 gm, 10%), m.p. 141.5-142.5°. IR ($CHCl_3$): 2225 cm^{-1} (CN). Mass spectrum: m/e 265 (M^+). Anal. calcd. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.23. Found: C, 81.66; H, 7.30; N, 5.16.

Fractions 10-18 from the above separation were concentrated and chromatographed using the same technique on a 25 mm diameter column with 20% ethyl acetate in 30-60 petroleum ether as eluent. 7 Ml fractions were collected and concentration of fractions 9-13 gave 35.6 mg of a solid, m.p. 90-105°. Two recrystallizations from absolute ethanol gave 6-cyano-1,10,10-trimethyl-7,8-benzo-3-oxatricyclo[5.3.1.1^{5,9}]-deca-5,7-diene (89) as white needles (3.8 mg), m.p. 119-120°. IR ($CHCl_3$): 2217 cm^{-1} (CN). Mass spectrum: m/e 265 (M^+). Anal. calcd. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.23. Found: C, 81.35; H, 7.34; N, 5.20.

Photoreaction of 2,3-dimethyl-2-butenyl 1-cyano-4-methylnaphthyl ether (54) in benzene. 2,3-Dimethyl-2-butenyl 1-cyano-4-methylnaphthyl ether (54) (0.395 gm, 1.5 mmoles) in benzene (50 ml) was purged with argon and irradiated with 14 RPR 3000 lamps through Pyrex for 40 minutes. Vpc analysis (6 ft x 1/4 in, 3% OV-1 on chromosorb WHP at 215°C) showed the presence of two products with retention times of 12.2 minutes and 15.8 minutes in a ratio of 4.8:1, respectively. The starting material (<u>54</u>) had a retention time of 19.6 minutes and represented 48% of the mixture. The solution was dark yellow in colour and the UV absorption showed a maximum at 372 nm (OD = 1.39). Upon evaporation of the benzene, the dark yellow colour faded.

The mixture was chromatographed using the technique of Still and coworkers.[73] A 50 mm diameter column was used with 10% ethyl acetate in 30-60 petroleum ether as eluent. 50 Ml fractions were collected. The fractions were assayed by TLC and vpc. Fractions 5-13 (0.139 gm) contained the starting material (<u>54</u>). Fractions 19-27 gave 0.108 gm of the major photoadduct (<u>91</u>) as a solid, m.p. 120-130°. 0.080 Gm was recrystallized from absolute ethanol to give 9-cyano-5,6,6-trimethyl-10,11-benzo-3-oxatricyclo[5.4.0.0^{1,5}]undeca-8,10-diene (<u>91</u>) as white needles (0.038 gm), m.p. 138.5-139.5°. IR ($CHCl_3$): 2220 cm^{-1} (CN). Mass spectrum: m/e 265 (M^+). Anal. calcd. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.23; O, 6.03. Found: C, 81.52; H, 7.37; N, 5.23.

Fractions 31-39 from the above column separation gave 0.040 gm of a yellow oil. Vpc analysis of this fraction indicated the presence of at least 3 components. Fractions 40-47 (0.058 gm) showed a carbonyl stretch (1710 cm^{-1}) in the

IR indicating that oxidation products were formed. The column was then washed with 500 ml ethyl acetate. Concentration of the ethyl acetate fraction gave 0.048 gm of material. These last two fractions were not investigated further.

Photoreaction of 2,3-dimethyl-2-butenyl 1-cyano-6-methylnaphthyl ether (55) in benzene. 2,3-Dimethyl-2-butenyl 1-cyano-6-methylnaphthyl ether (55) (0.179 gm, 0.68 mmoles) in benzene (50 ml) was deoxygenated with argon and irradiated with 14 RPR 3000 lamps through Pyrex. The progress of the reaction was monitored by vpc (6 ft x 1/4 in, 3% OV-1 on chromosorb WHP at 210°). After 90 minutes, one major product (retention time 6.0 min.) was observed which represented 17% of the mixture. The irradiation was terminated after 6.5 hours. The solution contained one photoproduct (retention time 6.0 min., 15%) and the starting material (55) (retention time 11.0 min., 81%). The mixture was chromatographed using the technique of Still and coworkers.[73] A 35 mm diameter column was used with 10% ethyl acetate in 30-60 petroleum ether as eluent. 25 Ml fractions were collected and were assayed by TLC and vpc. Fractions 4-13 (0.081 gm) contained the starting material (55). Fractions 14-17 (0.024 gm) consisted of a mixture of photoproduct (94) and (55). Fractions 18-24 (0.024 gm) contained 1,11,11-trimethyl-8,9-(6'-cyanobenzo)-3-oxatricyclo[$6.3.0.0^{5,10}$]-undeca-6,8-diene (94) as an oil in 95% purity. The major contaminant was 2,3-dimethyl-2-butenyl 1-cyano-6-methylnaphthyl ether (55). IR ($CHCl_3$): 2219 cm^{-1}.

Irradiation of 2,3-dimethyl-2-butenyl 1-cyano-4-methylnaphthyl ether (54) in benzene with subsequent addition of dimethylacetylene dicarboxylate. 2,3-Dimethyl-2-butenyl 1-cyano-4-methylnaphthyl ether (54) (0.400 gm, 1.5 mmoles) in 50 ml benzene was deoxygenated with argon and irradiated with 14 RPR 3000 lamps through Pyrex for 40 minutes. The solution became deep yellow. Dimethylacetylene dicarboxylate (0.089 gm, 0.63 mmoles) in benzene (5 ml) was added to the irradiated sample. The yellow colour of the solution was not dissipated. The solution was allowed to stand for 22 hours at room temperature followed by 1.5 hours at 70°. Evaporation of the benzene gave a yellow oil. NMR analysis indicated the presence of the starting material (54), the photoproduct (91) and residual dimethylacetylene dicarboxylate.

Irradiation of 2,3-dimethyl-2-butenyl 1-cyano-4-methylnaphthyl ether (54) in benzene-d_6. 2,3-Dimethyl-2-butenyl 1-cyano-4-methylnaphthyl ether (35) (0.050 gm, 1.9 mmoles) in benzene-d_6 (3 ml) was degassed by three freeze-pump-thaw cycles and was sealed in an NMR tube. The sample was irradiated with 14 RPR-3000 lamps in a Rayonet reactor and the progress of the reaction was followed by NMR. After 20 minutes, the reaction had been taken to 15% conversion and 36 minutes of irradiation resulted in 30% consumption of the starting material (54). No signals which could unambiguously assigned to compound (92) were detected.

FLUORESCENCE QUENCHING

1. Stern-Volmer Quenching Studies

Fluorescence cells fitted with a standard taper joint and a stopcock were used, and solutions were deaerated by purging with argon. The experiments were performed using the Aminco-Bowman spectrofluorimeter. Several fluorescence quenching studies were performed with three methyl-1-naphthonitriles. The 4-methyl-1-naphthonitrile-tetramethylethylene (TME) system in ethyl acetate and benzene will be used as examples to describe the general procedure used.

Fluorescence quenching of 4-methyl-1-naphthonitrile by TME in ethyl acetate. A stock solution of 0.253 M TME in ethyl acetate was prepared (534 mg in 25 ml). Successive dilutions resulted in TME solutions that were 0.127, 0.0635, 0.0318 and 0.0159 M.

3 Ml of the 4-methyl-1-naphthonitrile solution were mixed with equal volumes of each of the TME solutions to give the final solutions used in the measurement. Each sample was deoxygenated by purging with argon for 3 minutes.

The samples were excited at 300 nm, and the fluorescence of the naphthonitrile was monitored at 333 nm, which is off the emission maximum of 342 nm. The observed intensity at 342 nm was found to have a small contribution from the exciplex emission which has a maximum at 424 nm. Any error due to this overlap was minimized by using low concentrations of tetramethylethylene and by monitoring the 4-methyl-1-naphthonitrile emission off the maximum. Values of the unquenched emission of 4-methyl-1-naphthonitrile (1.6 x 10^{-4} M) were checked after each sample was run and these values typically differed by less than 5%. The results from this experiment are shown in Figure 5 of the Results section.

Fluorescence quenching of 4-methyl-1-naphthonitrile by TME in benzene. It was found that accurate intensity of monomer emission as a function of TME concentration in benzene could not be obtained because of substantial overlap of the naphthonitrile and exciplex emission. This problem can be overcome by using a system of simultaneous equations to determine monomer emission intensities at intermediate TME concentrations.[34] A requirement of this approach is the ability to obtain fluorescence spectra of "pure" monomer and "pure" exciplex. The former is obtained easily by recording the fluorescence spectrum of 4-methyl-1-naphthonitrile. The latter can be estimated by recording the spectrum at a high olefin concentration. In Figure 12, "pure" exciplex emission is represented by the curve labelled g(x) and the monomer emission is by F(x). The fluorescence envelope at an intermediate concentration of TME was a combination of g(x) and F(x). Measurement of the quantities $F(x_1)$, $F(x_2)$, $g(x_1)$ and $g(x_2)$ in one experiment, followed by

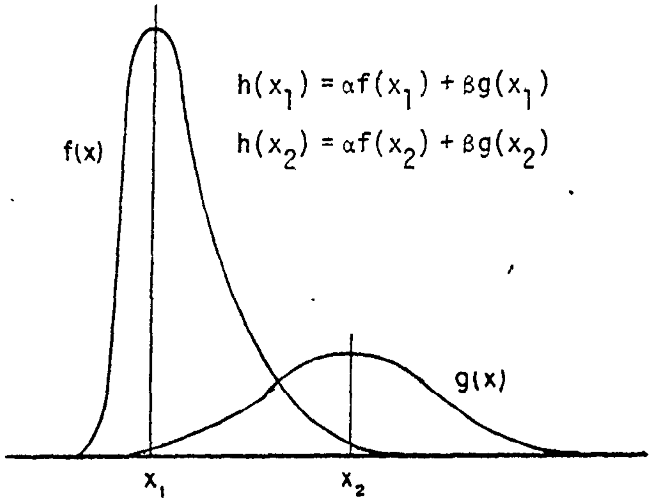


Figure 12. Simultaneous equation system for determining exciplex emission intensities as a function of quencher concentration $h(x_2)$ and $h(x_1)$ are observed intensities at the exciplex emission maximum (x_2) and the monomer emission maximum (x_1), respectively.

the determination of the values of $h(x_1)$ and $h(x_2)$ in another experiment, allow the calculation of the two coefficients α and β. Once the values of α and β are determined for one concentration of TME, the true monomer emission intensity at the emission maximum (x_1) can be computed $[\alpha F(x_1)]$ and the standard Stern-Volmer experiment can be performed.

In a typical experiment, the emission spectrum for 2.9×10^{-4} M 4-methyl-1-naphthonitrile in benzene was recorded. Similarly, a solution of 2.9×10^{-4} M 4-methyl-1-naphthonitrile and 2.0 M TME was used to record the "pure" exciplex emission.

The samples were deoxygenated by purging with a stream of argon for 3 minutes and the excitation wavelength was 310 nm. Values of the four parameters were found to be: $F(x_1) = 195$; $g(x_1) = 16$; $F(x_2) = 14$; and $g(x_2) = 46$.

Solutions were prepared that contained 2.9×10^{-4} M 4-methyl-1-naphthonitrile, and had TME concentrations that varied from 0.5 M to 0.0132 M. After deoxygenating with argon, emission spectra were recorded and the intensities at x_1 and x_2 were measured. These measurements coupled with the four parameters determined previously were used to calculate the true monomer emission intensities at x_1. The results are depicted in Figure 5 of the Results section.

2. Triplet Counting of Exciplexes using Biacetyl as the Monitor

Samples were contained in a Helma Q5 high vacuum fluorescence cell (1 cm) equipped with a side arm attached to a 10 ml peak-shaped reservoir. The cell and reservoir were sealed off by a rotoflo teflon stopcock externally equipped with a male B-14 joint for connection to a vacuum line. The sample was transferred to the reservoir for the freeze-pump-thaw cycles.

The detection of the 2-methyl-1-naphthonitrile-TME exciplex triplet state in benzene was attempted using biacetyl phosphorescence as monitor.[85] Two solutions contained in modified fluorescence cells (described above) were used for the study. One cell contained a solution of 2.0×10^{-4} M 2-methyl-1-naphthonitrile and 1.0×10^{-4} M biacetyl in benzene. The other consisted of a benzene solution which was 2.0×10^{-4} M in 2-methyl-1-naphthonitrile, 2.0 M in tetramethylethylene and 1.0×10^{-4} M in biacetyl. The TME concentration used resulted in 95% naphthonitrile quenching based on the value of the corresponding Stern-Volmer constant (KSV). Each sample underwent six freeze-pump-thaw cycles and was excited at 320 nm. In the cell containing only the naphthonitrile and biacetyl, the phosphorescence of biacetyl was observed with a maximum at 520 nm. No phosphorescence from biacetyl could be detected from the cell containing the naphthonitrile, tetramethylethylene and biacetyl.

In a similar experiment, an attempt was made to show the presence of the triplet state for the 2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether exciplex in benzene. Two solutions, one containing 2.0×10^{-4} 2-methyl-1-naphthonitrile and 1.0×10^{-4} M biacetyl in benzene and the other consisting of 2.2×10^{-4} M 2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether and 1.0×10^{-4} M biacetyl in benzene, underwent six freeze-pump-thaw cycles. The optical densities of the two naphthonitriles were both 0.56 at 320 nm. The samples were excited at 320 nm. Biacetyl phosphorescence at 520 nm was observed for the 2-methyl-1-naphthonitrile solution. However, no biacetyl phosphorescence could be detected for the

2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether solution.

3. Exciplex Quenching

The purpose of this series of experiments was to find a substance that would preferentially quench the exciplex emission over the 4-methyl-1-naphthonitrile emission.

Coumarin 102. Coumarin 102 (Eastman Kodak) was used without further purification.

Two stock solutions containing 4-methyl-1-naphthonitrile (4.25 mg, 2.5×10^{-4} M) in benzene (100 ml) and Coumarin 102 (1.45 mg, 5.7×10^{-5} M) in benzene (100 ml) were prepared. Two solutions, one containing 4-methyl-1-naphthonitrile (1.25×10^{-4} M) and Coumarin 102 (2.85×10^{-4} M) and the other containing only 4-methyl-1-naphthonitrile (1.25×10^{-4} M) were prepared by taking 10 ml of the appropriate stock solution and diluting to 25 ml. Both solutions were deoxygenated with argon and were excited at 300 nm. It was found that 14% of the emission of 4-methyl-1-naphthonitrile had been quenched by Coumarin 102.

An "Exciplex" solution was prepared using TME (3.2 gm, 1.5 M), 10 ml of the 4-methyl-1-naphthonitrile stock solution, and 10 ml of the Coumarin 102 stock solution followed by dilution to 25 ml with benzene. A second solution, identical to the first except that it did not contain Coumarin 102, was also prepared. Both solutions were deoxygenated with a stream of argon, and they were excited at 316 nm. Quenching of the exciplex emission was essentially complete in the presence of Coumarin 102.

Perylene. Perylene (Aldrich Gold Label) was used without further purification. Solutions of 4-methyl-1-naphthonitrile (4.3 mg, 2.6×10^{-4} M in 100 ml benzene) and perylene (0.107 gm, 1.7×10^{-2} M in 25 ml benzene) were prepared. Two solutions, one containing perylene (6.8×10^{-3} M) and 4-methyl-1-naphthonitrile (1.0×10^{-4} M) and the other containing 4-methyl-1-naphthonitrile (1.0×10^{-4} M) in benzene, were prepared from the appropriate stock solutions. The emission spectra of the two solutions were recorded and compared. Both solutions were deoxygenated by purging with argon and were excited at 300 nm. The fluorescence from 4-methyl-1-naphthonitrile was completely quenched by perylene.

Biacetyl. Biacetyl (Aldrich) was freshly distilled before use, b.p. 85-88°C. The fluorescence measurements were performed at -14.5° using the Aminco-Bowman spectrofluorimeter with an Aminco JA 8262 Thermostable cell compartment. Cooling was with cold nitrogen bled from a dewar containing liquid nitrogen. The nitrogen bleed was generated by a heating rod immersed in the liquid nitrogen. Samples were contained in a fluorescence cell (1 cm) with a standard taper joint fitted with a stopcock and were equilibrated for 20 minutes before the emission spectrum was recorded. The temperature of the cell was monitored by a Leeds and Northrup Co. Temperature Potentiometer and was found to be constant (± 0.2°) during acquisition of the fluorescence spectrum.

A stock solution of 4-methyl-1-naphthonitrile (4.3 mg, 2.6×10^{-4} M) in benzene (100 ml) was prepared. As well, a solution of biacetyl (0.115 gm, 5.4×10^{-2} M) in benzene (110 ml) was made. Tetramethylethylene (2.114 gm) was added to two 25 ml volumetric flasks. 10 Ml of the stock 4-methyl-1-naphthonitrile solution was added to both flasks. One flask was then diluted wo the mark with benzene to give a solution which was 1.0×10^{-4} M in 4-methyl-1-naphthonitrile and 1.0 M in TME. 2 Ml of the biacetyl stock solution was added to the other volumetric flask. Dilution to the mark with benzene gave a solution which was 1.0×10^{-4} M in 4-methyl-1-naphthonitrile, 1.0 M in TME and 4.3×10^{-3} M in biacetyl. Using the technique described above, the emission spectra of these two solutions were recorded and the exciplex emission intensities compared. Both solutions were deoxygenated by purging with argon and were excited at 320 nm.

