PHOTOPHYSICAL STUDIES:
I. SINGLET QUENCHING IN NAPHTHALENE-CONJUGATED DIENE BICHROMOPHORES
II. FLUORESCENCE OF AROMATIC HYDROCARBON-TERTIARY AMINE BICHROMOPHORES
III. INTERSYSTEM CROSSING IN THE METHYL BENZENES

Thesis by
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ABSTRACT

Part I describes the synthesis, photochemistry, and fluorescence of several naphthalene-conjugated diene bichromophores. The data for these systems and for suitable reference systems are used to discuss and develop models for the bimolecular singlet quenching phenomenon.

Part II describes the synthesis and fluorescence of several aromatic hydrocarbon-tertiary amine bichromophores. The fluorescence properties of these systems are related to the accessibility of various conformations and possible configurational requirements of amine singlet quenching are discussed.

Part III reports the results of a systematic study of intersystem crossing in the methyl benzenes. Along with measured singlet lifetimes and literature values for the fluorescence quantum yields, these data allow evaluation of the rate constants for deactivation of the first excited singlet state of the methyl benzenes in degassed cyclohexane solution. A qualitative dependence of the intersystem crossing rates on the symmetry of methyl substitution is found and mechanisms involving intersystem crossing to the second triplet state are proposed to account for this result. Non-radiative decay of the first excited singlet state *via* pathways other than fluorescence and intersystem crossing is found to be a significant process for all of the methyl benzenes except *p*-xylene.

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PART I

SINGLET QUENCHING IN NAPHTHALENE-CONJUGATED DIENE BICHROMOPHORES

INTRODUCTION

The Lamola-Hammond method[1] has been widely used to determine intersystem crossing quantum yields (ϕ_{isc}) in solution. Using piperylene (1,3-pentadiene) or other suitable isomerizable species as a triplet counter, sensitized photostationary state and isomerization quantum yield measurements allow determination of ϕ_{isc} of the sensitizer. ϕ_{isc} values obtained by this method for several aromatic hydrocarbons, particularly naphthalene and its derivatives, agreed poorly with those determined by independent methods.[2,3] That this was due to quenching of the aromatic singlet state by piperylene was shown by Stephenson.[4]

Studies on the quenching of naphthalene fluorescence by conjugated dienes have resolved several mechanistic features. Neither excited singlet nor excited triplet states of the diene are formed as a result of the quenching act; the quantum yield for disappearance of naphthalene is negligible under conditions where all the naphthalene singlets are being quenched; no new fluorescence is observed.[4] Studies on other singlet quenchers, such as quadricyclene,[5] indicated that a portion of the energy of excitation of the aromatic is converted to vibrational excitation in the quencher. This is compatible with a simple mechanism involving formation and decay of a non-fluorescent exciplex [eq. (1)]. The decay step (k_2) is envisioned as a conversion of the energy

$$A^{*(1)} + D \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (AD)^{*(1)} \xrightarrow{k_2} A^{*}(\text{vib}) + D^{*}(\text{vib}) \qquad (1)$$

of excitation to vibrational energy--in effect, an accelerated internal conversion process. Perdeuteration of either the aromatic or the diene leads to a small increase in the quenching rate[6] indicating that C-H vibrations are not involved in the quenching step (this assumes that k_1 is not rate limiting).

There has been much controversy in the literature regarding the nature of the binding (i.e., the factors affecting k_1/k_{-1}) in these complexes. Binding is probably due to a number of factors, with both excitation delocalization and charge transfer interactions contributing to the binding [eq. (2)].

$$\psi_{(AD)^{*(1)}} = a\,\psi_{A^*D} + b\,\psi_{AD^*} + c\,\psi_{A^+D^-} + d\,\psi_{A^-D^+} \quad . \qquad (2)$$

Energetic considerations and substituent studies[7,8] imply that $a > b$ and that $d > c$, but say nothing about the relative magnitudes of $a + b$ and $c + d$. Others have put forward reduction potential[8] and ionization potential[9] correlations as evidence for the dominance of charge transfer terms. The absence of a large (1-2 orders of magnitude) polar solvent effect on the quenching rates, however, indicates that charge transfer interactions are not large. Taylor[10] has recently seen emission from exciplexes of electron-rich olefins with 1-cyanonaphthalene. The dipole moments of these exciplexes (estimated from solvent-dependent emission shifts) are much smaller than those observed for naphthalene-amine exciplexes.[11] Typical quenching rates are listed in Table I.

The existence of a preferred configuration has been indicated in several studies. In general, bulky substituents in either the aromatic[4]

Table I

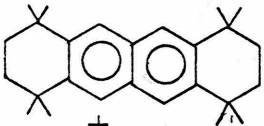
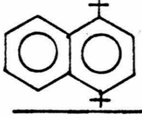
Effect of solvents and substituents on the rate of quenching of naphthalene fluorescence by conjugated dienes.

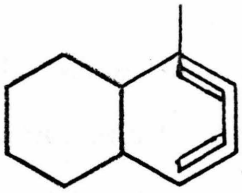
Aromatic	Quencher	Solvent	$k_Q \times 10^{-8}$ $M^{-1}sec^{-1}$	
Naphthalene	*cis*-piperylene	Hexane	1.11	(11)
"	"	Cyclohexane	1.31	(11)
"	"	Methanol	1.85	(11)
"	"	Acetonitrile	1.52	(11)
"	*trans*-piperylene	Hexane	1.29	(11)
"	"	Cyclohexane	1.98	(11)
"	"	Methanol	2.58	(11)
"	"	Acetonitrile	2.24	(11)
1-Methylnaphthalene	"	Hexane	0.79	(4)
2-Methylnaphthalene	"	Hexane	0.94	(4)
1-Methylnaphthalene	piperylene	Isoöctane	0.38	(8)
1-Cyanonaphthalene	"	Isoöctane	49	(8)

or the diene[11] hinder the quenching process. In addition, s-cis dienes are better quenchers than corresponding s-trans dienes.[4,11] Some relevant quenching rates are given in Table II. Calculations by Salem[12] using his intermolecular orbital theory of the interaction between conjugated systems (binding based on overlap with an arbitrary assumption concerning interplanar distance) had indicated that configurations I-V would lead to the greatest binding energy. With these calculations in mind and with a general interest in bichromophoric systems, we decided to synthesize and study the naphthyl diene bichromophores VI and VII.

Table II

Effects of steric bulk in the diene or the aromatic on singlet quenching rates.

Aromatic	Quencher	Solvent	$k_Q \times 10^{-7}$	
Naphthalene	*trans*-piperylene	Hexane	12.9	(11)
"	*trans*-5, 5-dimethyl-1, 3-hexadiene	"	3.9	(11)
"	isoprene	"	1.8	(11)
"	2-*tert*-butyl-1, 3-butadiene	"	5.0	(11)
1, 5-Dimethyl naphthalene	2, 5-dimethyl-2, 4-hexadiene	Hexane	110	(7)
2, 3-Dimethyl naphthalene	"	"	97	(7)
	*trans*-piperylene	"	0.87	(4)
	"	"	1.3	(4)



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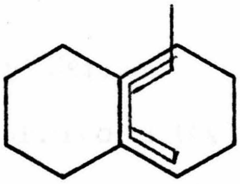
I



0.34ev

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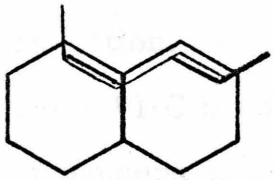
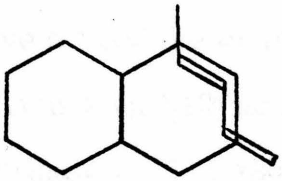


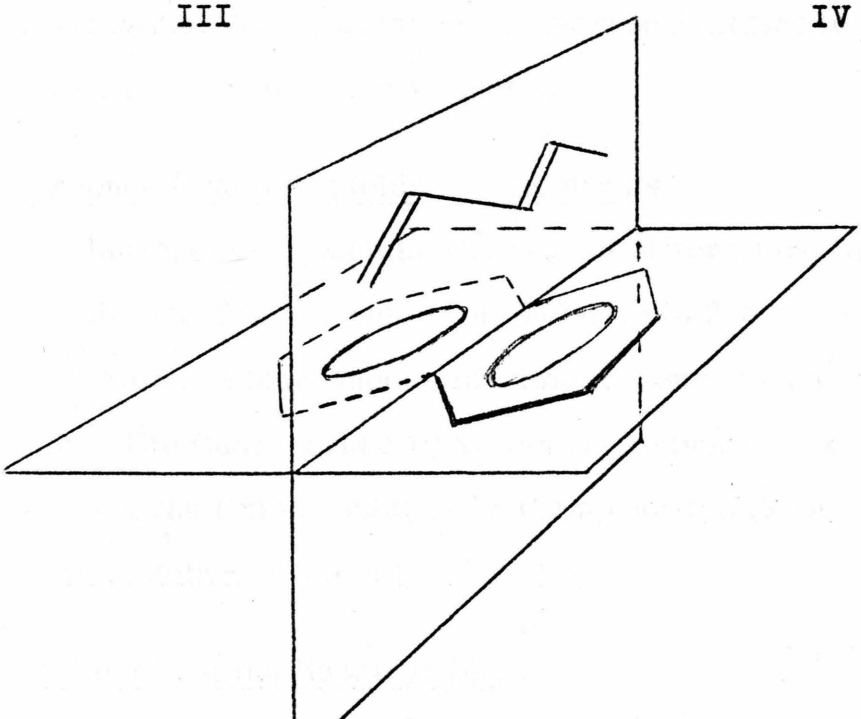
0.80ev

III



0.36ev

IV



1.2ev

V

RESULTS AND DISCUSSION

Syntheses

Syntheses of the α-naphthyl and β-naphthyl derivatives are outlined in Schemes I and II, respectively. The desired α,α-dimethylaldehydes (IX and XII) were synthesized from the corresponding naphthyl alkyl halides (VIII and XI) by a modification of the method of Stork and Dowd.[13] The reference compounds (X and XIII) were prepared from the corresponding aldehydes by the Huang-Minlon modification[14] of the Wolff-Kishner reduction. Wittig reaction with IXb gave a mixture of isomers of VI in which VI-C predominated; similar reaction with XIIb gave a mixture of isomers of VII in which VII-C predominated. The isomers of VI and VII were separated by dry-column chromatography on silver nitrate-alumina. The assignment of stereochemistry to the diene isomers is detailed in the experimental section.

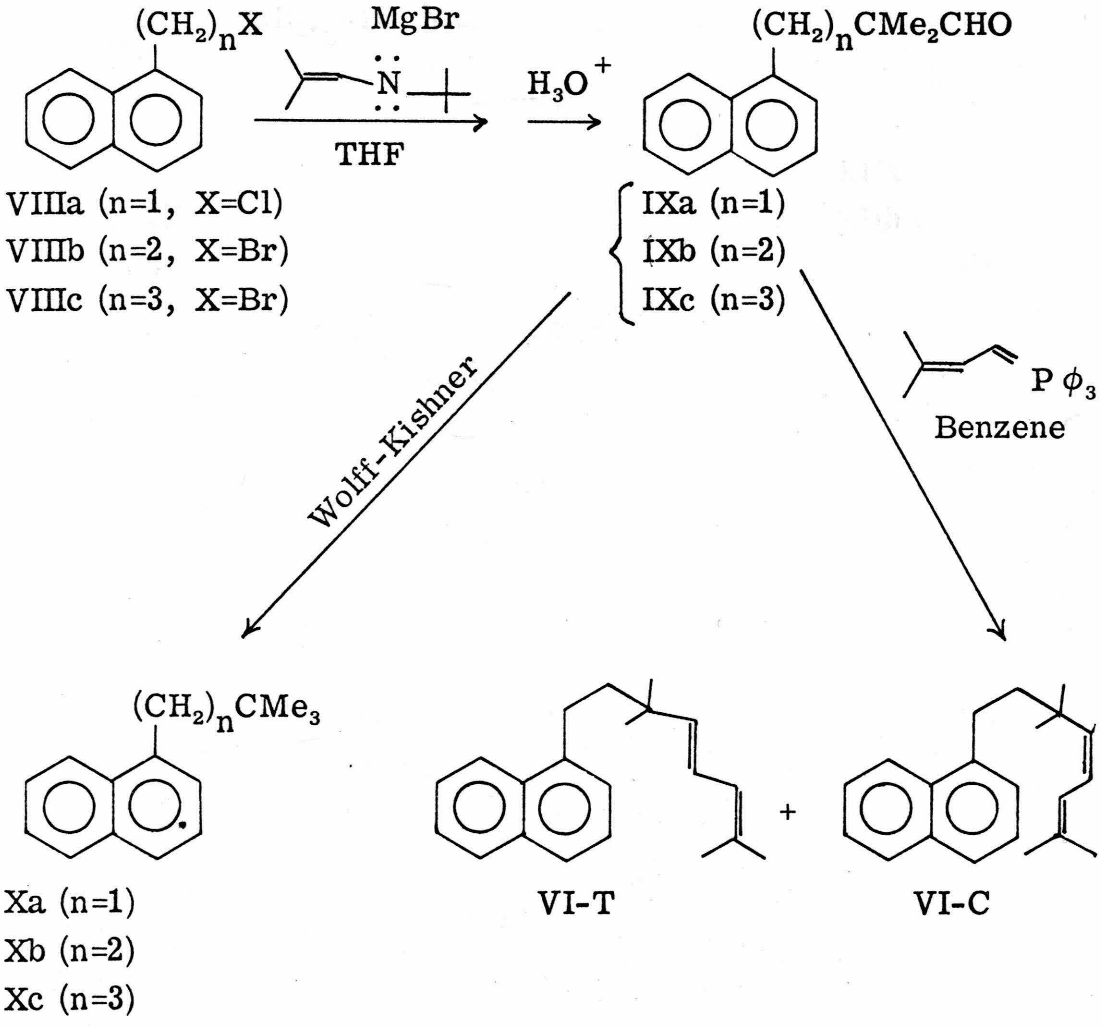
Fluorescence Quantum Yields and Lifetimes

Fluorescence quantum yields were determined in degassed cyclohexane solution (312 nm excitation) relative to 2,3-dimethylnaphthalene in cyclohexane. Fluorescence lifetime measurements were made when possible. The fluorescence lifetimes of the isomers of VI and VII were shorter than the time resolution of the apparatus (3 ns). Quantum yield and lifetime data are listed in Table III.

Energy Levels of the Naphthyl Dienes

The energy of the first singlet of Xb and XIIIb is about 89 kcal. The onset of S_2 is not well resolved, but is in the vicinity of 95 kcal.

Scheme 1: Synthesis of the α-series.



Scheme 2: Synthesis of the β-series.

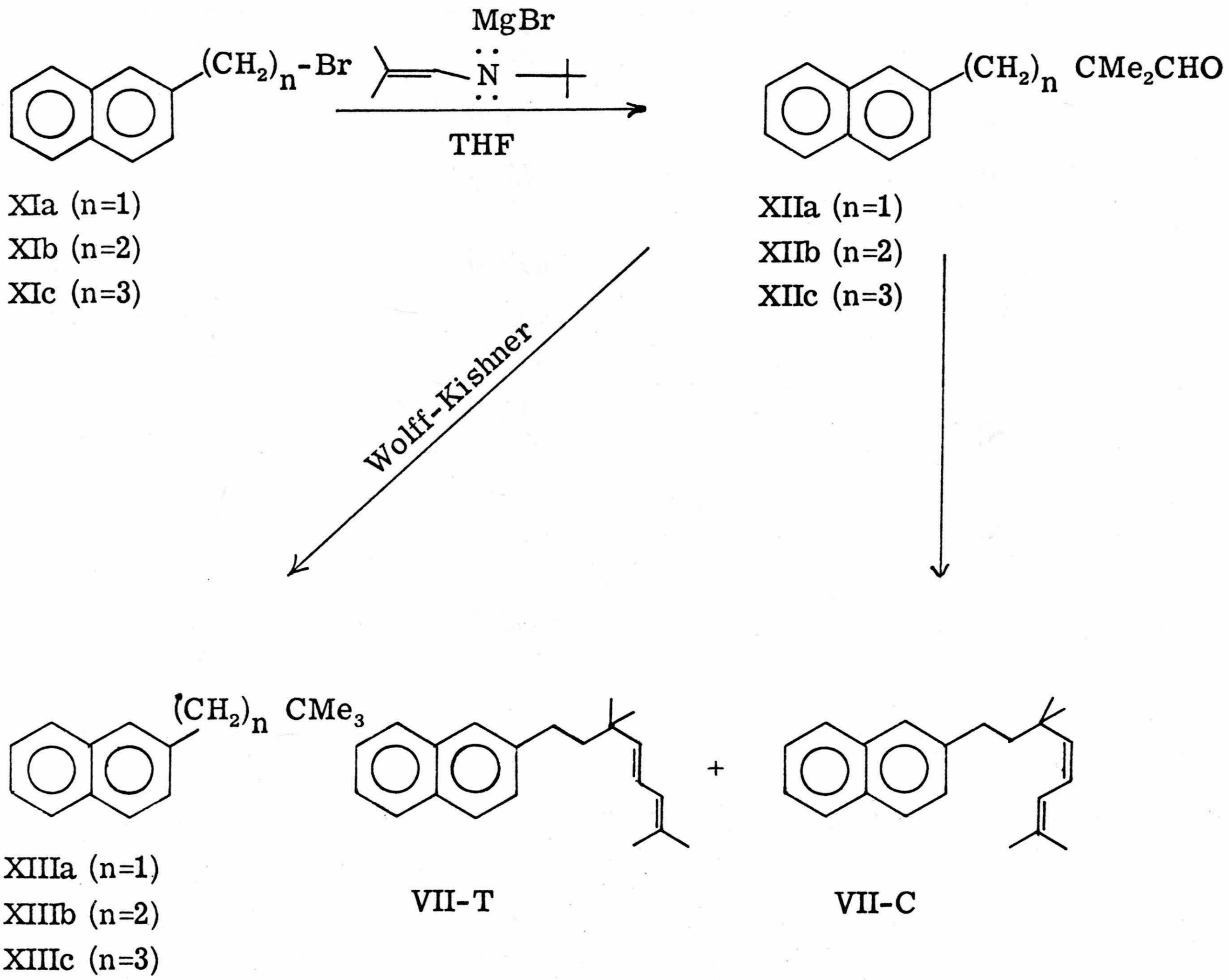


Table III

Fluorescence quantum yield and lifetime data for the naphthyl dienes and reference compounds.

Compound	ϕ_f ± 10%	τ_f (ns) ± 5%
Xa	0.20	57
Xb	0.22	55
Xc	0.22	56
VI-C	0.0086	<3
VI-T	0.0081	<3
XIIIa	0.21	54
XIIIb	0.25	50
XIIIc	0.24	54
VII-C	0.0086	<3
VII-T	0.010	<3

The first (spectroscopic) singlet of the diene occurs at an energy higher than 110 kcal. Thus, for the naphthyl diene bichromophores, the two lowest singlet states are localized on the naphthalene chromophore, with the third singlet potentially localized on the diene unit. In addition, there is probably a state of energy comparable to or below S_1 which corresponds to the bimolecular exciplex state.

In the triplet manifold, the ordering should be reversed, with the lowest triplet localized in the diene unit. Reasonable estimates are 55-57 kcal for the *cis* diene and 57-59 kcal for the *trans* diene lowest triplet energies. On the basis of phosphorescence spectra, the triplet energy of Xb is placed at 59.8 kcal and that of XIIIb at 61.0 kcal. Consistent with this ordering of triplet energies, no phosphorescence could be detected from either VI or VII.

Irradiations of VI and VII

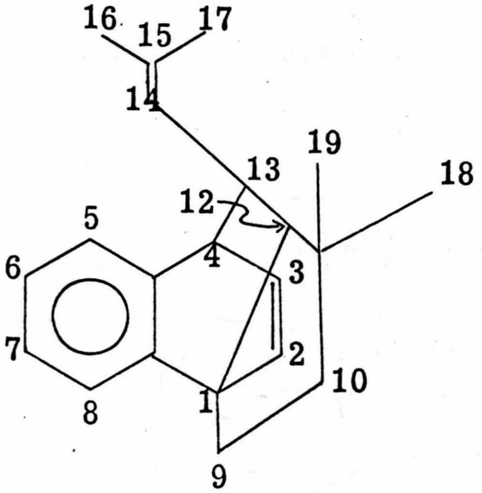
Direct irradiation of the synthetic mixture of isomers of VI (0.28 M in degassed benzene, 5 ml of solution) at 305 nm for one week gave a mixture consisting of VI-C (10%), VI-T (45%), and two products: **A** (20%) and **B** (25%). Irradiation in degassed cyclohexane solution gave similar results. Separate experiments in which the course of the irradiation was followed by NMR showed that isomerization of the diene is rapid relative to product formation.