4. Temperature Dependence of the Exciplex to Monitor Fluorescence Ratio for the 4-Methyl-1-Naphthonitrile-TME System

A stock solution of 4-methyl-1-naphthonitrile (2.7 mg, 1.62×10^{-4} M) in ethyl acetate (100 ml) was prepared. Tetramethylethylene (0.132 gm, 6.3×10^{-2} M) was added to a 25 ml volumetric flask and diluted to the mark with the naphthonitrile stock solution. The sample was deoxygenated with argon and was excited at 300 nm. The fluorescence measurements were obtained with an Aminco-Bowman spectrofluorimeter equipped with an Aminco JA8262 Thermostable cell compartment. Cooling was with cold nitrogen as described previously. The sample was equilibrated for 5 minutes at the desired temperature before the emissionspectrum was acquired. The temperature of the fluorescence cell was monitored by a Leeds and Northrup Co. temperature potentiometer and was found to be constant (± 0.5°) during the period required to obtain the emission spectrum. The emission intensity of the monomer was measured at 346 nm. The exciplex emission intensity was measured at its maximum, which was red shifted as the temperature decreased. The exciplex to monomer fluorescence ratio was then determined as shown in Table 4 of the Results section.

A similar experiment was performed with the 2-methyl-1-naphthonitrile-TME system using an ethyl acetate solution which was 1.2×10^{-4} M in 2-methyl-1-naphthonitrile and 0.064 M in tetramethylethylene. The results are shown in Figure 4 of the Results section.

5. <u>Exciplex Emission Quantum Yield</u>

The fluorescence quantum yields for the 2-methyl-1-naphthonitrile-TME, 4-methyl-1-naphthonitrile-TME and 6-methyl-1-naphthonitrile-TME exciplexes in benzene were determined. The relative quantum yield method was employed using anthranilic acid as standard.[101] The yield assumed for anthranilic acid in deoxygenated benzene was 0.58.[102] Measurements were made at ambient temperature (23°) and the exciting wavelength was 299 nm.

Each naphthonitrile was recrystallized twice and sublimed. The anthranilic acid was recrystallized three times from ethanol water, m.p. 144.5-145.5°.

The optical densities of all solutions were matched at 299 nm. Table 10 shows the concentrations of the three methyl-1-naphthonitriles used in the experiment.

Stock solutions of the 3-methyl-1-naphthonitriles in benzene (100 ml) were prepared. The tetramethylethylene concentration used in each solution was that which resulted in 96% naphthonitrile quenching, based on the values of the corresponding Stern-Volmer constants (K_{sv}). These values are summarized in Table 10.

Five ml of the stock methyl-1-naphthonitrile solution was transferred by pipette to the 10 ml volumetric containing the appropriate weight of tetramethylethylene, and the solutions were made up to the mark with benzene. The methyl-1-naphthonitrile concentrations of the final solutions are given in Table 10, and the absorbance of all the solutions at 299 was 1.0.

All solutions were deoxygenated with argon and were excited at 299 nm with an excitation band-pass of 10 nm. The emission spectra were recorded; the peaks were traced, cut and weighed, and the weights of the exciplex emission peaks compared to those of anthranilic acid. The results are shown in

Table 10. Methyl-1-Naphthonitrile and Tetramethylethylene Concentrations used for Exciplex Emission Quantum Yields in Benzene.

Fluorescer	Concentration, mole/liter x 10^4	KSV m^{-1}	[TME] mole/liter
2-methyl-1-naphthonitrile	1.52	10.1	2.38
4-methyl-1-naphthonitrile	1.25	15.7	1.53
6-methyl-1-naphthonitrile	1.83	9.0	3.31

Table 6 of the Results section.

6. Methyl-1-Naphthonitrile Emission Quantum Yields in Ethyl Acetate and Benzene

The fluorescence quantum yields for the three methyl-1-naphthonitriles in ethyl acetate were determined using the relative quantum yield method with anthranilic acid as standard. For the determinations in benzene 1-naphthonitrile was used as the standard. The yield assumed for 1-naphthonitrile in deoxygenated benzene was 0.21.[74] The procedure used was essentially the same as that described in the previous section. The optical densities of all solutions were matched at 299 nm. The determined fluorescence quantum yields are given in Table 8 of the Results section.

Product Quantum Yield Measurements

The product quantum yields were measured using the procedure of Bowman et al.[77] The irradiations were performed using a Bausch and Lomb model 33-86-01 U.V. grating monochromator coupled to an Osram HBO 220 W super-pressure lamp. The emtrance and exit slits were commonly adjusted to 5.7 and 3.2 mm, respectively, giving a band pass of 15 nm at 313 nm.

The parallel beam from the monochromator was split by a quartz plate (5.0 cm square, 2 mm thick) fixed at 45° to the beam. A typical splitting ratio, with 313 cm incident light, was 10:1. For runs using 0.001 M naphthonitrile, a neutral density filter (Model No. G-66-22, ORIEL Corporation) with a reported density of 0.37 at 300 nm was placed between the quartz plate and the reaction vessel. A typical splitting ratio, with 313 cm light, was 3.5:1.

The cells were of suprasil quartz, made by the Hellma Company, Gmbh, Germany. They were jacketed to allow water at 23° to be circulated by a Haake circulating bath. The cells were of two sizes: 2.5 cm in diameter with a path length of 5 cm, holding a volume of 26 ml; and 2.5 cm in diameter with a path length of 2.5 cm and a volume of 13 ml.

In a typical experiment, the solution to be irradiated was contained in the 26 ml cell. This cell was placed in the main beam of light, immediately followed by a 13 ml cell holding actinometer solution. A 13 ml cell holding actinometer was placed in the path of the secondary (reflected) beam. All cells were deoxygenated by purging with a stream of argon prior to and during the irradiation. Light intensities were measured by ferrioxalate actinometry.[113] The total light output was determined by measuring the light incident on the cell in the reflected beam taking into account the splitting ratio. The light absorbed by the organic solution was calculated on the basis of the total light output minus that light which was transmitted to the "back-up" actinometer solution.

The quantum yield determination for formation of cyclobutane adduct in reaction of 4-methyl-1-naphthonitrile and tetramethylethylene in ethyl acetate at -14.5° required a modification of the optical bench described above. The reaction cell was cooled by methanol from a Haake temperature bath modified in the following manner. Cooling of the methanol was with nitrogen which had passed through a coil of 1/4" copper tubing immersed in liquid nitrogen. Cold nitrogen was blown across the faces of the reaction cell to prevent condensation. The temperature of the ethyl acetate solution was monitored by a Leeds and Northrup temperature potentiometer and was found to be constant (± 0.5°) during the period of irradiation.

The extent of product formation was determined by vpc. Detector response was calibrated using solutions containing known weights of product and a suitable internal standard. In the case of the 4-methyl-1-naphthonitrile-TME system, phenanthrene was used as the internal standard. A 6' x 1/4" column of 3% OV1 on chromosorb WHP at 170° was employed. Peak areas measured with the varian integrator were typically reproducible to ± 5%. Figure 12 shows the calibration plot used in this determination. The irradiated naphthonitrile solution was evaporated and the internal standard in ethyl acetate was added for analysis by vpc.

The detector responses for the 2-methyl-1-naphthonitrile-TME and 6-methyl-1-naphthonitrile-TME cycloadducts were assumed to be the same as that determined for the 4-methyl-1-naphthonitrile-TME cycloadduct (64) with phenanthrene as the internal standard. This was a fair assumption since the cycloadducts are isomeric, and exhibit very similar retention times on the column used.

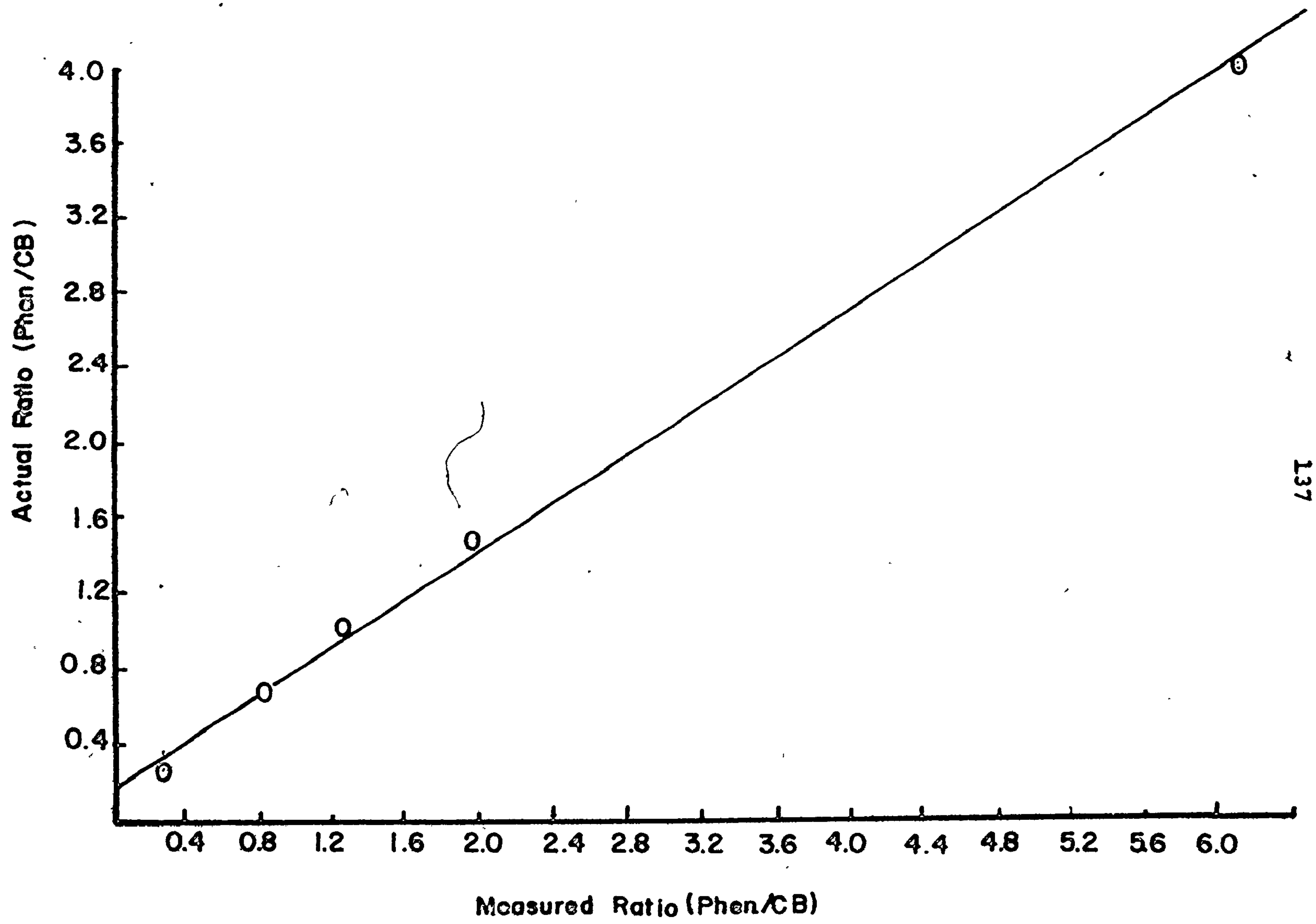


Figure 12. Typical vpc calibration plot for response to mixtures of cyclobutane 64 (CB) and phenanthrene (Phen).

In the case of 2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether, the detector response of the photoproduct (88) was measured using 4,4'-dichlorobenzophenone as the internal standard. It was assumed that this detector response would apply to the photoproducts from 2,3-dimethyl-2-butenyl 1-cyano-4-methylnaphthyl ether and 2,3-dimethyl-2-butenyl 1-cyano-6-methylnaphthyl ether. A 4' x 1/4" column of 3% OV1 on chromosorb WHP at 210° was used.

Selected product quantum yield determinations for the 4-methyl-1-naphthonitrile, 2,3-dimethyl-2-butenyl 1-cyano-2-methylnaphthyl ether and 2,3-dimethyl-2-butenyl 1-cyano-4-methylnaphthyl ether systems in benzene were monitored by UV to ensure the absence of light absorbing intermediates. Absorbance measurements were taken before and after irradiation and they were compared taking into account the degree of reaction. In all three cases there was good agreement. Since the product (94) from the irradiation of 2,3-dimethyl-2-butenyl 1-cyano-6-methylnaphthyl ether absorbed strongly at the wavelength used (ε = 2700 at 313 nm in ethanol), a correction for this was applied. In the direct irradiation, the rate of product (P) formation is given by:

$$\frac{d[P]}{dt} = -\frac{d[R]}{dt} = (\text{Quantum Yield}) \times \left(\begin{array}{c}\text{Fraction of light absorbed}\\ \text{by reactant}\end{array}\right)$$

or

$$\frac{d[P]}{dt} = \frac{d[R]}{dt} = \frac{\varepsilon_P[R]}{{}_R[R] + {}_P[P]} \cdot I \cdot \Phi \qquad (38)$$

where R is reactant, P is product, ε_R and ε_P are the extinction coefficients of R and P, respectively, I is the light intensity and Φ is the quantum yield of product formation. Integration of equation (38) gives:[114]

$$I \cdot \Phi \cdot t = ([R_o] - [R_t])(1-\varepsilon_P/\varepsilon_R) + (\varepsilon_P/\varepsilon_R)([R_o]/[R_t]) \qquad (39)$$

If [P] is the amount of product at time t, equation (39) gives

$$I \cdot \Phi \cdot t = (1 - \varepsilon_P/\varepsilon_R)[P] + \varepsilon_P/\varepsilon_R[R_o]\ell n[R_o]/[R_o-P] \qquad (40)$$

from which Φ can be calculated.

Measurement of Nanosecond Lifetimes

The technique used for excited state lifetime determinations was that of time-correlated single-photon counting.[115] The apparatus and procedure have been described by Miller.[34]

In a typical experiment, two decays were collected. The first was the lamp profile which was obtained by using Ludox SM to scatter light at the same wavelength as used for the sample excitation. The second decay was that of the emitting sample. The data from both decays was fed into the ITCONV computer program, kindly supplied by Dr. T. Nemzek. This program employed an iterative convolution procedure to correct the observed decay for the finite lifetime of the lamp discharge.

Two typical experiments are described. The measured lifetimes are recorded in Tables 3 and 6 of the Results section.

2-Methyl-1-Naphthonitrile Lifetime in Benzene.

A solution of 1.2×10^{-4} M 2-methyl-1-naphthonitrile in benzene was prepared. The solution was transferred to a Suprasil tube and was degassed by four cycles of freeze-pump-thaw, using an oil diffusion pump on a mercury-free vacuum line. The experiment was run on the 100 ns time base and the temperature was 23.0°C. The sample was excited at 310 nm and analysis of the data using the ITCONV program gave a lifetime of 10.94 nsec.

2-Methyl-1-Naphthonitrile-TME Exciplex Lifetime in Benzene.

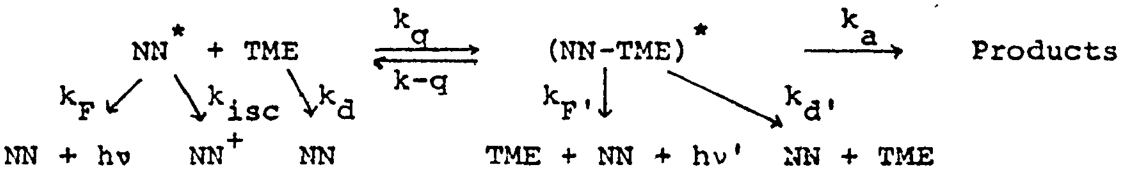
A solution was prepared that was 1.0×10^{-4} M in 2-methyl-1-naphthonitrile and 2.01 M in TME, in benzene (5 ml). The concentration of TME quenched approximately 95% of the 2-methyl-1-naphthonitrile fluorescence (as determined from the Stern-Volmer constant; $K_{SV} = 10.1$). The solution was transferred to a Suprasil tube and was degassed by four cycles of freeze-pump-thaw. The experiment was run on the 100 ns time base and the temperature was 24.0°C. The sample was excited at 310 nm and analysis of the data using the ITCONV program gave an exciplex lifetime of 14.11 ns.

APPENDICES AND REFERENCES

APPENDIX A

Steady State Conditions

Scheme



$$\frac{d[NN^*]}{dt} = I_a(t) + k_{-q}[NN^*] - (k_F + k_d + k_{isc} + k_q[TME][N^*])$$

$$\frac{d[(NN\text{-}TME)^*]}{dt} = k_q[TME][NN^*] - (k_{-q} + k_p)[(NN\text{-}TME)^*]$$

$$k_p = k_{F'} + k_{d'} + k_a = \tau_{lim}^{-1}\text{(Exciplex)}$$

$$\lambda_0 = k_F + k_{isc} + k_d = \tau_0^{-1}\text{(monomer)}$$

Stern-Volmer Relation

$$\frac{\Phi_0}{\Phi} = \frac{I_0}{I} = 1 + KSV[Q]$$

$$KSV = \frac{k_q k_p}{k_{-q} + k_p}\ \tau_0$$

Also,

$$KSV^{-1} = \frac{k_{-q} + k_p}{k_q k_p \tau_0} = \frac{k_{-q}}{k_q k_p \tau_0} + \frac{1}{k_q \tau_0}$$

$$= \frac{k_{-q} \cdot \tau_{lim}}{k_q \cdot \tau_0} + \frac{1}{k_q \cdot \tau_0}$$

$$= \frac{1}{k_q \tau_0}[k_{-q} \cdot \tau_{lim} + 1]$$

Or

$$k_q = \frac{KSV}{\tau_0}[k_{-q}\cdot\tau_{\lim} + 1]$$

k_q will equal $\frac{KSV}{\tau_0}$ if k_{-q} is small or $\tau_{\lim}$ is very short, i.e., conditions for irreversibility.