Irradiation of VI (0.28 M in degassed benzene, 5 ml of solution) at 360 nm for one week in the presence of benzophenone as sensitizer gave a mixture consisting of VI-C (5%), VI-T (20%), and **B** (75%). Benzophenone sensitized isomerization was rapid relative to the formation of

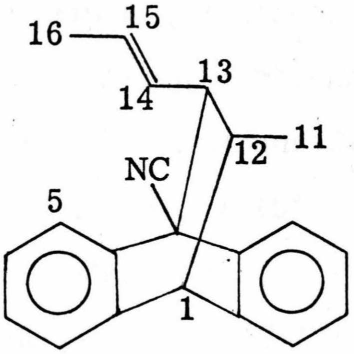
B. Sensitization with *m*-methoxyacetophenone (E_T = 72 kcal), 1-acetonaphthone (E_t = 56.4 kcal) or chrysene (E_t = 56.6-57 kcal) also resulted in formation of **B** in addition to isomerization. Attempts at sensitization using benzil (E_t = 53.7 kcal) resulted in consumption of the diene.

The photoproduct **B** was isolated from the *m*-methoxyacetophenone sensitized irradiation of VI by preparative thin layer chromatography (TLC) on silver nitrate impregnated silica gel. The nuclear magnetic resonance (NMR) spectrum ($CDCl_3$) showed two alkyl methyl groups (0.90δ, s, 6H, $C^{18}\underline{H}_3$ and $C^{19}\underline{H}_3$), two vinyl methyl groups (1.58δ and 1.69δ, d, 2 × 3 H, $J_{14-17} = J_{14-16} = 1.2$ Hz, $C^{16}\underline{H}_3$ and $C^{17}\underline{H}_3$), four aromatic protons (7.12δ, m, 4H, $C^5\underline{H}$-$C^8\underline{H}$), and three vinyl hydrogens at 6.09δ (d of d, 1H, $J_{2-3} = 7.5$ Hz, $J_{2-4} \approx 1.5$ Hz, $C^2\underline{H}$), 6.60δ (d of d, 1H, $J_{2-3} = 7.5$ Hz, $J_{3-4} = 6.2$ Hz, $C^3\underline{H}$), and 4.50δ (d of m, 1H, $J_{13-14} = 10.2$ Hz, $J_{14-16} = J_{14-17} = 1.2$ Hz, $C^{14}\underline{H}$). The remaining resonances occurred at 3.56δ (d of m, 1H, $J_{3-4} = 6.2$ Hz, $J_{2-4} \approx 1.5$ Hz, $J_{4-13} = 1.7$ Hz, $C^4\underline{H}$), 2.53δ (d of d of d, 1H, $J_{13-14} = 10.2$ Hz, $J_{4-13} = 1.7$ Hz, $J_{12-13} = 6.7$ Hz, $C^{13}\underline{H}$), 1.7-2.4δ (m, 4H, $C^9\underline{H}$ and $C^{10}\underline{H}$), and 1.03δ (d, 1H, $J_{12-13} = 6.7$ Hz, $C^{12}\underline{H}$). The infrared spectrum (liquid film) showed bands at 3040, 3020, 2950, 2868, 1465, 1455, 1387, 1375, 1364, 1180, 1120, 1030, 870, 850, 757, 715, and 693 cm^{-1}. The UV spectrum (hexane) had maxima at 272 (ε 370), 264 (ε 470), and 259 nm (ε 420). These data are sufficient to characterize the carbon framework as XIV. The UV spectrum is similar to that of the parent benzobicyclo[2.2.2]-octadiene.[15] The NMR data are quite similar to those reported for

XV:[16] 1.32-1.82δ (m, 1H, $C^{12}\underline{H}$), 1.60δ (d of d, 3H, $J_{14-16} = 1.5$ Hz, $J_{15-16} = 6.0$ Hz), 2.00δ (d of d, 1H, $J_{12-13(trans)} = 4.5$ Hz, $J_{13-14} = 9.0$ Hz, $C^{13}\underline{H}$), 3.98δ (d, 1H, $J_{1-12} = 2.0$ Hz), and 4.72δ (m, 1H, $J_{14-15} = 15.0$ Hz, $J_{13-14} = 9.0$ Hz, $J_{14-16} = 1.5$ Hz, $C^{14}\underline{H}$).

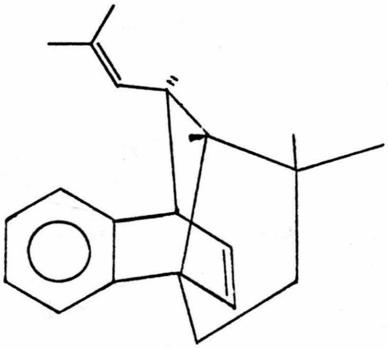


XIV



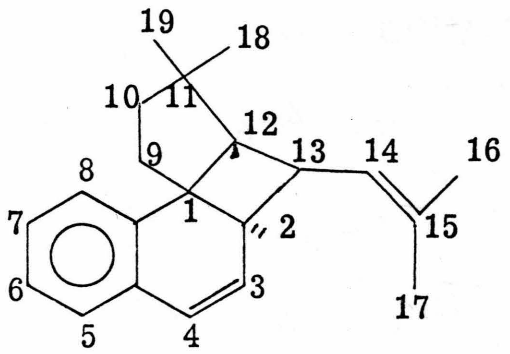
XV

Since there are four isomers of XIV, the stereochemistry at C^{12} and C^{13} must be clarified. The coupling constant $J_{12-13} = 6.2$ Hz is indicative of trans geometry. This was confirmed by quantitative conversion of B to VI-T at 208° (4 hrs) in a retro-Diels-Alder fashion. The upfield position of the $C^{14}\underline{H}$ (4.50δ) is consistent with a syn relationship of the vinyl group and the aromatic ring. The corresponding proton in XV suffers deshielding by the cyano group and appears at 4.72δ (the deshielding of the $C^5\underline{H}$ amounts to 0.35 ppm in this compound). Photoproduct B is therefore assigned the structure XVI.

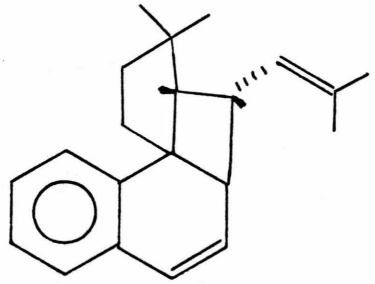


XVI

Small quantities of impure photoproduct A were isolated from the direct irradiations of VI by dry column chromatography on silver nitrate impregnated alumina. The NMR spectrum (CCl_4) showed two alkyl methyl groups (1.02δ, s, 3H, $C^{19}\underline{H}_3$; 1.10δ, s, 3H, $C^{18}\underline{H}_3$), two vinyl methyl groups (1.55δ and 1.63δ, s, 2 × 3H, $C^{16}\underline{H}_3$ and $C^{17}\underline{H}_3$), four aromatic protons (6.8-7.2δ, m, 4H, $C^5\underline{H}$-$C^8\underline{H}$), and three vinyl hydrogens at 6.25δ (d, 1H, $J_{3-4} = 10$ Hz, $C^4\underline{H}$), 5.43δ (d of d, 1H, $J_{3-4} = 10$ Hz, $J_{2-3} = 4.5$ Hz, $C^3\underline{H}$), and 5.30δ (d, 1H, $J_{13-14} = 10$ Hz, $C^{14}\underline{H}$). Two overlapping resonances occurred at 2.9-3.2δ (m, 2H, $C^2\underline{H}$ and $C^{13}\underline{H}$); the remaining resonances were not resolved due to impurities. The IR spectrum (liquid film) showed bands at 3090, 3050, 3020, 2950, 2924, 2860, 790, and 755 cm^{-1}. The UV spectrum (hexane) consisted of a broad, structureless absorption with a maximum at 273 nm ($\epsilon > 3000$). This is sufficient to establish the carbon framework as XVII, leaving only the stereochemistry at C^{13} in doubt. Since the downfield position of the alkyl methyl resonances is indicative of deshielding by the vinyl group, photoproduct A is assigned the structure XVIII.



XVII



XVIII

Direct irradiation of the synthetic mixture of isomers of VII (0.28 M in degassed benzene) as above resulted in a mixture consisting of 55% VII-C and 45% VII-T. No new products could be detected. Similarly, sensitized isomerization with benzophenone gave a mixture of isomers (48% VII-C and 52% VII-T), but no observable products.

Mechanism

The following mechanism, analogous to the bimolecular mechanism, is consistent with the results for the naphthyl dienes. To account for product formation from VI, eqs. (11) and (12) are included in the mechanism for VI.

$$A_0 \sim D \xrightarrow{h\nu} A^{*(1)} \sim D \tag{3}$$

$$A^{*(1)} \sim D \xrightarrow{k_4} A_0 \sim D + h\nu' \tag{4}$$

$$A^{*(1)} \sim D \xrightarrow{k_5} A^{*(3)} \sim D \tag{5}$$

$$A^{*(1)} \sim D \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} (A \sim D)^{*(1)} \tag{6}$$

$$(A \sim D)^{*(1)} \xrightarrow{k_7} A^{*}(\mathrm{vib}) \sim D^{*}(\mathrm{vib}) \tag{7}$$

$$A^{*(3)} \sim D \xrightarrow{k_8} A_0 \sim D^{*(3)} \tag{8}$$

$$A_0 \sim D^{*(3)} \xrightarrow{k_9} A_0 \sim C \tag{9}$$

$$A_0 \sim D^{*(3)} \xrightarrow{k_{10}} A_0 \sim T \tag{10}$$

$$(A \sim C)^{*(1)} \xrightarrow{k_{11}} \mathrm{XVIII} \tag{11}$$

$$A_0 \sim D^{*(3)} \xrightarrow{k_{12}} \mathrm{XVI} \tag{12}$$

Eq. (11) reflects the structure assigned to photoproduct **A** (XVIII) and assumes that formation of XVIII occurs with retention of stereochemistry. Since there is no reason to expect that singlet quenching leads to isomerization of the diene unit,[4] the slow formation of XVIII relative to isomerization and the efficiency of intramolecular singlet quenching (*vide infra*) imply that *stable* product formation is not an important consequence of singlet quenching ($k_7 \gg k_{11}$). Since sensitizers of lower triplet energy than the naphthyl chromophore are capable of sensitizing the formation of photoproduct **B** (XVI), eq. (12) best represents the formation of XVI.

Relationship to Singlet Quenching

For a suitable reference compound, only the processes in eqs. (13-15) deactivate the fluorescent state. By comparing the fluorescence

$$A_0 \xrightarrow{h\nu} A^{*(1)} \qquad (13)$$

$$A^{*(1)} \xrightarrow{k_4} A_0 + h\nu' \qquad (14)$$

$$A^{*(1)} \xrightarrow{k_5} A^{*(3)} \qquad (15)$$

of the naphthyl dienes (ϕ_f^D) to that of a suitable reference compound (ϕ_f^{Ref}), one may obtain the unimolecular quenching rates for the bichromophores [eq. (16)].

$$\frac{\phi_f^{Ref}}{\phi_f^D} = 1 + \frac{k_6 k_7}{k_{-6} + k_7}\tau_f^{Ref} = 1 + k_Q^D \tau_f^{Ref} \quad . \qquad (16)$$

The use of eq. (16) implies that the following conditions are met: (a) the fluorescences of the reference compound and the bichromophore arise from similar states; (b) the fluorescence and intersystem crossing rates (k_4 and k_5, respectively) are the same for both the bichromophore and the reference compound; (c) there is no ground-state interaction between the chromophores of the bichromophore. Since the spectral distributions of the fluorescence from X and VI and from XIII and VII are similar, condition (a) is met. Figure 1 shows absorption spectra for Xb, VI-C, and VI-T and Figure 2 shows absorption spectra for XIIIb, VII-C, and VII-T. The spectra in each figure are identical within experimental

Figure 1

Absorption Spectra of Xb, VI-C, and VI-T

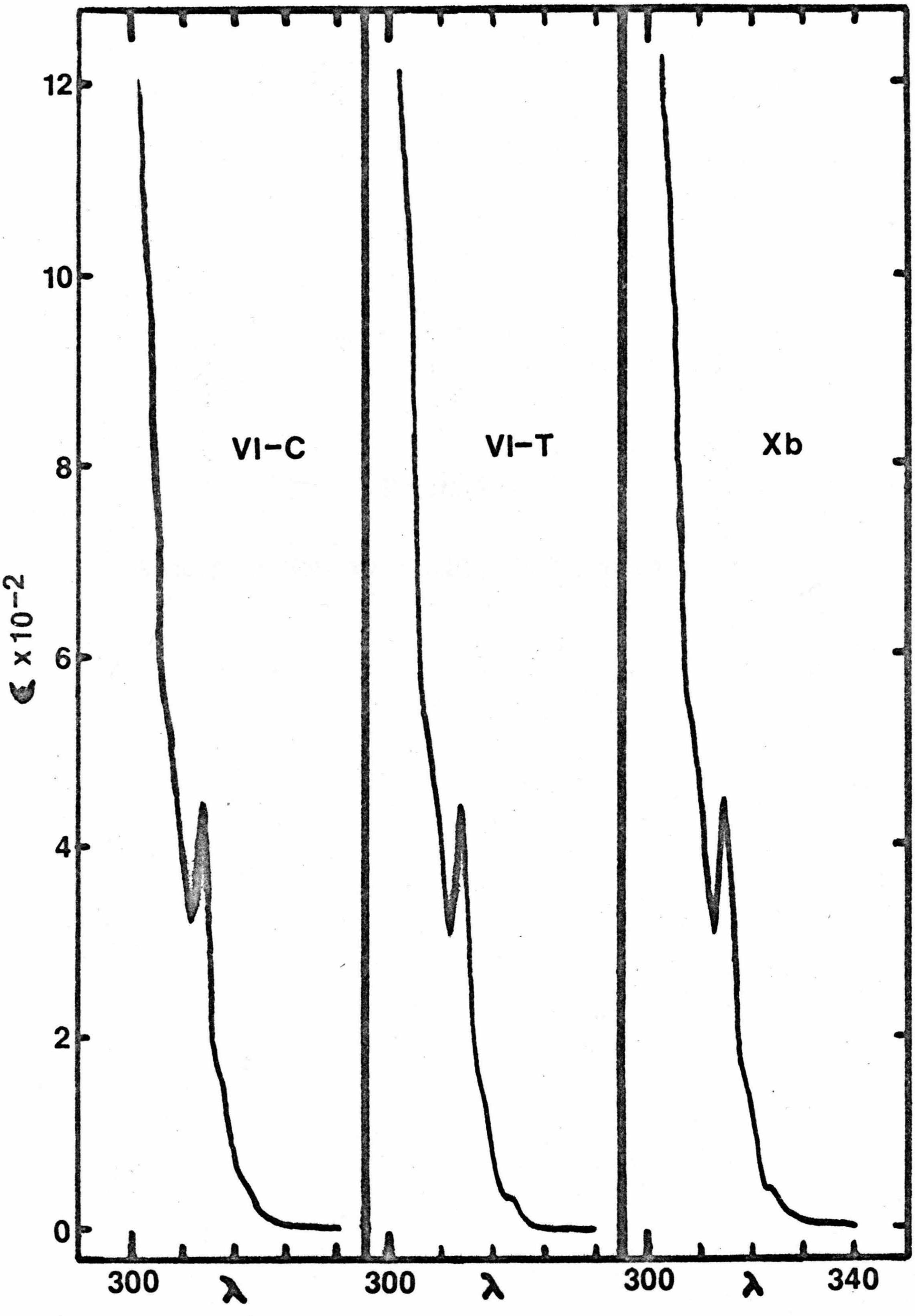
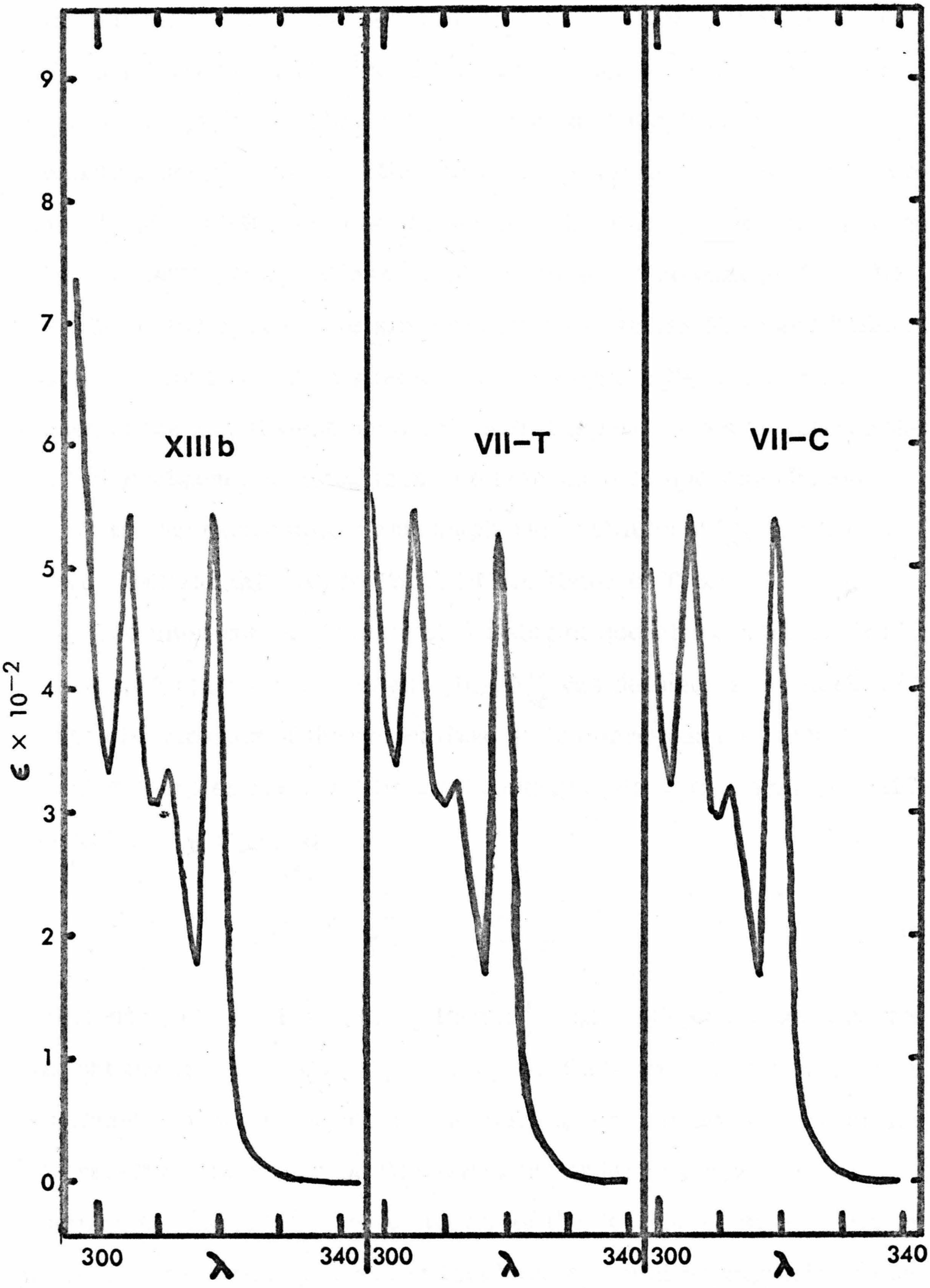

12
10
8
6
4
2
0
ϵ x10⁻²
VI-C
VI-T
Xb
300
λ
300
λ
300
λ
340

Figure 2

Absorption Spectra of XIIb, VII-C, and VII-T


XIII b
VII–T
VII–C
$\epsilon \times 10^{-2}$
0
1
2
3
4
5
6
7
8
9
300
340
300
340
300
340
λ
λ
λ

error, indicating that ground-state interactions between the chromophores in VI and VII are negligible [condition (c)]. Because the fluorescence rate constant may be related to the integrated absorption intensity for the emitting state[17] and condition (a) is met, values of k_4 for Xb and VI and for XIIIb and VII should be the same. The other portion of condition (b), that k_5 is constant, is less readily verified. The data in Table III show that ϕ_f and τ_f are quite similar within the series Xa-c and XIIIa-c. Thus, k_5 seems to be little affected by the length of the alkyl chain attached to the naphthalene nucleus[18] and it is reasonable to assume that k_5 will be unchanged in going from the reference compounds (Xb and XIIIb) to the corresponding bichromophores. Values of k_Q^D calculated from eq. (16) and the data in Table III are listed in Table IV.