Also,

$$\phi^{-1} = \phi_{\lim}^{-1}(1 + KSV^{-1}[TME]^{-1})$$

Φ = quantum yield of fluorescence or product formation

$$\phi_{\lim}^{f'} = k_{F'}/k_{F'} + k_{d'} + k_a = k_{F'}\tau_{\lim}$$

$$\phi_{\lim}^{Product} = k_a/k_{F'} + k_{d'} + k_a = k_a\cdot\tau_{\lim}$$

Transient Conditions

At relatively high temperatures (the "rapid equilibrium region"), $k_q, k_{-q} >> \lambda_0, k_p$. In this region, both NN* and (NN-TME)* show single exponential decay with the same decay constant, λ.[27,116]

$$\lambda = (\lambda_0 + k_q\cdot k_p/k_{-q})[TME]/1 + (k_q/k_{-q})[TME]$$

As [TME] → ∞

$$\lambda = (\lambda_0/1 + (k_q/k_{-q})[TME]) + ((k_q/k_{-q})k_p[TME])/(k_q/k_{-q})[TME] + 1$$

$$= k_p = (\tau_{\lim})^{-1}$$

At limiting quencher concentration, we are assuming the following approximation is valid.

$$[(NN\text{-}TME)^*]_t = [(NN\text{-}TME)^*]_0 e^{-k_p t}$$

APPENDIX B

Supplementary Material

A table of the moduli of F_o and F_c for (X10.0). (13 Pages) F(000) on the same scale is 5680, $C_{18}H_{19}NO$.

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_{18}H_{19}NO$

PAGE 1 OF13

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
0	0	2	313	329	9	0	4	14	151	148	5	0	10	5	7+	16	23
0	0	4	198	206	6	0	4	15	36+	46	9	0	10	6	24+	24	14
0	0	6	158	153	5	0	4	16	40	43	9	0	10	4	4+	10	24
0	0	8	266	263	3	0	4	17	21+	14	15	1	0	0	94	84	3
0	0	10	41	37	5	0	5	1	218	219	7	1	0	2	920	923	27
0	0	12	313	330	10	0	5	2	72	69	4	1	0	4	480	482	14
0	0	14	174	137	6	0	5	3	54	49	4	1	0	-4	186	183	6
0	0	16	40+	43	8	0	5	4	107	101	4	1	0	6	131	128	4
0	0	18	52+	55	7	0	5	5	69	67	4	1	0	-6	658	663	20
0	1	1	727	749	21	0	5	6	76	79	4	1	0	8	39	29	5
0	1	3	250	248	8	0	5	7	46	51	6	1	0	-8	87	94	3
0	1	4	162	162	5	0	5	8	80	83	4	1	0	10	77	81	4
0	1	5	15+	17	10	0	5	9	21+	32	11	1	0	-10	203	197	6
0	1	6	192	201	6	0	5	10	52	59	6	1	0	12	299	296	9
0	1	7	41	40	4	0	5	11	7+	3	18	1	0	-12	233	234	7
0	1	8	39	43	5	0	5	12	27+	30	10	1	0	14	44	46	6
0	1	9	24+	32	8	0	5	13	88	86	5	1	0	-14	85	87	5
0	1	10	41	46	6	0	5	14	42+	34	8	1	0	16	18+	8	13
0	1	12	93	101	4	0	5	15	12+	19	18	1	0	-16	82	83	5
0	1	13	82	86	5	0	6	0	67	72	4	1	0	18	63	43	6
0	1	14	151	158	5	0	6	1	81	84	4	1	0	-18	18+	13	14
0	1	16	22+	18	12	0	6	2	23+	21	9	1	1	0	927	919	27
0	1	17	27+	27	11	0	6	3	73	73	4	1	1	1	339	355	10
0	1	18	21+	10	14	0	6	4	27+	20	8	1	1	-1	211	216	6
0	2	0	1005	1013	30	0	6	5	55	58	5	1	1	2	372	364	11
0	2	1	282	297	9	0	6	6	28+	14	8	1	1	-2	98	98	4
0	2	2	39	49	5	0	6	8	21+	30	11	1	1	3	259	267	8
0	2	3	241	239	7	0	6	7	144	143	5	1	1	-3	54	54	4
0	2	5	137	140	4	0	6	9	13+	15	14	1	1	4	386	388	12
0	2	6	83	86	3	0	6	10	9+	23	18	1	1	-4	459	449	14
0	2	7	175	181	5	0	6	11	14+	12	17	1	1	5	350	366	11
0	2	8	29+	20	6	0	6	12	16+	22	16	1	1	-5	103	110	4
0	2	9	93	95	4	0	6	13	9+	27	20	1	1	6	138	138	4
0	2	10	41	37	6	0	6	14	22+	25	18	1	1	-6	207	204	6
0	2	11	14+	38	15	0	6	15	49	37	8	1	1	7	37	49	5
0	2	12	164	161	5	0	7	1	134	139	5	1	1	-7	18+	1	8
0	2	13	75	76	5	0	7	2	35+	36	7	1	1	8	70	74	4
0	2	14	103	105	5	0	7	3	105	109	4	1	1	-8	32+	22	6
0	2	15	15+	15	17	0	7	4	126	130	5	1	1	9	104	101	4
0	2	16	26+	19	11	0	7	5	60	54	5	1	1	-9	45	39	5
0	2	17	40+	49	9	0	7	6	54	58	5	1	1	10	40	43	5
0	2	18	6+	14	23	0	7	7	42	51	8	1	1	-10	229	230	7
0	3	1	352	342	11	0	7	8	11+	22	18	1	1	11	108	115	4
0	3	2	117	115	4	0	7	9	61	57	6	1	1	-11	82	76	4
0	3	3	153	153	5	0	7	10	6+	13	21	1	1	12	145	151	5
0	3	5	129	133	4	0	7	11	11+	19	19	1	1	-12	32+	8	8
0	3	6	131	132	4	0	7	12	15+	2	18	1	1	13	43	55	6
0	3	7	72	72	4	0	7	13	15+	10	19	1	1	14	153	155	5
0	3	8	12+	5	14	0	7	14	0+	11	28	1	1	-14	32+	47	9
0	3	9	28+	21	7	0	8	0	33+	44	9	1	1	15	52	56	6
0	3	10	154	157	5	0	8	1	40	37	7	1	1	-15	36+	48	9
0	3	11	212	216	6	0	8	2	17+	30	13	1	1	-16	40+	26	8
0	3	12	88	89	4	0	8	3	80	81	5	1	1	17	24+	10	11
0	3	13	133	139	5	0	8	6	16+	21	17	1	1	-17	16+	36	15
0	3	14	15+	9	17	0	8	7	21+	17	12	1	1	-18	62	64	7
0	3	15	94	93	5	0	8	8	20+	18	15	1	1	-19	24+	9	13
0	3	16	53	51	6	0	8	9	9+	9	20	1	2	0	806	824	24
0	3	17	28+	30	11	0	8	10	6+	26	22	1	2	1	490	503	15
0	3	18	10+	23	21	0	8	11	39+	48	10	1	2	-1	40	40	5
0	4	0	424	435	13	0	8	12	24+	13	15	1	2	2	951	962	28
0	4	1	256	261	9	0	9	2	44+	40	8	1	2	-2	384	386	12
0	4	2	414	425	13	0	9	3	76	73	5	1	2	3	97	99	3
0	4	3	66	66	4	0	9	4	52	41	7	1	2	-3	398	416	12
0	4	4	12+	31	14	0	9	7	45	28	7	1	2	4	259	263	8
0	4	5	15+	20	13	0	9	8	24+	26	13	1	2	-4	81	82	3
0	4	6	53	47	4	0	9	9	31+	32	11	1	2	5	394	396	12
0	4	7	77	78	4	0	9	10	22+	21	19	1	2	-5	243	229	7
0	4	8	109	113	4	0	10	0	57	41	6	1	2	6	235	239	7
0	4	9	22+	17	10	0	10	1	14+	6	19	1	2	-6	213	218	6
0	4	12	96	89	5	0	10	2	10+	9	20	1	2	7	303	315	9
0	4	13	66	71	5	0	10	3	3+	5	25	1	2	-7	140	138	4

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_{18}H_{19}NO$

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG
1	2	8	31+	48	6
1	2	-8	248	237	7
1	2	9	87	88	4
1	2	-9	34+	17	6
1	2	10	21+	22	9
1	2	-10	202	202	6
1	2	11	53	48	5
1	2	-11	207	209	6
1	2	12	142	147	5
1	2	-12	182	182	6
1	2	13	139	132	5
1	2	-13	23+	33	11
1	2	14	54	52	6
1	2	-14	86	82	5
1	2	15	15+	3	14
1	2	-15	32+	38	9
1	2	16	43+	36	7
1	2	-16	13+	14	16
1	2	-17	26+	53	12
1	2	18	34+	29	10
1	3	0	123	120	4
1	3	1	121	130	4
1	3	-1	535	542	16
1	3	2	23+	14	7
1	3	-2	59	65	4
1	3	3	128	121	4
1	3	-3	216	232	6
1	3	4	139	145	4
1	3	-4	68	70	3
1	3	5	45	53	4
1	3	-5	129	131	4
1	3	6	86	80	3
1	3	-6	41	41	5
1	3	7	17+	9	9
1	3	-7	155	151	5
1	3	8	74	75	4
1	3	-8	115	110	4
1	3	-9	128	132	4
1	3	10	62	67	4
1	3	11	37+	38	6
1	3	12	48	41	6
1	3	-12	165	170	5
1	3	13	71	78	5
1	3	-13	208	217	7
1	3	14	88	92	5
1	3	-14	54	53	6
1	3	15	23+	18	11
1	3	16	50	56	7
1	3	17	11+	22	17
1	3	-17	26+	9	11
1	4	0	212	194	6
1	4	1	309	326	9
1	4	-1	94	96	4
1	4	2	279	284	8
1	4	-2	79	77	3
1	4	3	111	108	4
1	4	-3	89	90	3
1	4	4	130	126	4
1	4	-4	103	97	4
1	4	5	78	81	4
1	4	-5	165	158	5
1	4	6	52	56	4
1	4	-6	72	68	4
1	4	-7	45	48	5
1	4	8	22+	0	8
1	4	9	173	174	5
1	4	-9	26+	35	9
1	4	10	61	59	5
1	4	-10	322	332	10
1	4	11	37+	24	6
1	4	-11	125	132	5
1	4	12	136	135	5
1	4	-12	31+	33	9
1	4	13	80	84	5
1	4	-13	77	69	5
1	4	14	108	104	5
1	4	-14	23+	28	11
1	4	16	25+	0	11
1	4	-16	33+	28	10
1	4	17	33+	31	10
1	4	-17	59	39	6
1	5	0	34+	36	6
1	5	1	47	54	5
1	5	-1	27+	21	7
1	5	2	225	227	7
1	5	-2	102	102	4
1	5	3	91	87	4
1	5	-3	129	131	4
1	5	4	198	197	6
1	5	-4	93	98	4
1	5	5	47	43	5
1	5	-5	115	116	4
1	5	6	56	63	5
1	5	7	33+	23	7
1	5	-7	22+	13	10
1	5	-8	144	149	5
1	5	-9	68	72	5
1	5	10	63	71	5
1	5	-10	74	80	5
1	5	11	66	71	5
1	5	-11	5+	41	20
1	5	12	9+	0	16
1	5	-12	79	85	5
1	5	13	26+	27	10
1	5	14	21+	15	12
1	5	15	44+	19	7
1	5	-15	22+	7	13
1	5	16	68	57	6
1	5	-16	18+	9	15
1	5	-17	15+	17	17
1	6	0	44	49	6
1	6	1	172	165	5
1	6	-1	28+	20	8
1	6	2	186	191	6
1	6	-2	58	62	5
1	6	3	142	149	5
1	6	-3	173	166	5
1	6	4	95	94	4
1	6	-4	47	48	6
1	6	5	42	31	6
1	6	6	59	55	5
1	6	-6	33+	40	8
1	6	7	47	53	6
1	6	-7	75	78	5
1	6	8	25+	29	9
1	6	-8	42+	25	7
1	6	9	35+	33	7
1	6	-9	28+	48	9
1	6	10	18+	37	13
1	6	-10	105	103	5
1	6	11	23+	33	10
1	6	-11	29+	23	10
1	6	12	12+	6	16
1	6	-12	43+	15	7
1	6	14	49	28	7
1	6	-14	28+	18	11
1	6	15	40+	45	9
1	7	0	69	65	5
1	7	1	221	221	7
1	7	-1	83	87	4
1	7	2	110	103	4
1	7	-2	169	170	5
1	7	3	122	127	5
1	7	4	94	100	4
1	7	-4	100	97	5
1	7	5	41+	32	6
1	7	6	56	51	5
1	7	-6	74	73	5
1	7	7	14+	26	14
1	7	-7	102	98	5
1	7	8	66	54	5
1	7	-8	40+	42	8
1	7	9	41+	21	7
1	7	-9	38+	44	8
1	7	10	39+	29	8
1	7	-10	33+	37	10
1	7	11	26+	35	11
1	7	-11	74	71	6
1	7	12	32+	11	9
1	7	-12	10+	17	19
1	7	13	38+	25	9
1	7	-13	35+	18	9
1	7	-14	20+	5	15
1	8	0	35+	29	8
1	8	1	54	54	6
1	8	2	24+	20	11
1	8	-2	30+	37	9
1	8	3	52	51	6
1	8	-1	21+	20	11
1	8	-3	29+	35	10
1	8	4	8+	2	18
1	8	-5	33+	19	9
1	8	-6	32+	20	9
1	8	7	29+	1	9
1	8	-7	20+	2	13
1	8	-8	41+	32	8
1	8	9	46+	52	8
1	8	-10	14+	12	17
1	8	-12	28+	25	12
1	9	1	38+	39	8
1	9	-1	44+	37	9
1	9	2	57	47	6
1	9	-2	28+	36	11
1	9	3	35+	9	8
1	9	-3	8+	10	19
1	9	4	26+	27	11
1	9	-4	29+	18	10
1	9	-5	34+	21	9
1	9	6	28+	2	10
1	9	-6	19+	24	14
1	9	-7	24+	18	12
1	9	-8	22+	9	14
1	9	9	53	41	7
1	9	-9	51	28	7
1	9	-10	38+	34	10
1	10	0	31+	25	10
1	10	1	16+	7	16
1	10	-1	32+	8	10
1	10	2	19+	34	15
1	10	-2	52	28	7
1	10	-3	22+	8	13
1	10	-4	53	31	7
1	10	-5	39+	13	9
1	10	-6	20+	16	15
2	0	0	151	160	5
2	0	2	1051	1050	31
2	0	-2	518	510	15
2	0	4	528	520	16
2	0	-4	915	900	27
2	0	6	37	28	5
2	0	-6	895	968	27
2	0	8	129	132	4
2	0	-8	29+	33	6