The most notable feature of the singlet quenching rates is that they are all quite similar. In eq. (16), k_Q^D was defined as a product of the rate of formation of the delocalized state corresponding to the bimolecular exciplex state (k_6) times the decay ratio of this state [eq. (17)]. The two limiting cases are

$$k_Q^D = \frac{k_6 k_7}{k_{-6} + k_7} \qquad (17)$$

of greatest interest. If $k_7 \gg k_{-6}$, then $k_Q^D = k_6$. Although this limit predicts that the rates of singlet quenching should be similar (affected only by the factors which influence k_6), it is not a very attractive explanation of the results. An activation barrier of the order of 6 kcal/mole (assuming $A = 10^{13}$ sec^{-1}) for formation of the "exciplex" state would be required. Since 3-4 kcal/mole of this barrier could be attributed to the

Table IV

Intramolecular singlet quenching rates for VI and VII.

Compound	k_Q^D (sec^{-1})[a]	k_4 (sec^{-1})[b]	k_5 (sec^{-1})[b]
VI-C	4.5×10^8	4×10^6	1.4×10^7
VI-T	4.8×10^8	4×10^6	1.4×10^7
VII-C	5.6×10^8	4.5×10^6	1.4×10^7
VII-T	4.7×10^8	4.5×10^6	1.4×10^7

[a] ± 20%. Calculated from eq. (16).

[b] ± 20%. Calculated from reference compound data in Table III assuming that $k_4 = \phi_f^{Ref}/\tau_f^{Ref}$ and $k_5 = (1 - \phi_f^{Ref})/\tau_f^{Ref}$.

effects of the alkyl chain (this is the observed barrier for intramolecular excimer formation in the α,ω-dinaphthylpropanes and is of the magnitude expected for rotation about a trimethylene chain[19]), an intrinsic barrier of about 2-3 kcal/mole would be predicted for the formation of the bimolecular exciplex. This is inconsistent with the formulation of the exciplex as a weakly bound molecular complex.[6,7]

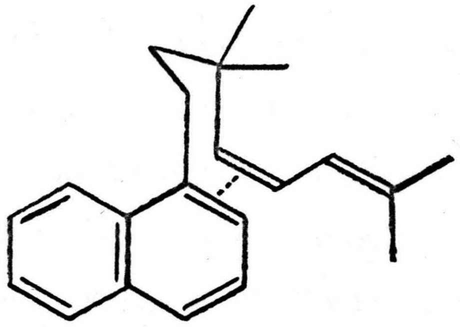
If $k_{-6} \gg k_7$, the rate of singlet quenching is equal to the rate of irreversible decay of the "exciplex" state attenuated by the equilibrium constant for formation of this state [eq. (18)]. Since K_{eq} is affected

$$k_Q^D = k_6k_7/k_{-6} = K_{eq}k_7 \qquad (18)$$

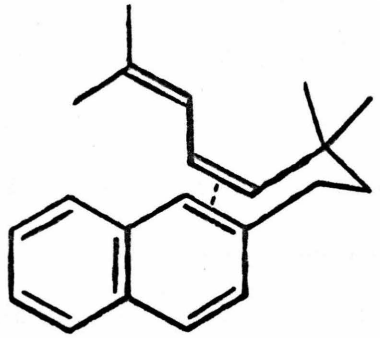
by the binding energy of the "exciplex" state, this limit allows interpretation of the observed (small) rate differences in terms of the configurations available to the bichromophore. Accepting this kinetic limit as valid, we examine some configurational models. Since the Salem configurations (I-V) provided the impetus for this study, they are an appropriate starting point. The substitution of the diene chromophores of VI and VII is sufficient to eliminate configurations I and II from consideration. If configuration V were important, the quenching rates for VI should be substantially higher than those of VII. Configuration III is available to both VI-C and VII-T; configuration IV is favored for VI-T. None of the configurations are accessible to VII-C, yet it shows the greatest quenching rate. Rather than postulate anomalous behavior for this compound, we conclude that the Salem model is inadequate for s-*trans* dienes.

Figure 3

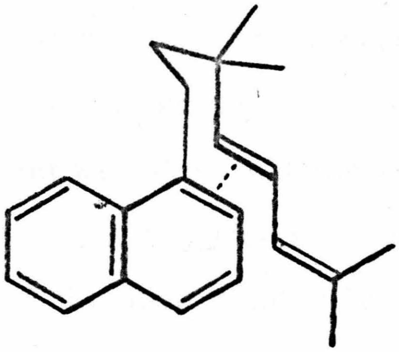
Possible Singlet Quenching Configurations



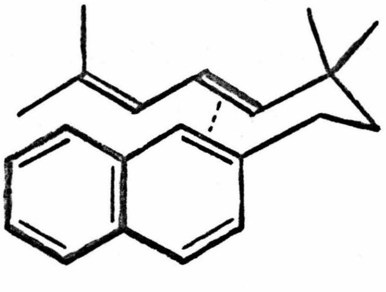
VI-C



VII-C



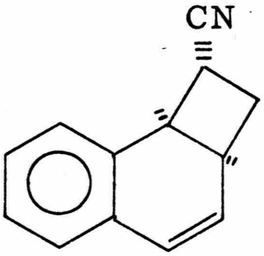
VI-T



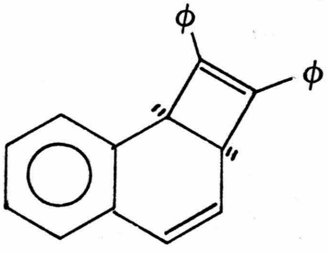
VII-T

The similarity of the quenching rate constants implies that if a preferred configuration exists, it must be readily accessible to all four bichromophores. The simplest model for a preferred binding configuration for s-trans dienes which is reasonably consistent with the results is one in which a double bond of the diene unit interacts with the 1,2-bond of the naphthalene nucleus (Figure 3). Because k_7 is sensitive to the precise nature of the diene unit, the quenching rate of VI-C should be compared to that of VII-C and similarly that of VI-T to VII-T. In his study of intramolecular excimer formation in the 1,3-dinaphthyl propanes, Chandross[19] found that the equilibrium lay further toward the excimer in 1,3-di-(2-naphthyl)-propane than in 1,3-di-(1-naphthyl)-propane at room temperature. This was attributed to steric differences in the 1- and 2-naphthylalkyl chains. The faster rate for VII-C relative to VI-C is consistent with a steric difference of this type. In VII-T, this effect is offset by an increase in steric interaction of the terminal end of the diene unit with the naphthalene ring; therefore, VII-T and VI-T exhibit essentially identical quenching rates.

This model implicitly accounts for the large variety of olefinic quenchers of naphthalene fluorescence. In this context, the formation of XVIII from VI is of importance. Both acrylonitrile[20] and tolan[21] quench naphthalene fluorescence with the formation of adducts of similar structure (XIX and XX, respectively).



XIX



XX

The product structure is established by the binding configuration and the efficiency of its formation is governed by the decay of the exciplex [the partitioning represented in eqs. (7) and (11)].

In the case of bimolecular singlet quenching, a number of interdependent factors influence the quenching rate. Changes in the structure of the diene may affect both k_7 and the coefficients of the charge transfer terms in eq. (2). These terms may also be affected by changes in the substitution pattern of the naphthalene nucleus. In weakly bound complexes, a preferred configuration may represent the minimum of a broad and shallow potential well. Thus, a large number of orientations of comparable binding energy are available to the system, and small steric perturbations on the preferred configurations may have little effect on the quenching rate. Such configurations may be indicated, and then only weakly, in systems such as VI and VII which incorporate large conformational restraints.

EXPERIMENTAL

Apparatus and General Techniques

All synthetic reactions were carried out under a nitrogen atmosphere as a matter of course. Solvent evaporations were carried out in vacuo using a Buchi rotary evaporator. Melting points (M. P.) were determined with a Thomas-Hoover Capillary Melting Point Apparatus and are uncorrected. Microanalyses were performed by Spang Microanalytical Service, Ann Arbor, Michigan. Ultraviolet absorption spectra (UV) were recorded using a Cary Model 14 spectrometer; wavelengths of maximum absorbance (λ_{max}) are reported in nanometers (nm) and extinction coefficients at these maxima (ϵ) are given in liters $mole^{-1}cm^{-1}$. Infrared spectra were recorded with a Perkin-Elmer Model 257 grating infrared spectrometer and are in units of cm^{-1}. Nuclear magnetic resonance (NMR) spectra were obtained with a Varian A-60 or HA-220 spectrometer and peak positions are reported as parts per million (δ) downfield from internal tetramethylsilane. Mass spectral analyses were performed by West Coast Technical Services, San Gabriel, California; mass peaks are reported at 70 eV.

Fluorescence samples were degassed in clean, dry, 13 × 100 mm Pyrex test tubes which had been constricted at a point about 30-40 mm below the top. Tubes were degassed on a mercury-free vacuum line by three freeze-pump-thaw cycles at a pressure of less than 5×10^{-4} torr and sealed under vacuum. Fluorescence spectra were recorded at room temperature (24 ± 2°) with either an Aminco-Bowman Spectrophotofluorometer or a Hitachi-Perkin-Elmer MPF-3 Spectrophotometer.

Fluorescence lifetimes were determined with a TRW Model 31A nanosecond spectral source (deuterium lamp) coupled to a Tektronix Type 556 dual-beam oscilliscope. A 340 nm interference filter was used to isolate the naphthalene emission. Phosphorescence spectra were recorded in EPA (5:5:2 ethylether: iso-pentane: ethyl alcohol) glasses at 77 °K using the MPF-3.

Materials and Fluorescence Quantum Yields

Cyclohexane (Matheson Coleman and Bell (MCB) Spectroquality) was purified by the method of Murray and Keller.[22] Benzene (MCB Spectroquality) was used as received. 2,3-Dimethylnaphthalene had been purified by D. A. Labianca for an earlier study.[7]

Cyclohexane solutions of the compound of unknown yield and the standard (2,3-dimethylnaphthalene) were adjusted to equal optical density (± 1%) at 312 nm using a Beckman DU. The solutions were degassed and relative fluorescence spectra recorded (312 nm excitation). Since positions and bandshapes of the fluorescence spectra were similar, fluorescence quantum yields were determined from ratios of intensities. The fluorescence quantum yield of 2,3-dimethylnaphthalene in cyclohexane was taken to be 0.32.[23]

The isomers of VI and VII were separated and rechromatographed on grade I alumina (*vide infra*). VI-T obtained in this manner exhibited anomalous fluorescence due to an impurity; therefore, material obtained from the pyrolysis of XVI (photoproduct **B**) was used in the fluorescence experiments.

General Procedure for $LiAlH_4$ Reductions in Tetrahydrofuran (THF)

A THF solution of the compound to be reduced was added dropwise to a slurry of excess $LiAlH_4$ in THF. The mixture was heated at reflux with stirring, generally overnight. After cooling, the reaction mixture was worked up as follows: 1 ml of water, 1 ml of 15% NaOH, and 3 ml of water per gram of $LiAlH_4$ were cautiously added and the reaction mixture again heated to reflux for 1-2 hrs. Cooling, filtration, and removal of the THF *in vacuo* gave the crude product in 90-100% yield.

The following known alcohols were prepared by this method: 1-naphthylethanol from 1-naphthylacetic acid (Eastman); 1-naphthylpropanol from 1-naphthylpropionic acid;[24] 2-naphthylethanol from 2-naphthylacetic acid (Eastman); 2-naphthylpropanol from 2-naphthylpropionic acid.[25]

General Procedure for Synthesis of Alkyl Bromides

The procedure of Huisgen and Rietz[26] was employed with slight modification. In general, the crude alcohol was used directly without purification; no difference in yield relative to purified alcohol was noticed. The following procedure for 2-naphthylpropyl bromide is typical.

23.0 gm (0.124 mole) of crude 2-naphthylpropanol, 50 ml of 48% HBr, and 0.15 gm of red phosphorus were heated at reflux with stirring for 20 hrs. The reaction mixture was poured into 200 ml of water and extracted with CH_2Cl_2 (3 × 80 ml). The CH_2Cl_2 extracts were washed with saturated $NaHCO_3$ (2 × 80 ml), water (1 × 80 ml), and saturated NaCl (2 × 80 ml) and dried ($MgSO_4$). Removal of the solvent *in vacuo* and short path distillation of the residue gave 22.2 gm (71%)

of 2-naphthylpropyl bromide (XIc), B. P. 128-132°/0.05 torr, which solidified upon standing, M. P. 44-45° (literature[25] M. P. 43.5-44.5°).

1-Naphthylethyl bromide (VIIIb), B. P. 118-123°/0.3 torr (literature[27], B. P. 135-8°/1.5 torr), 1-naphthylpropyl bromide (VIIIc), B. P. 125-128°/0.1 torr (literature[28] B. P. 127-130°/0.4 torr), and 2-naphthylethyl bromide (XIIb), M. P. 62-64° after sublimation (literature[25] M. P. 64.5-66.5°), were prepared by this procedure.

Preparation of Aldehydes

The method of Stork and Dowd[13] was used; however, an excess of the imine salt was employed to insure complete reaction of the alkyl halide. The following preparation is typical.

2,2-Dimethyl-4-(1-naphthyl)-butyraldehyde (IXb). To a solution of ethyl magnesium bromide (0.19 moles, from 4.70 gm Mg and 20.85 gm ethyl bromide) in dry THF (100 ml, freshly distilled from $LiAlH_4$) was added a solution of 24.4 gm (0.19 mole) of freshly prepared tert-butylimine of iso-butyraldehyde[29] in 50 ml of THF. The solution was refluxed until the evolution of ethane had ceased (about 2 days) and decanted to remove unreacted Mg. 29.4 gm (0.125 mole) of 1-naphthylethyl bromide (VIIIb) in THF (80 ml) were added dropwise to this solution and the resultant yellow solution refluxed 48 hrs. After cooling to room temperature, 150 ml of 10% HCl were cautiously added and the two-phase system refluxed 5 hrs. The phases were separated and the aqueous phase extracted with ether (2 × 100 ml). The organic phase and the ether extracts were combined, washed with saturated $NaHCO_3$ (1 × 100 ml), water (2 × 100 ml), and saturated NaCl (2 × 100 ml), and dried ($MgSO_4$). The solvent was removed by rotary evaporation and a low-boiling impurity removed by pumping at room temperature and 0.05 torr overnight. Short-path distillation gave 21.4 gm (75.7%) of product, B. P. 121-124°/0.08 torr and M. P. 29-31°C.

Analysis. Calculated for $C_{16}H_{18}O$: 84.91% C, 8.02% H
Found: 84.91% C, 7.78% H

NMR ($CDCl_3$): 1.12δ (s, 6H), 1.58-1.95δ (A_2B_2, 2H), 2.68-3.05δ (A_2B_2, 2H), 7.0-8.0δ (m, 7H), 9.62δ (s, 1H). IR (liquid film): 1723 (C=O), 3060, 3040, 2698, 1597, 1510, 1470, 1378, 1365, 800, 784. Mass spectrum: m/e 226 (M+, 16%), 154 (100), 142 (24), 141 (68), 115 (20).

2,2-Dimethyl-3-(1-naphthyl)-propionaldehyde (IXa) was prepared from 0.30 moles of imine salt and 0.20 moles (35.3 gm) of 1-chloromethylnaphthalene (VIIIa, Aldrich, chloride reacts exothermically) as above. Distillation of the residue gave 35.2 gm (83%) of product, B. P. 120-122°/0.05 torr.

Analysis: Calculated for $C_{15}H_{16}O$: 84.87% C, 7.60% H
Found: 84.95% C, 7.54% H

NMR ($CDCl_3$): 1.07δ (s, 6H), 3.27δ (s, 2H), 7.15-8.15δ (m, 7H), 9.62δ (s, 1H). IR (liquid film): 1720 (C=O), 3045, 2708, 1596, 1510, 1470, 1397, 1378, 1365, 805, 784. Mass spectrum: m/e 212 (M+, 12%), 142 (15), 141 (100), 115 (12).

2,2-Dimethyl-5-(1-naphthyl)-pentanaldehyde (IXc) was prepared from 0.20 moles of imine salt and 0.10 moles (24.9 gm) of 1-naphthylpropyl bromide (VIIIc) as above. Distillation of the residue gave 20.2 gm (84%) of product, B. P. 143-147°/0.20 torr.

Analysis. Calculated for $C_{17}H_{20}O$: 84.96% C, 8.39% H

Found: 85.15% C, 8.36% H

NMR ($CDCl_3$): 1.00δ (s, 6H), 1.45-1.75δ (m, 4H), 2.90-3.23δ (m, 2H), 7.2-8.15δ (m, 7H), 9.43δ (s, 1H). IR (liquid film): 1726 (C=O), 3060, 3045, 2695, 1598, 1512, 1472, 1398, 1379, 1368, 800, 780. Mass spectrum: m/e 240 (M+, 18%), 142 (24), 141 (100), 115 (21).

2,2-Dimethyl-3-(2-naphthyl)-propionaldehyde (XIIa) was prepared from 0.30 moles of imine salt and 0.20 moles (44.2 gm) of 2-bromomethylnaphthalene[30] (XIa, bromide reacts exothermically) as above. The residue was recrystallized from petroleum ether and sublimed (75°/0.05 torr) to give 30.2 gm (71%) of product, M.P. 82-83°.

Analysis. Calculated for $C_{15}H_{16}O$: 84.87% C, 7.60% H

Found: 84.76% C, 7.52% H

NMR ($CDCl_3$): 1.07δ (s, 6H), 2.94δ (s, 2H), 7.1-8.0δ (m, 7H), 9.71δ (s, 1H). IR (3% in CS_2): 1726 (C=O), 3055, 3015, 2695, 1635, 1601, 1375, 1366, 819, 749. Mass spectrum: m/e 212 (M+, 17%), 142 (23), 141 (100), 115 (12).

2,2-Dimethyl-4-(2-naphthyl)-butyraldehyde (XIIb) was prepared from 0.25 moles of imine salt and 0.125 moles (29.4 gm) of 2-naphthylethyl bromide (XIb) as above. Distillation of the residue gave 13.5 gm (52%) of product, B.P. 124-129°/0.07 torr and M.P. 42-44°.

Analysis. Calculated for $C_{16}H_{18}O$: 84.91% C, 8.02% H

Found: 84.96% C, 7.83% H

NMR ($CDCl_3$): 1.10δ (s, 6H), 1.6-2.0δ (A_2B_2, 2H), 2.46-2.9δ (A_2B_2, 2H), 7.1-7.95δ (m, 7H), 9.43δ (s, 1H). IR (3% in CS_2): 1727 (C=O), 3055, 3015, 2695, 1634, 1600, 1366, 817, 745. Mass spectrum: m/e 226 (M+, 18%), 154 (100), 142 (37), 141 (55), 115 (16).

2,2-Dimethyl-5-(2-naphthyl)-pentanaldehyde (XIIc) was prepared from 0.196 moles of imine salt and 0.089 moles (22.1 gm) of 2-naphthylpropyl bromide (XIc) as above. Distillation of the residue gave 17.9 gm (84%) of product, B. P. 142-146°/0.08 torr and M. P. 36-37°.

Analysis. Calculated for $C_{17}H_{20}O$: 84.96% C, 8.39% H

Found: 84.92% C, 8.34% H

NMR ($CDCl_3$): 1.04δ (s, 6H), 1.4-2.0δ (m, 4H), 2.5-3.0δ (m, 2H), 7.15-7.95δ (m, 7H), 9.44δ (s, 1H). IR (liquid film): 1725 (C=O), 3050, 3015, 2695, 1631, 1602, 1508, 1462, 1377, 1368, 817, 747. Mass spectrum: m/e 240 (M+, 32%), 142 (50), 141 (100), 115 (18).

Preparation of Reference Compounds

The aldehydes were reduced by the Huang-Minlon modification[14] of the Wolff-Kishner reduction. The following procedure is typical.