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_{18}H_{19}NO$ PAGE 3 OF13

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	0	10	56	50	4	2	2	14	57	53	5	2	5	3	38+	56	6
2	0	-10	142	137	5	2	2	-14	21+	3	10	2	5	-3	38+	33	6
2	0	12	175	187	6	2	2	15	18+	14	13	2	5	4	281	270	8
2	0	-12	148	149	5	2	2	15	31+	18	9	2	5	-4	101	99	4
2	0	14	0+	11	24	2	2	-16	5+	16	21	2	5	5	82	75	4
2	0	-14	33+	32	8	2	2	17	35+	7	9	2	5	-5	270	260	8
2	0	16	77	73	5	2	2	-18	50	41	7	2	5	6	58	51	5
2	0	-16	29+	20	9	2	3	1	114	107	4	2	5	-6	129	126	4
2	0	18	47+	48	8	2	3	0	285	275	9	2	5	7	64	62	4
2	0	-18	66	74	6	2	3	-1	82	75	3	2	5	-7	36+	27	7
2	1	0	480	477	14	2	3	2	401	394	12	2	5	8	84	89	4
2	1	1	20+	31	8	2	3	-2	245	242	7	2	5	-8	138	138	5
2	1	-1	31+	37	5	2	3	3	318	324	10	2	5	9	41	37	6
2	1	-2	57	51	4	2	3	-3	98	95	4	2	5	-9	58	62	5
2	1	2	395	399	12	2	3	4	335	316	10	2	5	10	47	51	6
2	1	3	89	82	3	2	3	-4	29+	14	6	2	5	-10	33+	35	8
2	1	-3	82	78	3	2	3	5	289	280	9	2	5	11	45	33	6
2	1	4	128	133	4	2	3	-5	96	97	4	2	5	12	13+	0	14
2	1	5	18+	30	9	2	3	6	99	92	4	2	5	-12	62	71	5
2	1	-5	268	268	8	2	3	-6	15+	18	10	2	5	13	5+	16	21
2	1	6	313	316	9	2	3	7	94	95	4	2	5	14	25+	3	11
2	1	-6	10+	17	12	2	3	-7	74	69	4	2	5	15	14+	19	17
2	1	7	147	153	5	2	3	8	27+	34	7	2	5	-17	23+	5	14
2	1	-7	256	250	8	2	3	-8	151	150	5	2	6	0	34+	2	7
2	1	8	34+	48	6	2	3	9	9+	6	15	2	6	1	224	237	7
2	1	-8	140	129	4	2	3	-9	45	48	5	2	6	-1	76	77	4
2	1	9	107	111	4	2	3	-10	220	215	7	2	6	2	178	185	6
2	1	-9	115	114	4	2	3	11	48	59	5	2	6	-2	24+	16	9
2	1	10	97	102	4	2	3	-11	195	195	6	2	6	3	227	232	7
2	1	-10	123	127	4	2	3	12	83	79	4	2	6	-3	106	99	4
2	1	11	91	90	4	2	3	13	55	48	5	2	6	4	58	54	5
2	1	-11	76	74	4	2	3	-13	27+	6	9	2	6	-4	96	97	4
2	1	12	47	47	6	2	3	14	53	55	6	2	6	-5	35+	25	7
2	1	-12	196	192	6	2	3	-14	60	59	5	2	6	6	19+	24	11
2	1	13	70	67	5	2	3	16	33+	18	9	2	6	-6	64	61	5
2	1	-13	84	92	4	2	3	-16	48	43	7	2	6	7	12+	12	14
2	1	14	12+	5	15	2	3	-17	50	51	7	2	6	-7	100	102	4
2	1	-14	42+	50	7	2	3	-18	42+	39	9	2	6	-8	17+	7	12
2	1	15	44+	42	7	2	4	0	287	282	9	2	6	9	35+	41	8
2	1	-15	23+	9	10	2	4	1	243	252	7	2	6	-9	62	54	5
2	1	17	27+	39	11	2	4	-1	108	104	4	2	6	10	51	63	6
2	1	-17	40+	21	8	2	4	2	571	551	18	2	6	-10	116	116	5
2	1	18	58	56	7	2	4	-2	232	225	7	2	6	11	34+	27	8
2	1	-18	40+	15	8	2	4	3	75	73	4	2	6	-11	30+	23	9
2	1	-19	27+	36	13	2	4	-3	38	37	5	2	6	12	25+	9	10
2	2	0	483	500	15	2	4	4	105	112	4	2	6	-12	43+	46	8
2	2	1	973	968	29	2	4	-4	150	144	5	2	6	-13	29+	39	10
2	2	-1	286	293	9	2	4	5	23+	4	8	2	6	14	48+	44	7
2	2	2	242	242	7	2	4	-5	73	68	4	2	6	-15	21+	15	14
2	2	-2	193	194	6	2	4	6	129	129	4	2	6	-16	6+	11	23
2	2	3	368	358	11	2	4	-6	162	153	5	2	7	1	104	102	4
2	2	-3	213	205	6	2	4	7	34+	41	6	2	7	-1	98	102	4
2	2	4	210	205	6	2	4	-7	28+	29	8	2	7	2	101	106	4
2	2	-4	200	198	6	2	4	8	76	73	4	2	7	-2	179	180	6
2	2	5	177	182	5	2	4	-8	21+	28	10	2	7	3	75	82	5
2	2	-5	57	54	4	2	4	9	58	59	5	2	7	-3	44	41	6
2	2	6	93	89	4	2	4	-9	89	95	4	2	7	4	113	125	5
2	2	-6	146	151	4	2	4	10	48	57	6	2	7	-4	35+	31	7
2	2	-7	56	58	4	2	4	-10	130	129	5	2	7	5	13+	17	13
2	2	8	19+	14	9	2	4	-11	71	67	5	2	7	-5	87	93	5
2	2	-8	119	121	4	2	4	-12	196	196	6	2	7	6	18+	25	12
2	2	9	157	155	5	2	4	-14	37+	40	8	2	7	7	50	43	6
2	2	-9	289	285	9	2	4	15	44+	31	7	2	7	-7	15+	14	13
2	2	10	84	94	4	2	4	-15	56	46	6	2	7	8	14+	23	14
2	2	-10	43	35	6	2	4	-16	35+	47	9	2	7	-8	55	50	6
2	2	11	12+	0	13	2	4	-18	19+	4	15	2	7	9	19+	8	13
2	2	-11	220	221	7	2	5	0	350	325	11	2	7	-9	44+	58	7
2	2	12	12+	33	14	2	5	1	198	201	6	2	7	10	12+	3	16
2	2	-12	183	192	6	2	5	-1	53	36	4	2	7	-11	39+	39	8
2	2	13	10+	10	15	2	5	2	40	46	6	2	7	-12	59	49	6
2	2	-13	80	84	4	2	5	-2	50	45	5	2	7	13	74	60	6

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_{18}H_{19}NO$

PAGE 4 OF13

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG
2	7	-13	25+	6	12
2	7	-14	11+	5	19
2	8	0	26+	32	10
2	8	1	34+	29	8
2	8	-1	63	72	5
2	8	2	16+	16	13
2	8	-2	5+	18	20
2	8	3	39+	52	7
2	8	4	26+	43	10
2	8	-4	35+	29	8
2	8	5	49	43	6
2	8	-5	40+	40	7
2	8	6	31+	4	9
2	8	-6	14+	4	15
2	8	7	21+	17	12
2	8	-7	39+	50	8
2	8	8	25+	28	11
2	8	-8	22+	42	12
2	8	9	23+	22	12
2	8	-9	50	35	7
2	8	10	19+	19	14
2	8	-11	34+	25	10
2	8	-12	43+	14	8
2	9	0	24+	2	11
2	9	2	34+	37	10
2	9	-2	40+	37	8
2	9	3	24+	5	11
2	9	-3	39+	12	8
2	9	4	53	45	7
2	9	-4	49	50	7
2	9	5	35+	33	9
2	9	6	29+	21	10
2	9	-6	30+	24	10
2	9	7	45+	34	8
2	9	-7	43+	35	8
2	9	8	42+	22	8
2	9	-8	61	59	7
2	9	9	35+	19	9
2	9	-9	59	63	7
2	9	-10	28+	17	12
2	10	2	31+	0	10
2	10	-2	17+	13	14
2	10	3	28+	3	11
2	10	-3	33+	19	10
2	10	-4	14+	2	17
2	10	-6	13+	28	19
3	0	0	467	469	14
3	0	2	239	242	7
3	0	-2	379	379	12
3	0	4	38	36	5
3	0	-4	1236	1217	37
3	0	6	563	567	17
3	0	-6	357	348	11
3	0	8	132	125	4
3	0	-8	644	600	20
3	0	10	100	97	4
3	0	-10	148	145	5
3	0	12	79	73	4
3	0	-12	8+	2	16
3	0	14	31+	48	9
3	0	-14	12+	21	14
3	0	16	34+	34	9
3	0	-16	60	58	6
3	1	0	232	224	7
3	1	1	227	226	7
3	1	-1	85	82	3
3	1	2	118	117	4
3	1	-2	235	230	7
3	1	3	95	93	3
3	1	-3	83	84	3
3	1	4	149	144	4
3	1	-4	59	54	4
3	1	5	185	172	6
3	1	-5	467	467	14
3	1	6	232	215	7
3	1	-6	721	701	22
3	1	7	194	192	6
3	1	-7	160	153	5
3	1	8	155	146	5
3	1	-8	109	112	4
3	1	9	37+	34	6
3	1	-9	104	100	4
3	1	-10	155	156	5
3	1	11	58	59	5
3	1	-11	56	58	5
3	1	12	63	53	5
3	1	-12	48	34	5
3	1	14	27+	32	9
3	1	-14	33+	37	8
3	1	15	46	30	6
3	1	-15	49	52	6
3	1	16	59	51	6
3	1	-16	30+	6	9
3	1	-18	49	50	7
3	1	-19	20+	3	14
3	2	0	26+	32	7
3	2	1	98	95	3
3	2	-1	178	183	5
3	2	2	115	114	4
3	2	-2	517	515	16
3	2	3	326	339	10
3	2	-3	101	101	3
3	2	4	69	77	4
3	2	-4	322	308	10
3	2	5	199	192	6
3	2	-5	63	70	4
3	2	6	105	104	4
3	2	-6	265	259	8
3	2	7	46	39	5
3	2	-7	331	328	10
3	2	8	127	126	4
3	2	-8	162	144	5
3	2	9	73	71	4
3	2	-9	100	92	4
3	2	10	147	140	5
3	2	-10	21+	3	9
3	2	11	74	77	4
3	2	-11	74	84	4
3	2	12	32+	38	8
3	2	-12	99	106	4
3	2	13	50	40	6
3	2	-13	11+	19	15
3	2	-15	43+	40	7
3	2	-16	44+	42	7
3	2	17	18+	20	15
3	2	-18	22+	5	13
3	3	1	79	80	3
3	3	-1	133	130	4
3	3	2	101	96	4
3	3	-2	141	130	4
3	3	3	83	75	3
3	3	-3	119	123	4
3	3	4	34+	42	6
3	3	-4	100	101	4
3	3	5	131	132	4
3	3	-5	6+	0	15
3	3	-6	145	143	4
3	3	7	117	123	4
3	3	-7	203	197	6
3	3	8	85	79	4
3	3	-8	29+	23	7
3	3	9	29+	32	8
3	3	10	83	85	4
3	3	-10	4+	23	19
3	3	11	12+	7	14
3	3	-11	44	39	6
3	3	-12	96	95	4
3	3	13	17+	11	13
3	3	-13	39+	30	7
3	3	14	24+	21	11
3	3	-14	18+	24	12
3	3	15	47+	49	7
3	3	16	19+	32	14
3	3	-16	35+	29	9
3	3	-18	19+	14	15
3	4	0	103	101	4
3	4	-1	30+	33	6
3	4	2	16+	27	10
3	4	-2	100	102	4
3	4	3	120	124	4
3	4	-3	88	85	4
3	4	4	83	80	4
3	4	-4	187	180	6
3	4	5	79	79	4
3	4	-5	265	249	8
3	4	6	109	108	4
3	4	-6	52	45	5
3	4	7	177	170	6
3	4	-7	91	85	4
3	4	8	45	32	6
3	4	-8	107	107	4
3	4	9	19+	25	11
3	4	-9	47	46	6
3	4	10	33+	38	8
3	4	-10	50	44	6
3	4	11	41+	41	6
3	4	-11	45	62	6
3	4	12	52	53	6
3	4	-12	37+	34	7
3	4	13	63	58	6
3	4	-13	15+	24	14
3	4	14	33+	28	9
3	4	-14	29+	16	9
3	4	15	14+	1	16
3	4	-15	56	62	7
3	4	-16	47+	46	7
3	4	-17	23+	32	14
3	4	-18	51+	48	8
3	5	0	43	49	6
3	5	1	47	41	5
3	5	-1	92	96	4
3	5	2	194	193	6
3	5	-2	115	121	4
3	5	3	77	77	4
3	5	-3	243	241	7
3	5	-4	19+	23	11
3	5	5	68	70	4
3	5	-5	179	175	6
3	5	6	43	30	6
3	5	-6	74	72	4
3	5	7	115	111	4
3	5	-7	24+	22	10
3	5	-8	76	72	5
3	5	9	115	116	5
3	5	-9	73	70	5
3	5	10	75	81	5
3	5	-10	79	85	5
3	5	11	17+	29	13
3	5	-11	86	85	5
3	5	12	38+	26	8
3	5	-12	39+	41	8
3	5	-13	29+	6	9
3	5	14	56	39	7

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_{18}H_{19}NO$

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
3	5	-14	11+	32	17	3	8	-10	21+	24	14	4	1	14	27+	23	10
3	5	15	14+	26	17	3	8	-11	34+	26	10	4	1	-14	20+	28	11
3	5	-15	42+	28	8	3	8	-12	41+	24	9	4	1	15	38+	7	9
3	5	-16	21+	25	13	3	9	0	27+	27	11	4	1	-15	40+	42	7
3	6	1	61	57	5	3	9	1	6+	14	21	4	1	16	25+	8	11
3	6	-1	168	164	5	3	9	-1	43+	20	7	4	1	-15	58	54	6
3	6	2	104	102	4	3	9	2	41+	45	9	4	1	-17	38+	24	8
3	6	-2	67	70	5	3	9	-2	38+	33	8	4	1	-18	54	42	7
3	6	3	63	71	5	3	9	3	93	84	5	4	1	-19	15+	5	17
3	6	-3	94	93	4	3	9	-3	20+	17	13	4	2	0	211	208	6
3	6	4	19+	26	11	3	9	5	41+	50	8	4	2	1	216	224	6
3	6	-4	87	91	4	3	9	-5	66	57	6	4	2	-1	44	49	4
3	6	5	15+	27	13	3	9	6	35+	30	9	4	2	2	24+	26	7
3	6	-5	50	44	6	3	9	-6	28+	0	11	4	2	-2	472	469	14
3	6	6	44	56	6	3	9	-7	70	57	6	4	2	3	435	431	13
3	6	-6	37+	32	7	3	9	8	23+	26	13	4	2	-3	373	368	11
3	6	7	82	82	4	3	9	-8	23+	40	14	4	2	4	230	226	7
3	6	8	24+	23	10	3	9	-9	58	33	7	4	2	-4	176	171	5
3	6	-8	36+	12	7	3	9	-10	62	60	7	4	2	5	104	96	4
3	6	-9	180	178	6	3	10	0	33+	18	10	4	2	-5	73	76	3
3	6	10	48	37	6	3	10	1	36+	22	9	4	2	6	73	78	4
3	6	-10	44+	35	7	3	10	-1	17+	17	15	4	2	-6	59	60	4
3	6	11	14+	2	15	3	10	2	25+	4	12	4	2	7	46	39	5
3	6	-11	17+	3	13	3	10	-2	36+	22	9	4	2	8	47	55	5
3	6	12	28+	40	11	3	10	-3	47+	40	8	4	2	-8	231	232	7
3	6	-12	27+	6	10	3	10	4	37+	23	10	4	2	9	42	20	6
3	6	13	60	61	7	3	10	-5	37+	2	10	4	2	-9	95	95	4
3	6	-13	32+	2	10	3	10	-6	13+	13	18	4	2	10	23+	15	9
3	6	14	21+	25	14	4	0	0	136	138	4	4	2	-10	162	163	5
3	6	-14	18+	7	14	4	0	2	428	424	13	4	2	11	67	55	5
3	6	-15	30+	17	11	4	0	-2	260	282	8	4	2	-11	30+	21	7
3	6	-16	28+	6	12	4	0	4	184	182	6	4	2	-12	57	56	5
3	7	0	158	162	5	4	0	-4	317	302	10	4	2	-13	29+	3	8
3	7	1	128	134	5	4	0	6	224	224	7	4	2	-14	46	46	6
3	7	2	74	76	5	4	0	-6	576	562	18	4	2	15	10+	5	18
3	7	3	47	47	6	4	0	8	213	205	6	4	2	-15	50	40	6
3	7	-3	44	40	6	4	0	-8	168	156	5	4	2	16	9+	11	19
3	7	4	36+	34	7	4	0	10	26+	26	9	4	2	-16	42+	43	7
3	7	-4	116	115	4	4	0	-10	192	186	6	4	2	-17	58	58	6
3	7	5	77	79	5	4	0	12	28+	0	9	4	2	-19	65	65	7
3	7	-5	27+	16	9	4	0	-12	41+	37	6	4	3	0	68	61	3
3	7	-6	29+	9	9	4	0	14	54	46	6	4	3	1	114	108	4
3	7	-7	73	79	5	4	0	-14	0+	12	24	4	3	-1	268	263	8
3	7	8	54	51	6	4	0	16	28+	33	11	4	3	2	125	121	4
3	7	-8	38+	41	8	4	0	-16	54	54	6	4	3	-2	181	174	5
3	7	9	19+	41	13	4	0	-18	0+	4	27	4	3	3	81	80	4
3	7	10	48	46	7	4	1	0	57	64	4	4	3	-3	245	243	7
3	7	-10	29+	19	10	4	1	1	323	307	10	4	3	4	95	95	4
3	7	11	37+	15	9	4	1	-1	208	211	6	4	3	-4	163	164	5
3	7	-11	39+	27	8	4	1	2	51	54	4	4	3	5	10+	17	14
3	7	-12	37+	11	9	4	1	-2	212	211	6	4	3	-5	265	265	8
3	7	-14	14+	14	18	4	1	3	35	17	5	4	3	6	143	146	5
3	8	0	25+	35	10	4	1	-3	281	295	8	4	3	-6	114	114	4
3	8	1	30+	24	9	4	1	4	5+	21	15	4	3	7	106	110	4
3	8	-1	24+	7	10	4	1	-4	199	196	6	4	3	-7	69	75	4
3	8	2	28+	38	9	4	1	5	69	68	4	4	3	8	82	72	4
3	8	-2	14+	21	14	4	1	-5	50	56	4	4	3	-8	142	137	5
3	8	3	86	89	5	4	1	6	300	283	9	4	3	9	61	44	5
3	8	-3	77	80	5	4	1	-6	105	96	4	4	3	-9	47	48	5
3	8	4	80	77	5	4	1	7	207	208	6	4	3	10	22+	20	10
3	8	-4	39+	48	9	4	1	-7	112	114	4	4	3	-10	34+	28	7
3	8	5	20+	31	13	4	1	-8	269	241	8	4	3	11	60	70	5
3	8	-5	25+	2	10	4	1	9	110	114	4	4	3	-11	30+	18	8
3	8	6	21+	35	13	4	1	-9	19+	27	9	4	3	-12	80	83	5
3	8	-6	58	57	6	4	1	10	28+	38	8	4	3	13	48	31	6
3	8	7	28+	14	10	4	1	-10	46	47	5	4	3	-13	77	75	5
3	8	8	13+	28	16	4	1	11	32+	26	7	4	3	14	13+	4	15
3	8	-8	74	66	6	4	1	-11	73	66	4	4	3	-14	55	55	6
3	8	9	41+	19	8	4	1	12	58	64	5	4	3	-15	48	54	7
3	8	-9	66	69	6	4	1	-12	38+	46	7	4	3	-16	67	62	6
3	8	10	34+	42	10	4	1	13	15+	12	13	4	3	-17	80	83	6