2,2-Dimethyl-1-(1-naphthyl)-propane (Xa). 4.0 gm (0.019 mole) of 2,2-dimethyl-3-(1-naphthyl)-propionaldehyde (IXa), 3.0 ml of 85% hydrazine hydrate, 41 ml of ethylene glycol, and 2.55 gm of NaOH were refluxed 1.5 hrs. The condenser was removed and the solution temperature allowed to rise to 190°. The condenser was replaced and the solution refluxed at 190-195° for 2.5 hrs. The reaction mixture was poured into 300 ml of 5% HCl and extracted with ether (3 × 100 ml). The ether extracts were washed with water (1 × 100 ml), saturated $NaHCO_3$ (1 × 100 ml), water (1 × 100 ml), and saturated NaCl (1 × 100 ml) and dried ($MgSO_4$). Removal of the ether *in vacuo* and distillation of the residual oil from $LiAlH_4$ gave 2.2 gm (58%), B. P. 71-72°/0.08 torr. The product had a purity of > 99.8% by glpc (5% SE-30 on Chromosorb W, 140°) and was stored in degassed ampoules until used.

Analysis. Calculated for $C_{15}H_{18}$: 90.85% C, 9.15% H

Found: 90.85% C, 9.06% H

NMR ($CDCl_3$): 0.96δ (s, 9H), 3.02δ (s, 2H), 7.17-8.30δ (m, 7H). IR (liquid film): 3040, 1597, 1510, 1396, 1364, 1235, 799, 780. Mass spectrum: m/e 198 (M+, 27%), 142 (100), 141 (64), 115 (18), 57 (38).

3,3-Dimethyl-1-(1-naphthyl)-butane (Xb) was prepared as above in 24% yield from 2,2-dimethyl-4-(1-naphthyl)-butyraldehyde (IXb) and purified by distillation from $LiAlH_4$, B. P. 86-87°/0.08 torr. The product had a purity of > 99% by glpc (5% SE-30, 160°) and was stored in degassed ampoules until used.

Analysis. Calculated for $C_{16}H_{20}$: 90.51% C, 9.49% H

Found: 90.60% C, 9.41% H

NMR ($CDCl_3$): 1.01δ (s, 9H), 1.61δ (A_2B_2, 2H), 3.01δ (A_2B_2, 2H), 7.17-8.15δ (m, 7H). IR (liquid film): 3060, 3040, 1599, 1511, 1478, 1469, 1398, 1367, 800, 781. Mass spectrum: m/e 212 (M+, 44%), 155 (16), 142 (41), 141 (100), 115 (16), 57 (21).

4,4-Dimethyl-1-(1-naphthyl)-pentane (Xc) was prepared as above in 32% yield from 2,2-dimethyl-5-(1-naphthyl)-pentanaldehyde (IXc) and purified by distillation from $LiAlH_4$, B. P. 95-97°/0.08 torr. The product had a purity of > 99% by glpc (5% SE-30, 160°) and was stored in degassed ampoules until used.

Analysis. Calculated for $C_{17}H_{22}$: 90.20% C, 9.80% H

Found: 90.18% C, 9.82% H

NMR ($CDCl_3$): 0.86δ (s, 9H), 1.10-2.05δ (m, 4H), 2.85-3.2δ (m, 2H), 7.2-8.2δ (m, 7H). IR (liquid film): 3060, 3040, 1600, 1512, 1478, 1470, 1397, 1368, 800, 780. Mass spectrum: m/e 226 (M+, 44%), 142 (29), 141 (100), 115 (11), 57 (11).

2,2-Dimethyl-1-(2-naphthyl)-propane (XIIIa) was prepared as above in 28% yield from 2,2-dimethyl-3-(2-naphthyl)-propionaldehyde (XIIa). The product was purified by recrystallization (EtOH), two sublimations, chromatography on silica gel (30 gm/gm product, spectroquality benzene solvent), and sublimation (65-68°/0.05 torr); M.P. 70.0-70.5°. Glpc (5% SE-30, 140°) showed only one peak.

Analysis. Calculated for $C_{15}H_{18}$: 90.85% C, 9.15% H
Found: 90.82% C, 9.13% H

NMR ($CDCl_3$): 0.95δ (s, 9H), 2.66δ (s, 2H), 7.15-8.0δ (m, 7H). IR (crystalline film): 3041, 1631, 1599, 1508, 1472, 1465, 1366, 830, 760. Mass spectrum: m/e 198 (M+, 27%), 142 (100), 141 (63), 115 (19), 57 (63).

3,3-Dimethyl-1-(2-naphthyl)-butane (XIIIb) was prepared as above in 38% yield from 2,2-dimethyl-4-(2-naphthyl)-butyraldehyde (XIIb). The product was purified by two sublimations, chromatography on silica gel (30 gm/gm product, spectroquality benzene solvent), and sublimation (37°/0.05 torr); M.P. 42-43°. Glpc (5% SE-30, 130°) indicated a purity of > 99%.

Analysis. Calculated for $C_{16}H_{20}$: 90.51% C, 9.49% H
Found: 90.50% C, 9.50% H

NMR ($CDCl_3$): 1.00δ (s, 9H), 1.59δ (A_2B_2, 2H), 2.75δ (A_2B_2, 2H), 7.2-8.0δ (m,7H). IR (liquid film): 3050, 3015, 1634, 1603, 1510, 1478, 1470, 1369, 820, 742. Mass spectrum: m/e 212 (M+, 67%), 155 (23), 141 (100), 115 (16), 57 (24).

4,4-Dimethyl-1-(2-naphthyl)-pentane (XIIIc) was prepared as above in 13% yield from 2,2-dimethyl-5-(2-naphthyl)-pentanaldehyde (XIIc). The product was purified by two sublimations, chromatography on silica gel (30 gm/gm product, spectroquality benzene solvent), and sublimation (33°/0.05 torr); M.P. 37.5-38.0°. Glpc (5% SE-30, 165°) showed only one peak.

Analysis. Calculated for $C_{17}H_{22}$: 90.20% C, 9.80% H

Found: 90.08% C, 9.81% H

NMR ($CDCl_3$): 0.87δ (s, 9H), 1.05-2.0δ (m, 4H), 2.57-2.95δ (m, 2H), 7.2-8.0δ (m, 7H). IR (liquid film): 3055, 3020, 1634, 1602, 1510, 1479, 1470, 1368, 828, 748. Mass spectrum: m/e 226 (M+, 52%), 142 (70), 141 (100), 115 (15), 57 (24).

Synthesis of Naphthyl Dienes

(3-Methyl-2-butenyl)-triphenylphosphonium chloride. 113 gm (0.43 mole) of triphenyl phosphine and 45 gm (0.43 mole) of 3-methyl-1-chloro-2-butene (Aldrich, practical) in 500 ml of reagent acetonitrile were refluxed with stirring for 48 hrs, cooled, and the solvent removed by rotary evaporation. Ether was added and the granular white product collected by vacuum filtration, washed liberally with ether, and air dried. Yield 124.4 gm (78.8%).

3,3,7-Trimethyl-1-(1-naphthyl)-octa-4,6-diene (VI). To 8.15 gm (0.023 mole) of finely ground phosphonium salt suspended in 50 ml of reagent benzene was added 0.025 mole of phenyl lithium (Alfa Inorganics, in 70:30 benzene:ether, titrated for concentration of organometallic base before use) and the dark red solution refluxed 1 hr. After cooling to room temperature, a solution of 4.52 gm (0.02 mole) of 2,2-dimethyl-4-(1-naphthyl)-butyraldehyde (IXb) in 50 ml of reagent benzene was added dropwise over a period of 15 min. The solution was heated to reflux for 1 hr, cooled, and the benzene cautiously removed in vacuo. 150 ml of petroleum ether were added and the precipitated triphenylphosphine oxide removed by filtration. The petroleum ether was removed in vacuo and the residual oil distilled to give 5.46 gm (95%) of product, B. P. 150-164°/0.1-0.2 torr. The product consisted of a 2.2:1 cis:trans mixture of isomers (by NMR).

Analysis. Calculated for $C_{21}H_{26}$: 90.59% C, 9.41% H
Found: 90.48% C, 9.47% H

Trans-isomer (VI-T). NMR (CCl_4): 1.13δ (s, 6H), 1.75δ (unresolved d, 6H), 1.5-1.9δ (A_2B_2, 2H), 2.7-3.1δ (A_2B_2, 2H), 5.49δ (d, 1H, J_{trans} = 15.8 Hz), 5.71δ (d, 1H, J_x = 10.4 Hz), 6.16δ (d of d, 1H, J_{trans} = 15.8 Hz, J_x = 10.4 Hz), 7.05-8.0δ (m, 7H). IR (liquid film): 3040, 2960, 2920, 2870, 1595, 1508, 1460 (broad), 1395, 1385, 1375, 1363, 987, 965, 802, 783.

Cis-isomer (VI-C). NMR (CCl_4): 1.24δ (s, 6H), 1.6-2.0δ (2s, 6H), 1.6-2.0δ (A_2B_2, 2H), 2.8-3.2δ (A_2B_2, 2H), 5.27δ (d, 1H, J_{cis} ≈ 11.5 Hz), 6.08δ (d of d, 1H, J_{cis} ≈ 11.5 Hz, J_x ≈ 12 Hz), 6.33δ (d, 1H, J_x ≈ 12 Hz), 7.1-8.1δ (m, 7H). IR (liquid film): 3040, 3005, 2955, 2920, 2865, 1647, 1597, 1510, 1460 (broad), 1394, 1383, 1374, 1361, 791.

3,3,7-Trimethyl-1-(2-naphthyl)-octa-4,6-diene (VII). This diene was prepared according to the preceding procedure, adding the ylide to 2,2-dimethyl-4-(2-naphthyl)-butyraldehyde (XIIb, 4.52 g, 0.02 mole). The crude product was distilled to give 3.49 gm (61%) of product, B. P.

124-129 °/0.04 torr. The product consisted of a 3.0_5:1 cis:trans mixture of isomers (by NMR).

Analysis. Calculated for $C_{21}H_{26}$: 90.59% C, 9.41% H

Found: 90.57% C, 9.48% H

Trans-isomer (VII-T). NMR ($CDCl_3$): 1.12δ (s, 6H), 1.78δ (d, 6H, $J_{Me} = 1.25$ Hz), 1.5-1.9δ (A_2B_2, 2H), 2.55-2.95δ (A_2B_2, 2H), 5.62δ (d, 1H, $J_{trans} = 15.1$ Hz), 5.87δ (d of m, 1H, $J_x = 10.1$ Hz, $J_{Me} = 1.25$ Hz), 6.31δ (d of d, 1H, $J_{trans} = 15.1$ Hz, $J_x = 10.1$ Hz), 7.2-8.0δ (m, 7H). IR (liquid film): 3045, 2960, 2923, 2865, 1602, 1510, 1450 (broad), 1384, 1376, 1362, 990, 965, 853, 814, 742. Mass spectrum: m/e 278 (M+, 43%), 155 (13), 154 (16), 141 (51), 123 (100), 115 (14).