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_{18}H_{19}NO$ PAGE 6 OF13

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
4	3	-18	41+	21	9	4	6	-8	36+	24	7	4	10	-3	38+	3	9
4	4	0	283	273	9	4	6	9	15+	37	14	4	10	-4	38+	5	9
4	4	1	94	96	4	4	6	-9	73	68	5	4	10	-5	16+	30	18
4	4	-1	17+	16	10	4	6	10	52	61	7	5	0	0	497	475	15
4	4	2	7+	12	15	4	6	-10	86	91	5	5	0	2	306	303	9
4	4	-2	100	102	4	4	6	11	61	62	6	5	0	-2	424	424	13
4	4	3	120	116	4	4	6	-11	91	97	5	5	0	4	144	147	4
4	4	-3	12+	13	12	4	6	12	26+	21	11	5	0	-4	77	68	3
4	4	4	34+	25	6	4	6	-12	26+	7	11	5	0	6	20+	20	9
4	4	-4	161	159	5	4	6	13	39+	40	9	5	0	-6	164	160	5
4	4	5	42	37	6	4	6	-13	34+	20	9	5	0	8	133	141	5
4	4	-5	86	81	4	4	6	-14	31+	39	11	5	0	-8	82	84	4
4	4	6	74	72	4	4	6	-16	18+	18	16	5	0	10	62	66	5
4	4	7	67	57	5	4	7	0	100	93	4	5	0	-10	88	94	4
4	4	-7	91	91	4	4	7	1	127	128	5	5	0	12	62	65	5
4	4	8	73	75	5	4	7	-1	30+	26	9	5	0	-12	88	86	4
4	4	-8	41+	48	6	4	7	-2	91	85	4	5	0	14	87	86	5
4	4	9	73	66	4	4	7	3	12+	2	15	5	0	-14	0+	8	24
4	4	-9	65	64	4	4	7	-3	94	98	5	5	0	16	34+	25	10
4	4	10	37+	42	7	4	7	4	53	47	6	5	0	-16	35+	42	9
4	4	11	53	52	6	4	7	-4	71	79	5	5	0	-18	36+	44	9
4	4	-11	104	106	4	4	7	5	33+	40	8	5	1	0	112	109	4
4	4	12	58	60	6	4	7	-5	74	66	5	5	1	1	386	380	12
4	4	-12	89	84	5	4	7	6	23+	16	11	5	1	-1	164	160	5
4	4	13	47	43	7	4	7	-6	42+	36	6	5	1	2	158	153	5
4	4	-13	51	55	6	4	7	7	26+	14	10	5	1	-2	499	468	15
4	4	-16	21+	15	13	4	7	-7	31+	24	9	5	1	3	185	181	6
4	4	-17	50+	50	8	4	7	8	14+	14	15	5	1	-3	392	379	12
4	4	-18	58	58	7	4	7	-8	104	103	5	5	1	4	26+	34	7
4	5	0	37+	44	6	4	7	-9	35+	40	8	5	1	-5	40	36	5
4	5	1	147	145	5	4	7	10	50	52	7	5	1	6	75	79	4
4	5	-1	27+	26	8	4	7	-10	28+	36	10	5	1	-6	74	83	4
4	5	2	111	109	4	4	7	11	42+	38	9	5	1	7	44	41	6
4	5	-2	70	59	4	4	7	-11	15+	5	15	5	1	8	87	92	4
4	5	3	114	118	4	4	7	-12	34+	30	9	5	1	-8	98	100	4
4	5	-3	52	55	5	4	7	-13	19+	3	14	5	1	9	22+	21	10
4	5	4	14+	9	13	4	8	0	26+	8	10	5	1	-9	114	109	4
4	5	-4	139	138	5	4	8	1	33+	37	9	5	1	10	87	98	4
4	5	-5	39+	32	6	4	8	-1	17+	30	14	5	1	-10	23+	28	9
4	5	6	38+	28	7	4	8	3	53	60	6	5	1	11	27+	20	9
4	5	-6	60	62	5	4	8	4	20+	27	13	5	1	-11	48	60	6
4	5	7	188	190	6	4	8	-4	54	57	6	5	1	12	86	87	5
4	5	-7	63	71	5	4	8	5	52	40	6	5	1	-12	38+	52	7
4	5	8	78	84	5	4	8	-5	37+	28	8	5	1	14	39+	20	8
4	5	-8	65	57	5	4	8	6	22+	24	12	5	1	15	22+	29	13
4	5	9	71	67	5	4	8	7	44+	21	7	5	1	-15	29+	39	10
4	5	-9	171	168	6	4	8	-7	41+	27	8	5	1	16	13+	28	18
4	5	10	27+	21	10	4	8	8	40+	43	9	5	1	-16	63	66	6
4	5	-10	40+	46	7	4	8	-8	34+	15	9	5	1	-17	47+	44	7
4	5	11	31+	38	9	4	8	9	33+	10	9	5	1	-18	50	32	7
4	5	-11	96	104	5	4	8	-10	87	79	5	5	1	-19	33+	28	10
4	5	12	25+	8	11	4	8	-11	43+	35	8	5	2	0	195	192	6
4	5	13	37+	32	8	4	8	-12	30+	8	11	5	2	1	251	249	8
4	5	-13	37+	26	8	4	9	0	45+	30	8	5	2	-1	244	229	7
4	5	-14	17+	20	14	4	9	1	52	54	7	5	2	2	116	108	4
4	5	-15	55	38	7	4	9	-1	39+	24	9	5	2	-2	280	270	8
4	5	-16	34+	26	10	4	9	-2	15+	15	16	5	2	3	104	98	4
4	5	-17	31+	8	11	4	9	4	48+	53	8	5	2	-3	341	340	10
4	6	0	64	58	5	4	9	-4	36+	15	9	5	2	4	38	28	5
4	6	1	72	83	5	4	9	5	83	72	5	5	2	-4	345	337	10
4	6	-1	11+	43	15	4	9	-6	48+	52	8	5	2	5	163	162	5
4	6	2	28+	20	9	4	9	7	22+	3	13	5	2	-5	226	235	7
4	6	3	134	146	5	4	9	-7	50+	38	8	5	2	6	70	71	4
4	6	-3	51	47	5	4	9	-8	48+	45	8	5	2	-6	60	61	4
4	6	4	40+	36	7	4	9	-9	32+	38	11	5	2	7	27+	34	8
4	6	-4	36+	35	7	4	9	-10	17+	5	17	5	2	-7	8+	2	14
4	6	5	73	86	5	4	10	0	24+	6	13	5	2	8	58	60	5
4	6	-5	73	77	5	4	10	1	33+	26	11	5	2	-8	201	207	6
4	6	6	54	57	6	4	10	-1	32+	41	11	5	2	9	42+	41	6
4	6	-7	123	129	5	4	10	2	43+	29	9	5	2	10	105	103	4
4	6	8	77	81	5	4	10	-2	13+	14	18	5	2	-10	144	140	5

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_{18}H_{19}NO$

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
5	2	11	55	61	6	5	5	-6	84	71	4	5	8	8	31+	29	11
5	2	-11	41	39	6	5	5	7	42+	35	7	5	8	-8	24+	26	12
5	2	12	73	79	5	5	5	-7	57	53	5	5	8	9	35+	9	10
5	2	-12	18+	36	12	5	5	8	79	80	5	5	8	-9	48+	35	7
5	2	13	14+	32	15	5	5	9	26+	7	10	5	8	-10	47+	39	9
5	2	14	33+	50	10	5	5	-9	193	196	6	5	8	-12	35+	25	11
5	2	-15	48	47	6	5	5	10	35+	38	9	5	9	0	24+	4	12
5	2	-16	59	60	6	5	5	-10	45	38	7	5	9	1	20+	22	14
5	2	-17	29+	22	11	5	5	11	28+	16	10	5	9	-1	46+	51	8
5	3	0	120	114	4	5	5	12	18+	13	15	5	9	2	23+	24	13
5	3	1	122	117	4	5	5	-12	29+	2	9	5	9	-2	43+	34	8
5	3	-2	328	321	10	5	5	13	57	51	7	5	9	3	51	49	7
5	3	3	44	54	5	5	5	-14	35+	41	9	5	9	-3	24+	3	12
5	3	-3	196	188	6	5	5	-17	45+	47	9	5	9	4	55	28	7
5	3	4	108	106	4	5	6	0	32+	15	8	5	9	-4	27+	15	11
5	3	5	69	77	4	5	6	1	60	65	5	5	9	5	35+	18	10
5	3	-5	157	144	5	5	6	-1	50	48	6	5	9	-5	28+	15	11
5	3	-6	22+	17	9	5	6	2	50	46	6	5	9	6	17+	14	16
5	3	7	10+	14	15	5	6	-2	93	83	4	5	9	-6	6+	15	23
5	3	-7	158	158	5	5	6	3	20+	14	12	5	9	-8	40+	35	9
5	3	8	34+	20	7	5	6	-3	156	153	5	5	9	-9	11+	20	21
5	3	-8	58	57	5	5	6	-4	70	66	5	5	10	0	48+	50	9
5	3	9	152	158	5	5	6	5	69	70	5	5	10	-1	31+	25	12
5	3	-9	25+	19	9	5	6	-5	170	180	6	5	10	-2	13+	14	18
5	3	10	77	78	5	5	6	-6	55	48	5	5	10	-3	42+	37	10
5	3	-10	103	94	4	5	6	-7	135	141	5	6	0	0	384	376	12
5	3	11	11+	27	16	5	6	8	26+	35	11	6	0	2	421	416	13
5	3	-11	132	136	5	5	6	-8	40+	43	7	6	0	-2	197	198	6
5	3	12	20+	1	12	5	6	9	22+	6	12	6	0	4	106	101	4
5	3	-12	27+	8	9	5	6	-9	18+	17	13	6	0	-4	29+	34	6
5	3	-13	39+	32	7	5	6	10	12+	25	17	6	0	6	83	84	4
5	3	-14	37+	40	8	5	6	-10	49	44	7	6	0	-6	190	191	6
5	3	15	33+	8	10	5	6	-11	33+	32	9	6	0	8	75	74	4
5	3	-15	26+	0	10	5	6	-12	39+	33	8	6	0	-8	129	138	4
5	3	-16	40+	27	8	5	6	-13	17+	20	15	6	0	10	7+	20	18
5	3	-17	39+	29	9	5	6	-16	28+	29	12	6	0	-10	50	53	5
5	3	-18	95	81	6	5	7	0	87	88	5	6	0	12	108	113	5
5	4	0	21+	17	9	5	7	1	73	68	5	6	0	-12	39+	55	7
5	4	1	67	64	4	5	7	-1	12+	10	15	6	0	-14	99	91	5
5	4	-1	50	47	5	5	7	2	18+	15	13	6	1	0	228	228	7
5	4	2	34+	33	7	5	7	-2	50	49	6	6	1	1	56	65	4
5	4	-2	135	138	4	5	7	3	62	53	5	6	1	-1	220	213	7
5	4	3	160	162	5	5	7	-3	78	78	5	6	1	2	54	63	4
5	4	-3	121	118	4	5	7	4	73	73	5	6	1	-2	124	119	4
5	4	4	29+	24	8	5	7	-4	30+	17	9	6	1	3	315	316	10
5	4	-4	117	117	4	5	7	5	23+	13	11	6	1	4	25+	6	8
5	4	5	62	58	5	5	7	-5	88	99	5	6	1	-4	103	96	4
5	4	-5	46	43	5	5	7	6	29+	8	9	6	1	5	92	86	4
5	4	6	48	45	6	5	7	-6	124	120	5	6	1	-5	70	75	4
5	4	-6	267	273	8	5	7	-7	12+	13	16	6	1	6	24+	4	9
5	4	8	52	50	6	5	7	8	21+	5	12	6	1	-6	75	71	4
5	4	-8	52	49	5	5	7	-8	27+	24	11	6	1	7	41+	53	6
5	4	-9	9+	6	16	5	7	9	45+	39	8	6	1	-7	82	79	4
5	4	10	54	55	6	5	7	-9	18+	0	14	6	1	8	47	46	6
5	4	-10	88	89	5	5	7	10	31+	18	10	6	1	-8	170	172	5
5	4	-11	97	93	4	5	7	-10	61	62	6	6	1	9	27+	1	9
5	4	-14	74	69	5	5	7	11	26+	0	12	6	1	-9	162	162	5
5	4	-15	40+	32	8	5	7	-11	29+	32	11	6	1	10	72	80	5
5	4	-16	43+	58	9	5	7	-12	45+	42	8	6	1	-10	49	48	5
5	4	-18	42+	29	10	5	7	-13	15+	13	17	6	1	-11	29+	22	8
5	5	0	80	84	4	5	7	-14	21+	6	14	6	1	12	18+	21	13
5	5	1	108	110	4	5	8	0	38+	28	8	6	1	-12	81	90	5
5	5	-1	81	78	4	5	8	1	56	56	6	6	1	13	50	38	7
5	5	2	19+	40	11	5	8	2	26+	28	10	6	1	-13	28+	21	9
5	5	-2	12+	10	14	5	8	-3	38+	32	8	6	1	14	64	59	6
5	5	-3	183	197	6	5	8	4	41+	48	8	6	1	-14	112	115	5
5	5	4	74	74	5	5	8	-4	38+	43	8	6	1	-15	13+	11	15
5	5	-4	73	79	5	5	8	5	47+	21	7	6	1	-16	30+	0	10
5	5	5	10+	0	16	5	8	-5	38+	11	8	6	1	-17	16+	5	15
5	5	-5	105	110	4	5	8	-6	28+	38	10	6	1	-18	33+	31	10
5	5	6	69	70	5	5	8	7	25+	22	12	6	1	-19	17+	17	16

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_{18}H_{19}NO$

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
6	2	0	48	47	4	6	4	7	27+	27	9	6	7	-2	60	60	5
6	2	1	153	148	5	6	4	-7	16+	19	12	6	7	3	20+	18	12
6	2	-1	30+	18	6	6	4	-8	26+	38	9	6	7	-3	72	73	5
6	2	2	170	174	5	6	4	9	44+	46	7	6	7	4	40+	45	8
6	2	-2	56	53	4	6	4	-9	98	95	4	6	7	-4	97	99	5
6	2	3	134	132	4	6	4	10	5+	4	20	6	7	5	35+	16	9
6	2	-3	46	41	4	6	4	-10	103	97	4	6	7	-5	28+	27	10
6	2	4	249	253	8	6	4	11	35+	43	9	6	7	6	60	50	6
6	2	-4	105	103	4	6	4	-11	21+	15	11	6	7	-6	12+	27	16
6	2	5	119	114	4	6	4	12	28+	18	11	6	7	7	29+	36	11
6	2	-5	207	209	6	6	4	-12	93	101	5	6	7	8	37+	39	9
6	2	6	129	125	5	6	4	13	33+	19	10	6	7	-8	31+	41	10
6	2	-6	154	163	5	6	4	14	24+	29	13	6	7	9	30+	10	11
6	2	7	18+	11	11	6	4	-14	33+	8	9	6	7	-9	53	54	7
6	2	-7	5+	17	16	6	4	-15	28+	24	11	6	7	-10	14+	21	16
6	2	8	7+	5	17	6	4	-17	23+	22	13	6	7	-11	68	74	6
6	2	-8	231	235	7	6	4	-18	60	49	7	6	7	-12	43+	36	9
6	2	9	75	80	5	6	5	0	62	61	5	6	7	-14	26+	8	13
6	2	-9	137	145	5	6	5	1	127	136	5	6	8	0	31+	21	10
6	2	10	99	102	5	6	5	-1	42+	39	6	6	8	1	17+	35	15
6	2	-10	92	93	4	6	5	2	260	262	8	6	8	-1	53	59	7
6	2	11	41+	44	8	6	5	-2	22+	16	10	6	8	2	104	88	5
6	2	-11	55	41	5	6	5	3	172	169	6	6	8	-2	35+	14	8
6	2	12	45+	66	8	6	5	-3	34+	23	7	6	8	3	63	60	6
6	2	-12	124	122	5	6	5	4	26+	14	9	6	8	-4	20+	6	13
6	2	13	42+	34	8	6	5	-4	18+	5	12	6	8	5	31+	9	10
6	2	-13	44	52	6	6	5	5	38+	47	7	6	8	-5	52	44	7
6	2	14	24+	17	13	6	5	-5	40+	31	6	6	8	6	31+	29	11
6	2	-14	36+	9	8	6	5	-6	31+	41	8	6	8	-6	17+	4	14
6	2	15	6+	29	23	6	5	7	38+	33	7	6	8	-7	8+	17	19
6	2	-15	8+	1	18	6	5	-7	127	134	5	6	8	8	43+	7	8
6	2	-19	49+	41	8	6	5	8	43+	60	7	6	8	-8	35+	31	9
6	3	0	107	102	4	6	5	-8	57	62	5	6	8	-9	67	69	6
6	3	1	36+	29	6	6	5	9	44+	37	7	6	8	-10	71	66	6
6	3	-1	102	96	4	6	5	-9	101	110	5	6	8	-11	72	64	6
6	3	2	206	205	6	6	5	10	42+	38	9	6	8	-12	52+	36	8
6	3	3	37+	39	6	6	5	-10	94	89	5	6	9	1	27+	23	11
6	3	-3	78	79	4	6	5	11	28+	29	11	6	9	-1	63	59	6
6	3	4	77	79	4	6	5	-11	144	145	5	6	9	2	11+	29	19
6	3	-4	47	50	5	6	5	12	26+	6	12	6	9	-2	52	24	7
6	3	-5	116	118	4	6	5	-12	67	70	5	6	9	-3	24+	21	12
6	3	6	72	69	4	6	5	13	17+	8	15	6	9	4	16+	29	17
6	3	-6	182	187	6	6	5	-14	24+	4	12	6	9	-4	56	42	7
6	3	7	43+	38	6	6	5	-15	67	57	6	6	9	-5	28+	22	11
6	3	-7	68	70	4	6	5	-16	31+	15	11	6	9	-7	35+	31	10
6	3	8	20+	25	11	6	5	-17	51+	20	9	6	9	-8	18+	5	16
6	3	-8	135	132	5	6	6	0	26+	36	9	7	0	0	251	240	8
6	3	9	7+	9	18	6	6	-1	66	70	5	7	0	2	218	219	7
6	3	-9	78	81	4	6	6	2	156	156	5	7	0	-2	211	214	6
6	3	-10	30+	40	8	6	6	-2	47	45	6	7	0	4	128	130	4
6	3	11	50	55	7	6	6	3	130	127	5	7	0	-4	236	232	7
6	3	-11	42+	41	6	6	6	-3	37+	38	7	7	0	6	67	66	5
6	3	-12	23+	21	10	6	6	4	109	113	5	7	0	-6	82	83	4
6	3	13	34+	37	9	6	6	-4	26+	14	9	7	0	8	76	82	5
6	3	-13	48	52	6	6	6	5	34+	22	8	7	0	-8	93	90	4
6	3	14	43+	24	8	6	6	-5	129	130	5	7	0	10	47	28	6
6	3	-15	84	69	5	6	6	6	12+	15	17	7	0	-10	37+	52	7
6	3	-16	81	73	5	6	6	-6	14+	15	14	7	0	12	23+	35	12
6	3	-17	59	48	6	6	6	7	70	67	5	7	0	-12	121	124	5
6	3	-18	31+	18	11	6	6	-7	17+	14	12	7	0	14	34+	24	10
6	4	0	162	164	5	6	6	8	6+	10	20	7	0	-14	130	135	5
6	4	1	109	109	4	6	6	-8	51	46	6	7	0	-16	14+	33	15
6	4	-1	180	171	6	6	6	9	46+	49	8	7	0	-18	81	71	5
6	4	2	34+	38	7	6	6	-9	105	118	5	7	1	0	149	153	5
6	4	-2	44	44	5	6	6	-10	47+	58	7	7	1	1	63	61	4
6	4	3	135	135	5	6	6	11	22+	13	13	7	1	-1	22+	19	8
6	4	4	104	109	4	6	6	-11	77	72	5	7	1	2	35+	20	6
6	4	-4	64	63	4	6	6	-14	20+	22	14	7	1	-2	332	318	10
6	4	5	68	58	5	6	7	0	58	59	6	7	1	3	25+	19	8
6	4	-5	15+	15	12	6	7	1	33+	29	8	7	1	-3	129	130	4
6	4	-6	69	69	4	6	7	-1	53	62	6	7	1	4	73	77	4

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_{18}H_{19}NO$ PAGE 9 OF13
(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG
7	1	-4	102	106	4
7	1	5	130	131	5
7	1	6	10+	0	15
7	1	-6	36+	42	6
7	1	7	15+	15	13
7	1	-7	182	182	6
7	1	8	27+	0	8
7	1	-8	308	315	9
7	1	9	24+	8	10
7	1	-9	191	194	6
7	1	-10	41+	40	6
7	1	11	22+	0	11
7	1	-11	44	54	6
7	1	-12	19+	32	11
7	1	13	31+	11	10
7	1	-13	62	58	5
7	1	14	70	58	6
7	1	-14	84	99	5
7	1	-15	42+	20	7
7	1	-16	43+	18	7
7	1	-17	19+	20	14
7	1	-18	10+	6	19
7	2	0	120	111	4
7	2	1	106	103	4
7	2	-1	179	177	5
7	2	2	105	103	4
7	2	3	123	122	4
7	2	-3	152	153	5
7	2	4	144	147	5
7	2	-4	36+	36	6
7	2	5	167	170	5
7	2	-5	82	72	4
7	2	6	26+	28	9
7	2	-6	147	150	5
7	2	7	82	87	4
7	2	-7	190	189	6
7	2	8	33+	33	8
7	2	-8	100	98	4
7	2	9	54	48	6
7	2	-9	61	58	5
7	2	-10	145	149	5
7	2	-11	167	165	5
7	2	-12	31+	28	8
7	2	13	47+	30	7
7	2	-17	34+	40	10
7	2	-18	63	59	7
7	3	0	169	170	5
7	3	1	113	113	4
7	3	-1	117	117	4
7	3	2	84	81	4
7	3	-2	54	48	5
7	3	3	167	171	5
7	3	-3	68	64	4
7	3	4	20+	34	11
7	3	-4	41	41	6
7	3	6	18+	18	12
7	3	-6	40+	45	6
7	3	-7	6+	29	18
7	3	8	44+	37	7
7	3	-8	130	135	5
7	3	9	47	35	6
7	3	-9	105	100	4
7	3	10	22+	9	11
7	3	-10	88	90	4
7	3	11	26+	24	11
7	3	-11	115	113	5
7	3	12	49+	52	7
7	3	-12	97	96	5
7	3	13	21+	30	14
7	3	-13	37+	34	8
7	3	-14	29+	14	9
7	3	-15	49	48	7
7	3	-17	39+	29	9
7	3	-18	26+	29	13
7	4	0	63	69	5
7	4	1	12+	13	15
7	4	-1	24+	23	10
7	4	2	304	313	9
7	4	-2	38+	35	7
7	4	3	148	150	5
7	4	-3	98	90	4
7	4	4	163	162	5
7	4	-4	82	77	4
7	4	-5	50	56	6
7	4	-6	40+	39	6
7	4	-7	27+	19	9
7	4	8	37+	30	7
7	4	-8	71	76	5
7	4	9	59	36	6
7	4	-9	73	69	5
7	4	10	33+	20	9
7	4	-10	152	151	5
7	4	11	45+	44	8
7	4	-11	62	64	5
7	4	-12	26+	24	10
7	4	-13	14+	10	14
7	4	-14	28+	15	10
7	4	-15	69	65	6
7	4	-16	55	45	7
7	5	0	191	192	6
7	5	1	91	83	4
7	5	-1	51	50	6
7	5	2	72	63	5
7	5	-2	7+	24	18
7	5	3	171	175	6
7	5	-3	71	75	5
7	5	4	179	188	6
7	5	5	62	57	5
7	5	-5	58	54	5
7	5	-6	57	66	5
7	5	7	23+	39	11
7	5	-7	91	91	4
7	5	8	47	33	6
7	5	-8	75	70	5
7	5	-9	40+	49	7
7	5	10	16+	13	15
7	5	-10	75	76	5
7	5	11	38+	18	9
7	5	-11	23+	12	11
7	5	-12	26+	43	11
7	5	-13	39+	33	8
7	5	-14	32+	27	10
7	5	-15	55	51	7
7	6	0	51	51	6
7	6	1	186	194	6
7	6	-1	56	56	5
7	6	2	103	113	5
7	6	3	34+	37	9
7	6	-3	55	55	6
7	6	4	28+	10	10
7	6	-4	39+	31	7
7	6	5	18+	3	13
7	6	-5	79	78	5
7	6	6	30+	15	9
7	6	-6	53	48	6
7	6	7	19+	25	13
7	6	-7	32+	31	8
7	6	8	33+	20	9
7	6	-8	93	89	5
7	6	-9	36+	23	8
7	6	10	31+	6	10
7	6	-10	68	68	5
7	6	-11	51	51	6
7	6	-12	26+	7	11
7	6	-13	20+	22	14
7	6	-14	34+	36	10
7	6	-15	48+	43	8
7	7	0	31+	30	9
7	7	-1	59	45	6
7	7	-2	26+	15	10
7	7	3	49	51	7
7	7	-3	64	54	5
7	7	4	29+	23	9
7	7	-4	40+	31	7
7	7	-5	36+	31	8
7	7	6	52	35	7
7	7	-6	5+	25	20
7	7	7	42+	37	8
7	7	-8	35+	21	8
7	7	9	13+	13	18
7	7	-9	30+	32	10
7	7	-10	21+	11	13
7	7	-11	28+	13	11
7	7	-12	58	48	7
7	7	-13	66	63	7
7	8	0	22+	23	12
7	8	1	72	58	6
7	8	-1	23+	10	12
7	8	2	46+	19	7
7	8	-2	14+	30	16
7	8	3	12+	23	17
7	8	-3	43+	39	8
7	8	-4	33+	40	9
7	8	-5	30+	22	10
7	8	6	57	55	7
7	8	-6	12+	26	18
7	8	-7	29+	13	10
7	8	-9	27+	23	12
7	8	-10	9+	4	21
7	8	-11	118	103	5
7	9	0	42+	32	9
7	9	-1	15+	4	17
7	9	2	47+	44	8
7	9	-2	19+	32	15
7	9	3	30+	22	11
7	9	-3	12+	21	18
7	9	-4	28+	16	12
7	9	-5	33+	23	10
7	9	-6	41+	18	9
8	0	0	9+	0	15
8	0	2	125	126	4
8	0	-2	175	175	5
8	0	4	140	141	5
8	0	-4	231	232	7
8	0	6	197	199	6
8	0	-6	232	236	7
8	0	8	9+	0	17
8	0	-8	297	300	9
8	0	10	23+	28	12
8	0	-10	52	49	5
8	0	12	26+	21	12
8	0	-12	43+	42	6
8	0	-14	41+	30	7
8	0	-15	40+	32	8
8	1	0	77	80	4
8	1	1	16+	4	11
8	1	-1	81	87	4
8	1	2	146	148	5
8	1	-2	21+	9	9
8	1	3	59	59	5
8	1	-3	150	153	5
8	1	4	333	342	10
8	1	-4	67	61	4

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_{18}H_{19}NO$

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
8	1	5	37+	54	7	8	3	-16	40+	28	8	8	7	-6	14+	8	15
8	1	-5	73	74	4	8	3	-17	32+	21	10	8	7	7	11+	1	19
8	1	6	88	93	5	8	3	-18	38+	29	12	8	7	-8	8+	7	19
8	1	-6	153	148	5	8	4	0	65	56	5	8	7	-9	46+	47	8
8	1	7	13+	21	14	8	4	1	61	68	5	8	7	-10	45+	43	8
8	1	-7	241	247	7	8	4	-1	30+	37	8	8	7	-11	16+	39	16
8	1	-8	103	104	4	8	4	2	59	62	5	8	8	0	27+	29	12
8	1	-9	77	83	4	8	4	-2	46	44	6	8	8	1	53	52	7
8	1	-10	322	330	10	8	4	3	120	123	5	8	8	2	26+	8	12
8	1	11	21+	19	12	8	4	4	26+	18	9	8	8	-2	12+	14	17
8	1	-11	115	116	4	8	4	-5	18+	24	11	8	8	3	38+	27	9
8	1	12	31+	27	10	8	4	6	25+	27	10	8	8	4	44+	34	9
8	1	-12	31+	9	8	8	4	-6	93	103	4	8	8	-4	23+	23	12
8	1	13	28+	4	11	8	4	7	69	53	5	8	8	-6	12+	18	19
8	1	-13	20+	13	12	8	4	-7	63	63	5	8	8	-7	16+	35	16
8	1	-14	72	64	5	8	4	8	46+	59	7	8	8	-8	40+	26	9
8	1	-15	69	67	5	8	4	-8	114	119	5	8	8	-9	38+	38	10
8	1	-16	31+	15	9	8	4	-9	124	125	5	8	8	-10	33+	26	11
8	1	-18	84	81	6	8	4	10	17+	14	15	8	9	0	17+	31	16
8	2	0	98	94	4	8	4	-10	96	100	5	8	9	-1	9+	8	21
8	2	1	109	113	4	8	4	11	11+	19	19	8	9	-2	54	42	8
8	2	-1	44	41	6	8	4	-11	42+	26	7	8	9	-4	32+	20	11
8	2	-2	76	75	4	8	4	12	18+	35	16	9	0	0	23+	30	10
8	2	3	276	286	8	8	4	-13	25+	4	11	9	0	2	132	134	5
8	2	-3	51	58	5	8	4	-14	60	47	6	9	0	-2	335	325	10
8	2	4	282	284	9	8	4	-15	41+	16	8	9	0	4	383	371	12
8	2	5	17+	23	13	8	4	-17	23+	0	13	9	0	-4	25+	19	8
8	2	-5	33+	27	7	8	5	0	7+	11	18	9	0	6	151	151	5
8	2	6	220	221	7	8	5	1	73	76	5	9	0	-6	175	183	6
8	2	-6	60	62	5	8	5	-1	20+	8	11	9	0	8	81	78	5
8	2	7	29+	22	9	8	5	2	89	91	5	9	0	-8	281	294	8
8	2	-7	12+	4	14	8	5	-2	56	48	5	9	0	10	39+	40	9
8	2	8	25+	10	10	8	5	-3	106	108	4	9	0	-10	53	55	6
8	2	-8	364	364	11	8	5	4	9+	6	17	9	0	12	17+	21	16
8	2	-9	367	374	11	8	5	-4	39+	38	7	9	0	-12	131	134	5
8	2	10	37+	15	8	8	5	5	44+	44	7	9	0	-14	60	62	6
8	2	-10	141	140	5	8	5	-5	71	77	5	9	0	-16	32+	7	10
8	2	11	13+	0	16	8	5	6	29+	27	10	9	0	-18	123	99	5
8	2	-11	26+	34	9	8	5	-6	34+	15	8	9	1	0	54	47	5
8	2	12	48+	22	7	8	5	-8	141	145	5	9	1	-1	89	91	4
8	2	-12	63	60	5	8	5	-9	11+	3	16	9	1	2	200	198	6
8	2	13	32+	24	11	8	5	-10	46+	42	7	9	1	-2	19+	37	11
8	2	-13	36+	31	8	8	5	-12	70	70	6	9	1	3	65	55	5
8	2	-14	28+	35	10	8	5	-13	50	49	7	9	1	-3	80	78	4
8	2	-15	49	29	6	8	5	-14	66	57	6	9	1	4	51	50	6
8	2	-16	51	42	7	8	5	-16	30+	8	12	9	1	-4	32+	37	7
8	2	-18	32+	17	10	8	6	0	33+	6	8	9	1	5	62	68	5
8	3	0	107	115	4	8	6	-1	42+	33	7	9	1	-5	163	169	5
8	3	-1	60	52	5	8	6	2	52	59	6	9	1	6	147	145	5
8	3	2	58	57	5	8	6	3	22+	22	12	9	1	7	39+	23	7
8	3	3	43+	43	7	8	6	-3	31+	30	9	9	1	-7	111	119	4
8	3	-3	12+	10	14	8	6	4	52	39	6	9	1	8	11+	2	16
8	3	4	76	74	5	8	6	-4	43+	39	7	9	1	-8	50	53	6
8	3	-4	62	62	5	8	6	5	32+	21	9	9	1	-9	90	89	5
8	3	5	229	227	7	8	6	-5	40+	40	7	9	1	10	53	44	7
8	3	-5	18+	34	11	8	6	-6	67	68	5	9	1	-10	79	72	5
8	3	6	46	53	7	8	6	7	67	50	6	9	1	-11	19+	2	11
8	3	-6	74	78	5	8	6	-8	8+	29	19	9	1	12	20+	5	14
8	3	7	16+	5	13	8	6	9	25+	2	12	9	1	-13	118	121	5
8	3	-7	123	117	5	8	6	-9	62	58	6	9	1	-15	6+	3	21
8	3	8	29+	1	9	8	6	-10	112	110	5	9	1	-16	24+	33	12
8	3	-8	89	95	4	8	6	-11	87	85	5	9	1	-17	17+	14	15
8	3	9	28+	23	10	8	6	-14	18+	20	16	9	1	-18	66	54	7
8	3	10	51	38	7	8	7	0	50	60	7	9	2	0	118	118	4
8	3	-10	123	126	5	8	7	1	66	55	6	9	2	1	41+	39	6
8	3	11	39+	22	9	8	7	2	16+	31	15	9	2	-1	43	41	6
8	3	-11	45	45	6	8	7	3	52	47	7	9	2	2	85	85	5
8	3	-12	68	75	5	8	7	4	38+	29	9	9	2	-2	89	86	4
8	3	-13	79	80	5	8	7	-4	24+	13	11	9	2	3	63	72	5
8	3	-14	40+	49	8	8	7	-5	22+	6	12	9	2	-3	28+	17	8
8	3	-15	29+	36	10	8	7	6	21+	18	13	9	2	4	229	229	7

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_{18}H_{19}NO$ PAGE11 OF13

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
9	2	-4	67	71	5	9	5	5	33+	47	9	10	1	-1	87	88	5
9	2	5	86	87	5	9	5	-5	141	150	5	10	1	2	128	128	5
9	2	-5	44	23	6	9	5	7	68	61	6	10	1	-2	69	70	5
9	2	6	14+	20	15	9	5	-7	95	91	5	10	1	-3	50	52	6
9	2	-6	120	123	4	9	5	9	37+	24	9	10	1	4	5+	24	21
9	2	7	35+	39	9	9	5	-10	61	67	6	10	1	-4	35+	44	7
9	2	-7	114	121	4	9	5	-11	44+	39	8	10	1	5	12+	21	16
9	2	-8	57	56	5	9	5	-12	71	79	6	10	1	-5	43+	46	6
9	2	9	56	59	7	9	5	-13	41+	46	9	10	1	6	26+	29	11
9	2	-9	80	87	5	9	5	-14	17+	20	15	10	1	-6	209	217	6
9	2	10	41+	36	8	9	5	-15	53	37	8	10	1	8	18+	24	14
9	2	-10	85	87	5	9	6	0	8+	19	20	10	1	-8	89	94	4
9	2	11	21+	7	14	9	6	1	46+	35	7	10	1	9	39+	29	9
9	2	-11	9+	12	16	9	6	-1	19+	6	13	10	1	-9	57	65	5
9	2	12	45+	35	8	9	6	-2	54	42	6	10	1	10	51	37	8
9	2	-13	64	59	6	9	6	3	16+	24	14	10	1	-10	47	49	6
9	2	-14	61	62	6	9	6	-3	29+	17	9	10	1	11	27+	21	12
9	2	-15	26+	47	12	9	6	-4	57	55	6	10	1	-11	69	67	5
9	2	-16	38+	34	9	9	6	5	45+	38	8	10	1	-12	28+	26	10
9	2	-18	47+	41	9	9	6	-5	56	46	6	10	1	-13	10+	24	17
9	3	0	64	56	5	9	6	6	34+	8	10	10	1	-14	63	61	6
9	3	1	37+	43	7	9	6	-6	59	51	6	10	1	-15	30+	46	11
9	3	-1	143	149	5	9	6	7	14+	16	18	10	1	-16	96	94	5
9	3	2	35+	39	8	9	6	-7	57	55	6	10	1	-17	53	46	8
9	3	3	80	83	5	9	6	8	55	37	8	10	2	0	148	148	5
9	3	4	47	59	6	9	6	-8	74	62	6	10	2	1	33+	23	8
9	3	5	102	101	5	9	6	-9	68	59	6	10	2	-1	29+	28	9
9	3	-5	73	73	4	9	6	-10	49	35	7	10	2	2	12+	0	15
9	3	6	13+	26	15	9	6	-11	20+	3	13	10	2	-2	43+	44	6
9	3	-6	102	102	4	9	6	-12	42+	31	8	10	2	3	44+	50	7
9	3	7	41+	55	8	9	6	-13	9+	1	20	10	2	-3	96	102	5
9	3	-7	207	209	6	9	6	-14	19+	29	16	10	2	4	21+	5	11
9	3	-9	46	34	6	9	7	0	8+	5	20	10	2	-5	23+	11	10
9	3	10	6+	10	22	9	7	1	32+	12	9	10	2	6	100	99	5
9	3	11	27+	16	12	9	7	-1	50	47	7	10	2	-6	167	168	6
9	3	-11	63	68	5	9	7	2	24+	25	13	10	2	-7	86	87	5
9	3	-12	16+	29	14	9	7	-2	37+	17	9	10	2	8	85	83	6
9	3	-14	47+	11	7	9	7	4	26+	7	12	10	2	-8	166	170	5
9	3	-17	40+	37	10	9	7	5	45+	37	9	10	2	9	37+	36	9
9	4	0	85	77	5	9	7	-5	30+	38	10	10	2	10	37+	4	9
9	4	1	41+	36	7	9	7	6	17+	0	16	10	2	-10	41+	31	7
9	4	-1	42+	45	7	9	7	-6	44+	37	8	10	2	-11	29+	12	9
9	4	2	73	59	5	9	7	-7	41+	39	9	10	2	-12	23+	0	11
9	4	-2	62	62	5	9	7	-8	20+	19	13	10	2	-13	45+	36	7
9	4	-3	63	71	5	9	7	-9	12+	4	18	10	2	-14	107	97	5
9	4	4	52	49	6	9	7	-10	22+	13	14	10	2	-15	85	76	5
9	4	-4	151	158	5	9	7	-11	32+	20	11	10	2	-16	31+	31	11
9	4	5	48	47	7	9	7	-12	24+	14	14	10	2	-17	23+	11	14
9	4	-5	84	76	5	9	8	0	46+	43	8	10	3	0	15+	10	13
9	4	6	82	76	5	9	8	1	39+	34	10	10	3	1	63	59	5
9	4	-6	59	56	6	9	8	-1	23+	18	13	10	3	-1	69	69	5
9	4	7	42+	33	8	9	8	2	22+	9	13	10	3	2	22+	3	11
9	4	-7	39+	29	7	9	8	-2	41+	24	9	10	3	-2	35+	32	8
9	4	8	73	70	6	9	8	-3	29+	19	11	10	3	-3	37+	43	7
9	4	-8	64	62	5	9	8	-7	43+	27	8	10	3	4	68	64	6
9	4	9	34+	29	10	9	8	-8	42+	40	10	10	3	-4	90	97	4
9	4	-9	129	133	5	9	8	-9	33+	43	12	10	3	5	38+	40	8
9	4	10	16+	25	16	10	0	0	174	174	6	10	3	-5	135	135	5
9	4	-10	112	109	5	10	0	2	0+	0	24	10	3	6	5+	20	21
9	4	-11	24+	9	11	10	0	-2	78	73	4	10	3	7	55	47	7
9	4	-12	26+	16	11	10	0	4	59	47	5	10	3	-7	19+	31	12
9	4	-14	12+	8	17	10	0	-4	28+	22	8	10	3	8	68	60	6
9	4	-15	6+	0	22	10	0	6	54	64	6	10	3	-8	110	112	5
9	4	-16	53	48	8	10	0	-6	38+	48	7	10	3	9	17+	28	16
9	5	0	30+	25	9	10	0	8	70	56	6	10	3	-9	76	77	5
9	5	1	31+	28	9	10	0	-8	424	425	13	10	3	-10	29+	39	9
9	5	-1	32+	27	8	10	0	10	82	64	6	10	3	-12	25+	22	11
9	5	2	72	73	5	10	0	-10	79	71	5	10	3	-14	34+	25	9
9	5	-2	25+	36	10	10	0	-14	30+	30	10	10	3	-15	54	51	7
9	5	3	27+	13	10	10	0	-16	52	49	7	10	4	0	38+	32	7
9	5	-3	69	65	5	10	1	1	63	58	5	10	4	1	55	52	6

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_{18}H_{19}NO$. PAGE12 OF13

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
10	4	-1	13+	12	15	11	0	6	52	41	7	11	3	-15	36+	36	10
10	4	2	57	52	6	11	0	-6	113	113	5	11	3	-16	20+	40	15
10	4	-2	71	76	5	11	0	8	41+	45	9	11	4	-1	56	51	6
10	4	3	34+	31	8	11	0	-8	31+	19	8	11	4	2	45+	51	7
10	4	-3	63	62	5	11	0	-10	38+	0	7	11	4	-2	15+	19	14
10	4	4	25+	15	11	11	0	-12	0+	36	26	11	4	4	36+	38	9
10	4	-4	55	60	6	11	0	-14	69	76	6	11	4	-4	37+	41	8
10	4	5	35+	14	9	11	0	-16	145	126	6	11	4	5	64	66	6
10	4	-5	32+	37	9	11	1	0	26+	27	10	11	4	-5	29+	15	10
10	4	6	115	120	5	11	1	1	55	45	6	11	4	6	49+	44	8
10	4	-6	225	236	7	11	1	2	5+	7	20	11	4	-6	47	38	7
10	4	7	27+	53	13	11	1	-2	58	62	5	11	4	7	15+	21	18
10	4	-7	133	130	5	11	1	-3	36+	41	8	11	4	-7	26+	17	10
10	4	8	50+	43	8	11	1	4	47+	52	7	11	4	-9	24+	10	11
10	4	-8	44+	48	7	11	1	-4	134	139	5	11	4	-10	11+	17	17
10	4	9	53	37	8	11	1	5	8+	17	20	11	4	-11	44+	39	8
10	4	-9	32+	16	9	11	1	-5	24+	18	10	11	4	-13	8+	22	21
10	4	-11	8+	34	19	11	1	6	38+	38	9	11	4	-14	0+	1	28
10	4	-13	16+	0	15	11	1	-6	10+	32	16	11	4	-15	45+	31	8
10	4	-14	8+	2	20	11	1	-7	81	81	5	11	5	0	29+	7	10
10	4	-16	15+	22	18	11	1	8	26+	38	13	11	5	1	13+	19	17
10	5	0	20+	12	12	11	1	-8	35+	37	8	11	5	-1	12+	38	18
10	5	-1	59	51	6	11	1	9	26+	9	13	11	5	-2	24+	37	11
10	5	2	10+	2	18	11	1	-10	20+	15	12	11	5	3	31+	48	11
10	5	-2	31+	31	9	11	1	-11	46	29	7	11	5	4	37+	15	9
10	5	3	13+	5	16	11	1	-12	63	60	6	11	5	-4	30+	31	10
10	5	-4	143	148	5	11	1	-13	42+	43	8	11	5	-5	19+	31	13
10	5	5	109	96	5	11	1	-14	96	92	5	11	5	-6	17+	14	14
10	5	6	36+	44	10	11	1	-15	78	75	6	11	5	-7	35+	20	9
10	5	-7	66	57	5	11	1	-16	44+	40	9	11	5	-8	26+	22	11
10	5	8	37+	43	10	11	1	-17	33+	1	11	11	5	-10	34+	18	9
10	5	-8	110	110	5	11	2	0	82	72	5	11	5	-11	19+	28	14
10	5	-11	16+	14	15	11	2	1	44+	46	7	11	5	-12	29+	30	11
10	5	-12	16+	7	15	11	2	-1	111	117	5	11	5	-13	35+	15	10
10	5	-13	41+	23	9	11	2	-2	141	142	5	11	6	0	49+	41	8
10	5	-14	20+	29	15	11	2	3	34+	12	9	11	6	1	35+	25	10
10	6	0	31+	26	10	11	2	-3	72	85	5	11	6	-1	58	41	6
10	6	1	14+	19	16	11	2	4	31+	33	10	11	6	2	35+	9	9
10	6	-1	55	51	6	11	2	-4	57	56	5	11	6	-2	29+	27	11
10	6	-2	39+	22	8	11	2	5	32+	17	9	11	6	3	55	38	7
10	6	3	31+	6	10	11	2	-5	65	56	5	11	6	-3	19+	22	14
10	6	-3	29+	44	10	11	2	6	76	79	6	11	6	-4	53	43	7
10	6	-4	43+	17	7	11	2	-6	101	99	5	11	6	-5	64	62	6
10	6	6	47+	36	9	11	2	7	8+	2	20	11	6	-6	22+	34	13
10	6	-6	88	89	5	11	2	8	29+	28	11	11	6	-8	47+	37	8
10	6	-7	47+	49	7	11	2	-8	113	116	5	11	6	-11	32+	16	11
10	6	-8	22+	1	13	11	2	-10	41+	26	7	11	7	0	51+	45	8
10	6	-9	19+	27	14	11	2	-11	71	65	5	11	7	1	72	57	6
10	6	-11	44+	29	8	11	2	-12	30+	23	9	11	7	-1	31+	10	11
10	6	-12	38+	20	10	11	2	-13	70	63	6	11	7	-2	54	50	8
10	7	0	31+	19	10	11	2	-14	12+	4	18	11	7	-4	50+	58	8
10	7	-1	58	47	7	11	2	-15	27+	26	12	11	7	-5	49+	55	8
10	7	2	16+	14	16	11	2	-16	74	61	6	11	7	-6	31+	35	11
10	7	-2	14+	36	17	11	3	1	65	58	5	11	7	-7	50+	47	9
10	7	3	17+	12	16	11	3	-1	39+	33	7	11	7	-8	28+	7	12
10	7	4	22+	0	14	11	3	2	35+	19	8	12	0	0	20+	7	12
10	7	-4	36+	37	10	11	3	3	25+	6	10	12	0	2	46+	43	7
10	7	-5	82	71	6	11	3	-3	113	115	5	12	0	-2	35+	35	8
10	7	-7	24+	9	13	11	3	4	20+	17	13	12	0	4	49	15	7
10	7	-9	6+	4	23	11	3	-4	70	72	5	12	0	-4	166	176	6
10	7	-10	18+	9	15	11	3	5	6+	19	22	12	0	6	29+	10	10
10	8	-1	45+	4	8	11	3	-5	42+	47	7	12	0	-6	203	211	6
10	8	-2	14+	15	17	11	3	6	50	50	7	12	0	8	0+	26	28
10	8	-3	20+	29	15	11	3	-6	65	66	5	12	0	-8	0+	10	25
10	8	-4	14+	1	18	11	3	8	50+	42	8	12	0	-10	33+	37	8
10	8	-5	49+	50	9	11	3	-9	22+	22	11	12	0	-12	37+	16	9
11	0	0	91	94	5	11	3	-10	11+	2	16	12	0	-14	32+	34	10
11	0	2	139	139	5	11	3	-11	57	54	6	12	0	-16	35+	32	10
11	0	-2	155	161	5	11	3	-12	6+	5	21	12	1	-1	16+	5	14
11	0	4	63	70	6	11	3	-13	36+	25	9	12	1	2	20+	21	13
11	0	-4	113	109	4	11	3	-14	15+	27	17	12	1	-2	160	169	5

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $C_{18}H_{19}NO$ PAGE13 OF13

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
12	1	-3	16+	32	14	12	5	-6	47+	49	8	13	4	-6	41+	17	8
12	1	4	34+	15	9	12	5	-7	59	62	7	13	4	-7	38+	27	9
12	1	-4	57	59	6	12	5	-8	20+	4	13	13	4	-8	44+	24	8
12	1	-5	53	51	6	12	5	-9	25+	10	12	13	4	-9	47+	30	9
12	1	6	33+	20	9	12	5	-11	61	43	7	13	4	-10	6+	6	23
12	1	-6	19+	19	12	12	5	-12	29+	9	12	13	4	-11	28+	30	12
12	1	7	36+	6	9	12	6	0	23+	13	13	13	4	-12	24+	21	13
12	1	-7	85	87	5	12	6	1	28+	25	12	13	5	0	37+	19	10
12	1	-8	37+	44	8	12	6	-2	49+	48	8	13	5	1	70	68	7
12	1	-9	34+	32	8	12	6	-5	18+	37	15	13	5	-3	24+	13	13
12	1	-10	23+	23	11	12	6	-7	58	56	7	13	5	-5	43+	45	9
12	1	-12	28+	24	10	12	6	-8	40+	51	10	13	5	-6	22+	7	14
12	1	-13	37+	30	9	13	0	0	45+	54	7	13	5	-7	30+	38	12
12	1	-14	40+	33	8	13	0	2	49	40	7	13	5	-8	38+	19	9
12	1	-15	28+	34	12	13	0	-2	30+	21	10	13	5	-9	9+	7	21
12	1	-16	45+	39	8	13	0	4	10+	8	19	13	5	-10	42+	43	9
12	2	1	38+	25	8	13	0	-4	123	118	5	14	0	0	34+	38	10
12	2	2	31+	31	10	13	0	-6	46+	44	7	14	0	-2	61	68	7
12	2	3	33+	34	9	13	0	-8	50	56	6	14	0	-4	40+	27	9
12	2	-3	75	76	5	13	0	-10	32+	1	9	14	0	-6	119	123	5
12	2	4	25+	13	11	13	0	-12	119	118	5	14	0	-8	23+	40	13
12	2	-4	54	47	6	13	0	-14	23+	20	14	14	0	-10	0+	4	28
12	2	-5	28+	0	9	13	1	0	73	68	5	14	0	-12	18+	16	16
12	2	6	8+	17	19	13	1	1	29+	15	10	14	1	-1	31+	20	10
12	2	-6	37+	37	7	13	1	-1	8+	1	19	14	1	2	49+	31	8
12	2	7	22+	17	14	13	1	2	44+	31	8	14	1	3	11+	4	20
12	2	-7	71	72	5	13	1	-2	25+	14	11	14	1	-3	10+	30	18
12	2	-8	9+	20	17	13	1	3	12+	32	18	14	1	-4	86	82	5
12	2	-9	80	75	5	13	1	4	51	42	7	14	1	-5	20+	3	14
12	2	-12	24+	30	12	13	1	-4	30+	46	10	14	1	-7	51	45	7
12	2	-13	34+	39	9	13	1	-5	72	82	6	14	1	-8	27+	29	11
12	2	-14	19+	12	14	13	1	6	22+	8	14	14	1	-10	46+	33	8
12	2	-15	45+	36	8	13	1	-6	5+	23	21	14	1	-11	27+	19	12
12	3	0	10+	4	17	13	1	-9	51	53	6	14	1	-13	15+	23	18
12	3	1	15+	2	16	13	1	-10	39+	40	8	14	2	0	33+	8	10
12	3	-1	34+	17	9	13	1	-12	27+	39	12	14	2	2	19+	17	15
12	3	2	30+	8	10	13	1	-13	33+	43	10	14	2	3	69	58	7
12	3	3	35+	26	9	13	1	-14	44+	53	9	14	2	-3	12+	15	18
12	3	-3	12+	9	16	13	2	1	50	42	7	14	2	-4	54	52	7
12	3	4	43+	38	8	13	2	2	40+	18	9	14	2	-6	20+	11	13
12	3	5	51	51	7	13	2	-2	20+	32	13	14	2	-9	23+	30	14
12	3	-5	83	74	5	13	2	-3	13+	7	16	14	2	-10	58	54	7
12	3	6	14+	3	18	13	2	-4	66	63	6	14	2	-11	47+	22	8
12	3	-6	18+	3	13	13	2	5	79	64	6	14	2	-12	60	56	7
12	3	7	28+	7	12	13	2	-5	43+	12	7	14	3	0	27+	3	13
12	3	-7	53	49	6	13	2	-6	22+	33	13	14	3	2	23+	13	14
12	3	-9	37+	30	8	13	2	-7	51	55	7	14	3	-3	47+	30	8
12	3	-10	57	55	6	13	2	-8	46+	43	7	14	3	-5	9+	14	20
12	3	-11	28+	8	11	13	2	-9	56	43	6	14	3	-6	38+	30	9
12	3	-13	50	45	7	13	2	-12	39+	33	9	14	3	-8	35+	28	10
12	3	-14	9+	7	20	13	2	-13	14+	14	17	14	3	-9	14+	25	18
12	4	1	49	46	7	13	2	-14	39+	47	9	14	4	0	31+	14	11
12	4	2	54	33	7	13	3	0	54	54	7	14	4	-2	29+	39	12
12	4	-2	23+	13	12	13	3	1	55	39	7	14	4	-3	33+	8	10
12	4	3	24+	25	13	13	3	2	59	47	7	14	4	-9	29+	7	12
12	4	-3	13+	4	16	13	3	3	41+	48	9	15	0	0	19+	22	16
12	4	4	19+	31	14	13	3	-3	49	43	7	15	0	-2	13+	19	19
12	4	-4	85	82	5	13	3	-4	39+	22	8	15	0	-4	94	92	6
12	4	5	28+	9	12	13	3	-5	8+	4	20	15	0	-8	55	49	8
12	4	-5	55	51	6	13	3	-6	37+	33	9	15	0	-10	104	85	6
12	4	-6	42+	49	8	13	3	-7	31+	38	10	15	1	-2	11+	30	20
12	4	-7	56	49	6	13	3	-8	43+	35	8	15	1	-6	55	54	8
12	4	-8	40+	35	8	13	3	-10	38+	13	9	15	1	-8	52+	37	8
12	4	-9	15+	11	15	13	3	-11	61	43	7	15	1	-10	53+	43	8
12	4	-11	39+	48	9	13	3	-13	43+	46	10	15	2	-1	9+	19	21
12	4	-12	25+	3	12	13	4	0	24+	6	12	15	2	-2	33+	17	11
12	4	-13	78	74	6	13	4	-1	86	81	6	15	2	-4	13+	17	18
12	5	1	58	41	7	13	4	2	25+	3	13	15	2	-5	32+	33	10
12	5	-1	33+	32	10	13	4	3	26+	39	13	15	2	-6	47+	39	8
12	5	2	31+	33	11	13	4	-3	10+	18	19	15	2	-8	64	52	7
12	5	-2	35+	38	9	13	4	-4	25+	20	12	15	2	-9	33+	24	12
12	5	-3	38+	0	8	13	4	-5	17+	7	15	15	3	-5	42+	19	9
12	5	-4	34+	34	9												

REFERENCES

1. For a general review of introductory photochemical concepts see:
   a) J.G. Calvert and J.N. Pitts, Jr., "Photochemistry", John Wiley and Sons, New York, New York (1966).
   b) N.J. Turro, "Modern Molecular Photochemistry", Benjamin/Cummings, Menlo Park, California (1978).
2. A.A. Lamola and N.J. Turro, "Organic Photochemistry and Energy Transfer", Interscience, New York (1969).
3. M. Kasha, J. Chem. Phys., 20, 71 (1952).
4. D.S. McClure, N.W. Blake and P.L. Hanst, J. Chem. Phys., 22, 255 (1954).
5. L.M. Stephenson and G.S. Hammond, Angew. Chem. Int. Ed. Engl., 8, 261 (1969).
6. A. Weller, A.R. Watkins and K.H. Grellman, J. Phys. Chem., 76, 469 (1972).
7. J.B. Birks, "The Exciplex", M. Gordon and W.R. Ware, Ed., Academic Press, New York, New York (1975), p. 39.
8. Th. Förster and K. Kasper, Z. Phys. Chem., N.F., 1, 275 (1954).
9. a) Th. Förster, Angew. Chem. Int. Ed., 8, 333 (1969).
   b) Th. Förster, "The Exciplex", M. Gordon and W.R. Ware, Ed., Academic Press, New York, New York (1975), p. 1 and references therein.
10. H. Leonhardt and A. Weller, Ber. Bunsenges Phys. Chem., 67, 791 (1963).

11. A. Weller, "The Exciplex", M. Gordon and W.R. Ware, Ed., Academic Press, New York, New York (1975), p. 23, and references therein.
12. N. Mataga, ibid., p. 113, and references therein.
13. See B. Stevens, Adv. Photochem., 8, 161 (1971) for a useful review.
14. H. Knibbe, K. Rollig, F.P. Schafer and A. Weller, J. Chem. Phys., 47, 1184 (1967).
15. F.D. Lewis, Acc. Chem. Res., 12, 152 (1979) and references therein.
16. N. Mataga, Y. Torihashi and K. Ezumi, Theor. Chim. Acta, 2, 158 (1964).
17. H. Knibbe, D. Rehm and A. Weller, Ber. Bunsenges. Phys. Chem., 73, 839 (1969).
18. H. Matuhara, T. Hino and N. Mataga, J. Phys. Chem., 79, 994 (1975).
19. N. Mataga, T. Okada and N. Yamamoto, Chem. Phys. Lett., 1, 119 (1967).
20. C. Pac and H. Sakurai, Tetrahedron Lett., 43, 3829 (1969).
21. R.S. Davidson, J. Chem. Soc., Chem. Commun., 1450 (1969).
22. G.S. Cohen, A. Parola and G.H. Parson, Jr., Chem. Rev., 73, 141 (1973).
23. N.C. Yang and J. Libman, J. Am. Chem. Soc., 95, 5783 (1973).
24. F.D. Lewis and C.E. Hoyle, J. Am. Chem. Soc., 97, 5950 (1975).

25. G.N. Taylor, Chem. Phys. Lett., 10, 355 (1971).

26. a) R. Srinivasan, J. Am. Chem. Soc., 93, 3555 (1971).

    b) K.E. Wilzbach and L. Kaplan, ibid., 93, 2073 (1971).

27. W.R. Ware, D. Watt and J.D. Holmes, J. Am. Chem. Soc., 96, 7853 (1974).

28. J.J. McCullough, R.C. Miller, D. Fung and W.S. Wu, J. Am. Chem. Soc., 97, 5942 (1975).

29. D.R. Arnold, P.C. Wong, A.J. Maroulis and T.S. Cameron, Pure and Appl. Chem., 52, 2609 (1980).

30. a) G. Buchi, J.G. Atkinson, D.E. Ayer and E.W. Robb, J. Am. Chem. Soc., 85, 2257 (1963).

    b) T.S. Cantrell, J. Am. Chem. Soc., 94, 5929 (1972).

    c) T.S. Cantrell, J. Org. Chem., 42, 4238 (1977).

31. N.C. Yang, B. Kin, W. Chiang and T. Hamada, J. Chem. Soc., Chem. Commun., 729 (1976).

32. J.J. McCullough, R.C. Miller and W.-S. Wu, Can. J. Chem., 55, 2909 (1977).

33. a) A.J. Maroulis and D.R. Arnold, J. Chem. Soc., Chem. Commun., 351 (1979).

    b) R.A. Neunteufel and D.R. Arnold, J. Am. Chem. Soc., 95, 4080 (1973).

    c) A.J. Maroulis and D.R. Arnold, Synthesis, 819 (1979).

34. R.C. Miller, Ph.D. Thesis, McMaster University, 1978.

35. F.D. Lewis and C.E. Hoyle, J. Am. Chem. Soc., 99, 3779 (1977).

36. a) J. Michl, Photochem. Photobiol., 25, 141 (1977).

    b) R.A. Caldwell, J. Am. Chem. Soc., 102, 4004 (1980).

37. H. Knibbe, D. Rehm and A. Weller, *Z. Phys. Chem. (Frankfurt-am-Main)*, *56*, 95 (1967).

38. D. Rehm and A. Weller, *Isr. J. Chem.*, *8*, 259 (1970).

39. S. Masaki, T. Okada, N. Mataga, Y. Sakata and S. Misumi, *Bull. Chem. Soc. Japn.*, *49*, 1277 (1966).

40. N. Mataga, T. Okada, H. Masuhara, N. Nakashima, Y. Sakata and S. Misumi, *J. Lumin.*, *12*, 159 (1976).

41. N. Mataga, Y. Taniguchi and Y. Nishina, *Bull. Chem. Soc. Jpn.*, *45*, 764 (1972).

42. R.A. Caldwell, D. Creed, *J. Am. Chem. Soc.*, *100*, 2905 (1978).

43. W.K. MacInnis, unpublished results.

44. R.A. Caldwell and L. Smith, *J. Am. Chem. Soc.*, *96*, 2994 (1974).

45. K. Sakurai and C. Pac, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, *37*, 59 (1980).

46. R.A. Caldwell, D. Creed, D.C. DeMarco, L.A. Melton, H. Ohta and P.H. Wine, *J. Am. Chem. Soc.*, *102*, 2369 (1980).

47. P.M. Frochlich and H.A. Morrison, *J. Am. Chem. Soc.*, *96*, 332 (1974).

48. a) L.M. Stephenson, D.G. Whitten, G.F. Vesley and G.S. Hammond, *J. Am. Chem. Soc.*, *88*, 3665 (1966).

    b) D.A. Labianca, G.N. Taylor and G.S. Hammond, *ibid.*, *94*, 3679 (1972) and references therein.

49. F. Meeus, M. van der Auweraer, J.D. Dederin and F.C. De Schryver, *Rec. Trav. Chim. Pays-Bas*, *98*, 219 (1979).

50. a) For a useful review of the bichromophoric photochemistry of non-conjugated chromophores, see: F.C. De Schryver,

N. Boens and J. Put, "Advances in Photochemistry", J. Pitts, G.S. Hammond and K. Golenich, Ed., J. Wiley, Intersciences, New York, 1977, 10, 359;

b) R.S. Davidson, "Molecular Association", Vol. 1, ed., R. Foster, Academic Press, New York, 1975, p., 216, and references therein.

51. F. Hirayama, J. Chem. Phys., 42, 3163 (1965).

52. E. Chandross and C. Dempster, J. Am. Chem. Soc., 92, 3586 (1970).

53. M.T. Vala, J. Houlig and S.A. Rice, J. Chem. Phys., 43, 886 (1965).

54. F.C. De Schryver, I. Bhardwaj and J. Put, Angew. Chem., Int. Ed., 18, 213 (1969).

55. J. Put and F.C. De Schryver, J. Am. Chem. Soc., 95, 137 (1973).

56. K. Zachariasse and W. Kühnle, Z. Phys. Chem., N.F., 101, 267 (1976).

57. F.C. De Schryver, M. De Brackeleire, S. Toppet and M. Van Schoor, Tetrahedron Lett., 1253 (1973).

58. D. Georgescauld and H. Duclohier, Biochem. Biophys. Res. Commun., 85, 1186 (1978).

59. D. Georgescauld, J.P. Desmasez, R. Lapouyade, A. Babeau, H. Richard and M. Winnik, Photochem. Photobiol., 31, 539 (1980).

60. E.A. Chandross and H.T. Thomas, Chem. Phys. Lett., 9, 393 (1971).

61. T. Okada, T. Fiyita, M. Kubota, S. Masaki, and N. Mataga, Chem. Phys. Lett., 14, 563 (1972).

62. R.S. Davidson, R. Bonneau, J. Joussot-Dubien and K. Toyne, *Chem. Phys. Lett.*, 63 (1979).

63. D. Bryce-Smith, A. Gilbert and G. Klunkin, *J. Chem. Soc., Chem. Commun.*, 330 (1973).

64. M. Van der Auweraer, A. Gilbert and F.C. De Schryver, *J. Am. Chem. Soc.*, 102, 4007 (1980).

65. F. Meeus, M. Van der Auweraer and F.C. De Schryver, *Chem. Phys. Lett.*, 74, 218 (1980).

66. H. Morrison, *Acc. Chem. Res.*, 12, 389 (1979).

67. H. Morrison, "Organic Photochemistry", Vol. 4, A. Padwa, Ed., Marcel Dekker, New York, 1979, p. 143.

68. a) A. Gilbert and G. Taylor, *J. Chem. Soc., Chem. Commun.*, 229 (1979).

    b) A. Gilbert and G. Taylor, *J. Chem. Soc., Chem. Commun.*, 129 (1978).

69. P.A. Wender and J.J. Howbert, *J. Am. Chem. Soc.*, 103, 688 (1981).

70. a) J.L. Marshall, O. Saracoglu, C.R. McDaniel, Jr., N.L. Holy, H.P. Vail, A. Nijad, S. Huang, *J. Org. Chem.*, 45, 4271 (1980);

    b) J.L. Marshall, L.G. Fuchl, C.R. McDaniel, Jr., and D.N. Ledford, *J. Am. Chem. Soc.*, 99, 321 (1977);

    c) J.L. Marshall and T.K. Folson, *J. Org. Chem.*, 36, 2011 (1971).

71. P.W. Rabideau, *Acc. Chem. Res.*, 11, 141 (1978).

72. Formation of (61) is formally an 8-electron ene-type addition (photochemically allowed) which has been observed

in benzene photochemistry: D. Bryce-Smith, B.E. Foulger, A. Gilbert and P.J. Twitchett, J. Chem. Soc., Chem. Commun., 794 (1971).

73. W.C. Still, M. Kahn and A. Mitra, J. Org. Chem., 43, 2923 (1978).

74. W.R. Ware, D. Watt and J.D. Holmes, J. Am. Chem. Soc., 96, 7853 (1974).

75. J.G. Calvert and J.N. Pitts, Jr., "Photochemistry", John Wiley and Sons, New York, New York, 1966, p. 627.

76. J.G. Calvert and J.N. Pitts, Jr., ibid., p. 309.

77. R.M. Bowman, T.R. Chamberlain, C.-W. Huang and J.J. McCullough, J. Am. Chem. Soc., 96, 692 (1974).

78. E.F. Ullman and P. Singh, J. Am. Chem. Soc., 94, 5077 (1972).

79. H. Ohta, D. Creed, P.H. Wine, R.A. Caldwell and L.A. Melton, J. Am. Chem. Soc., 98, 2002 (1976).

80. T.R. Evans, private communication.

81. a) E.J. Bowen and B. Brocklehurst, Trans. Faraday Soc., 51, 774 (1955).
    b) E.J. Bowen and R. Livingston, J. Am. Chem. Soc., 76, 6300 (1954).

82. A.A. Lamola, "Techniques of Organic Chemistry", Vol. 14, P.A. Leermakers and A. Weissberger, Ed., John Wiley and Sons, New York, New York (1969), p. 38.

83. D.V. O'Connor and W.R. Ware, J. Am. Chem. Soc., 98, 4706 (1976).

84. For a discussion of the temperature dependence of exciplex formation see: R.J. McDonald and B.K. Sellinger, Mol. Photochem., 3, 99 (1971) and M. Cohen and B.K. Selinger, Mol. Photochem., 1, 371 (1969).

85. F. Wilkinson and J.T. Dubois, J. Chem. Phys., 39, 377 (1963).

86. H. Bouas-Laurent, A. Castellan and J.-P. Desvergne, Pure and Appl. Chem., 52, 2633 (1980).

87. E.L. Eliel, N.L. Allinger, S.J. Angyal and G.A. Morrison, "Conformational Analysis", Interscience-Wiley, New York, 1965, p. 203; J. Dale, Tetrahedron, 30, 1683 (1974).

88. G.A. Russel and J.M. Pecoraro, J. Am. Chem. Soc., 101, 3331 (1979).

89. J.J. McCullough, W. Keith MacInnis, C.J.L. Lock, and R. Faggiani, J. Am. Chem. Soc., 102, 7780 (1980).

90. C.R. Flynn and J. Michl, J. Am. Chem. Soc., 96, 3280 (1974).

91. T.R. Chamberlain and J.J. McCullough, Can. J. Chem., 51, 2578 (1973).

92. TME dimerizes slowly to give octamethylcyclobutane, D.R. Arnold and V.Y. Abraitys, J. Chem. Soc., Chem. Commun., 794 (1971).

93. F.D. Lewis, private communication.

94. R. Srinivason and K.L. Carlough, J. Am. Chem. Soc., 89, 4932 (1967); R.S. Liu and G.S. Hammond, ibid., 89, 4936 (1967).

95. E.A. Chandross and A.H. Schiebel, J. Am. Chem. Soc., 95, 611 (1973).

96. Compare R.S. Davidson and K.R. Tretheway, J. Chem. Soc., Chem. Commun., 827 (1976).

97. A. Streitweiser, Jr., L. Verbit and P. Stang, J. Org. Chem., 29, 3706 (1964).

98. P. Singh, D.G. Boocock and E.F. Ullman, Tetrahedron Lett., 3935 (1971).

99. R.C. Fuson, C.H. McKeever and L.C. Behr, J. Amer. Chem. Soc., 63, 2648 (1941).

100. H.G. Rule, J. Chem. Soc., 1816 (1950).

101. C.C. Price, E.C. Chapin, A. Goldman, E. Krebs and H.M. Shafer, J. Am. Chem. Soc., 63, 1857 (1941). The structure was determined by oxidation to 1,6-naphthoic acid and by decarboxylation to β-methylnaphthalene.

102. M.S. Newman and A.I. Kosak, J. Org. Chem., 14, 375 (1949).

103. M.F. Hebbelynck and R.H. Martin, Bull. Soc. Chim. Belges., 61, 635 (1952).

104. G.I. Samokhvalov, M.A. Miropolskaya, L.A. Vakulova and N.A. Preobsazhensky, J. Gem. Chem. U.S.S.R., 25, 515 (1955).

105. G.W. Stacy, A.J. Papa, F.W. Villaescusa and S.C. Ray, J. Org. Chem., 29, 607 (1964).

106. Y. Hirshberg, D. Lavie and E.D. Bergmann, J. Chem. Soc., 1030 (1951).

107. R.C. Huston and G.L. Goerner, J. Am. Chem. Soc., 68, 2504 (1946).

108. L.F. Fieser and W.S. Johnson, J. Am. Chem. Soc., 62, 575 (1940).

109. M.B. Green and W.J. Hickenbottom, J. Chem. Soc., 3262 (1957).

110. I.K. Saycheva, G.A. Vorob'eva, L.G. Kucheryavenko and N.A. Preobrazhenskii, Zhur. Obschei. Khim., 27, 2994 (1957). (Chemical Abstracts, 52, 8036d.)

111. For a review of the measurement of photoluminescence quantum yields see J.N. Demas and G.A. Croby, J. Phys. Chem., 75, 991 (1971).

112. W.H. Melhuish, J. Phys. Chem., 65, 229 (1961).

113. C.G. Hatchard and C.A. Parker, Proc. Roy. Soc., Ser. B, 140, 470 (1953).

114. H.E. Zimmerman, R.D. Rieke and J.R. Scheffer, J. Am. Chem. Soc., 89, 2033 (1967); H.E. Zimmerman, R.C. Hahn, H. Morrison, and M.C. Wani, ibid., 87, 1138 (1965).

115. For a useful description of general technique and the theory involved in time-correlated single photon counting see: L.J. Cline Love and L.A. Shaver, Analytical Chemistry, 48, 365A (1976).

116. J.B. Birks, "Photophysics of Aromatic Molecules", Wiley Interscience, New York (1970), p. 310-311.