Cis-isomer (VII-C). NMR ($CDCl_3$): 1.24δ (s, 6H), 1.76δ (s, 3H), 1.82δ (s, 3H), 1.6-2.0δ (A_2B_2, 2H), 2.6-3.0δ (A_2B_2, 2H), 5.31δ (d, 1H, $J_{cis} \approx 11.5$ Hz), 6.15δ (d of d, 1H, $J_{cis} \approx 11.5$ Hz, $J_x \approx 12$ Hz), 6.41δ (d, 1H, $J_x \approx 12$ Hz), 7.2-8.0δ (m, 7H). IR (liquid film): 3055, 3010, 2960, 2923, 2860, 1645, 1600, 1509, 1460 (broad), 1382, 1373, 1362, 852, 815, 741. Mass spectrum: m/e 278 (M^+, 44%), 155 (14), 154 (16), 141 (56), 123 (100), 115 (16).

Separation and Stereochemistry of Naphthyl Dienes

The diene isomers could not be separated by glpc or regenerated from their mercuric acetate adducts.[31] Preparative scale separation of diene isomers was achieved by dry column chromatography[32] on 10% $AgNO_3$/alumina[22] (150 gm/0.2 gm of diene) deactivated to grade III. Columns were developed with p-xylene. The diene isomers were located by thin layer chromatography on $AgNO_3$ impregnated plates and each isomer washed from the appropriate segment of absorbent with ether. The ether was removed by rotary evaporation and the residual xylene by pumping overnight at room temperature and 0.05 torr. Each isomer was rechromatographed on grade I alumina (5 gm/100 mg of diene, spectroquality benzene solvent). The solvent was removed by pumping overnight at room temperature and 0.05 torr to give dienes of > 98% isomeric purity (NMR).

Attempts to assign stereochemistry by iodine equilibration[33] failed, resulting in destructive consumption of the dienes. Therefore, 2,6,6-trimethylhepta-2,4-diene was prepared in 15% yield by reaction of the above ylide with pivalaldehyde in ether. The product, B. P. 140°, was about 95% pure and consisted of a 2.1:1 cis:trans mixture of isomers. A sample of this diene was equilibrated to the trans isomer with iodine. The NMR spectrum (CCl_4) of the trans isomer showed resonances at 1.01δ (s, 9H), 1.72δ (s, 3H), 1.74δ (s, 3H), 5.57δ (d, 1H, J_{trans} = 15.8 Hz), 5.75δ (d, 1H, J = 10.4 Hz), 6.18δ (d of d, 1H, J_{trans} = 15.8 Hz, J = 10.4 Hz). The alkyl methyl resonance of the cis isomer occurred at 1.13δ (s, 9H). Comparison of vinyl hydrogen patterns and coupling constants with those of the naphthyl dienes was used to assign stereochemistry to the latter. Subsequent iodine equilibration of the corresponding phenyl dienes by Dr. E. C. Sanford[34] provided further confirmation of the assignments.

Irradiations

Direct irradiations of VI and VII were carried out as follows: 0.5 gm of the synthetic diene mixture was diluted to 5.0 ml with solvent (benzene or cyclohexane). The solution was transferred to a 13 × 100 mm test tube, degassed by three freeze-pump-thaw cycles, and the tube sealed. Tubes were irradiated for one (benzene solution) or two (cyclohexane solution) weeks in an Ultraviolet Products PCQ-X1 lamp with 305 nm phosphor. Product ratios were determined by integration of the NMR spectrum of the photolysate.

Sensitized irradiations of VI and VII were carried out as follows: 0.5 gm of synthetic diene mixture and 0.018 gm of benzophenone were diluted to 5.0 ml with benzene and the solutions degassed as above. Irradiation was for one week in an UV Products PXQ-X1 lamp with 360 nm phosphor. Product ratios were determined by NMR.

Irradiations were also followed by NMR. Benzene solutions of the diene (approximately 0.2 M) were placed in Pyrex NMR tubes and the tubes sealed with serum caps. In sensitized irradiations, sensitizer concentrations were: benzophenone, 0.01 M; 1-acetonaphthone, 0.01 M; benzil, 0.02 M, chrysene, saturated. After outgassing with nitrogen, the tubes were irradiated at 305 nm (direct) or 360 nm (sensitized), monitoring periodically by NMR.

Isolation of Photoproduct A (XVIII)

2.0 ml of the benzene solution of VI which has been subjected to direct irradiation at 305 nm for 1 week were evaporated to dryness. The oily residue was subjected to dry column chromatography on silver nitrate-alumina (p-xylene) as described for separation of the diene isomers. About 20 mg of impure material (an oil) were obtained by this method. The NMR (220 MHz), IR, and UV data for this compound are given in the Results and Discussion. Pyrolysis of this material at 190° in an evacuated flask gave a complex mixture of products in which the isomers of VI were minor constituents.

Preparation and Isolation of Photoproduct B (XVI)

1.54 gm of synthetic VI and 0.12 gm of m-methoxyacetophenone were diluted to 15.0 ml with benzene. The solution was deoxygenated by bubbling with N_2 and irradiated for one month at 360 nm. The conversion was about 40-50% (NMR). The irradiated solution was chromatographed on grade I alumina (30 gm, reagent benzene solvent, 30 ml fractions) to remove the sensitizer. The second chromatography fraction was evaporated to dryness in vacuo at room temperature to give 1.06 gm of oil. This material was taken up in 3 ml of petroleum ether, cooled, and centrifuged to remove a small amount of white precipitate (polymer?). Additional petroleum ether was added to give 6 ml of solution. 3.0 ml of this solution were streaked on a Brinkman preparative TLC plate (2 mm thick silica gel layer) which had been impregnated with silver nitrate (the plate was impregnated by development with 10% methanolic silver nitrate followed by air-drying overnight). The plate was developed with p-xylene and allowed to air dry overnight. The appropriate portion of the layer was scraped from the plate and extracted with dry ether. The ether was removed by rotary evaporation and the residual p-xylene by pumping at 0.05 torr for 6 hrs. The remaining oil was rechromatographed on grade I alumina (5 gm, spectroquality benzene solvent.) Removal of the benzene (0.05 torr for 5 hrs) gave 0.16 gm of XVI as a colorless oil.

Analysis. Calculated for $C_{21}H_{26}$: 90.59% C, 9.41% H

Found: 90.58% C, 9.25% H

The spectral data are given in the Results and Discussion.

Pyrolysis of XVI

26.6 mg of XVI were degassed and sealed in a constricted Pyrex test tube. The tube was immersed in an oil bath maintained at 207-8° for four hours. The NMR and IR spectra and TLC behavior of the product were identical to those of VI-T and no other products could be detected. Later experiments indicated that the pyrolysis is complete after two hours. Control experiments with the synthetic diene mixture showed that the diene did not isomerize under the pyrolysis conditions.

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PART II

FLUORESCENCE OF AROMATIC HYDROCARBON-TERTIARY AMINE BICHROMOPHORES

INTRODUCTION

The quenching of the fluorescence of aromatic hydrocarbons by tertiary amines has been the subject of much study in this[1] and other[2,3,4,5,6] laboratories. The quenching rate exhibits quite large substituent effects. Substituents which decrease the ionization potential of the amine or increase the electron affinity of the aromatic greatly accelerate the quenching rate. An increase in the dielectric constant of the solvent also results in increased quenching efficiency. These correlations imply that the quenching process involves appreciable charge-transfer from the amine to the excited aromatic. In non-polar solvents, a broad, structureless emission to the red of the fluorescence of the aromatic accompanies the quenching process. This emission, attributed to fluorescence of the exciplex, shifts further to the red as the dielectric constant of the solvent is increased, implying that the emitting species is quite polar. As the exciplex fluorescence shifts to the red, it decreases in intensity. In polar solvents such as acetonitrile, this emission is not observed.

Most of the mechanistic controversy has revolved around the observation that the decrease in intensity of the exciplex emission with increasing dielectric constant of the solvent is not accompanied by a compensating decrease in the exciplex fluorescence lifetime. Weller and co-workers[4] postulated the existence of an intervening state which either underwent dissociation into separated radical ions or relaxed to the emissive exciplex [eq. (1)]. The intensity-lifetime discrepancy was attributed to the solvent-dependent partitioning of this intervening state.

$$\begin{tikzcd}
Ar^{*(1)} + Q \arrow[r, shift left, "k_1"] & (Ar \cdots Q)^{*(1)} \arrow[l, shift left, "k_{-1}"] \arrow[dl, "k_{ion}"] \arrow[dr, "k_2"] & & \\
Ar^{\dot{-}} + Q^{\dot{+}} & & (ArQ)^{*(1)} \arrow[ll, "k'_{ion}"'] \arrow[r, "k'_f", "-h\nu'"'] \arrow[r, bend right, "k'_d"'] & Ar + Q
\end{tikzcd} \qquad (1)$$

The increased yield of ions in polar solvents[4,7] was consistent with this formulation of the mechanism. Mataga,[5] however, proposed that the discrepancy was due to a change in the electronic structure of the exciplex in polar solvents. The highly polar exciplex might interact quite strongly with polar solvents, resulting in a decrease in the exciplex radiative rate constant. Little change in the lifetime would be expected if the non-radiative decay rates were relatively unaffected.

An interest in this controversy and in the use of bichromophoric systems to study bimolecular phenomena led to this study of the solvent dependence of the fluorescence of some aromatic hydrocarbon-tertiary amine bichromophores. Since, by appropriate choice of the amine chromophore, it is possible to design systems in which the fluorescence of the aromatic is essentially completely quenched, the effects of binding equilibria on the exciplex decay should be negligible. Observed differences should therefore be more readily attributable to differences in orientation of the chromophores. In order to restrict the number of configurations available to the component chromophores, bichromophoric systems in which the aromatic hydrocarbon and the amine were incorporated into a ring system (I-IV) were chosen for study. Three acyclic systems (V-VII) of diverse types were also studied in some detail.

RESULTS AND DISCUSSION

Synthetic

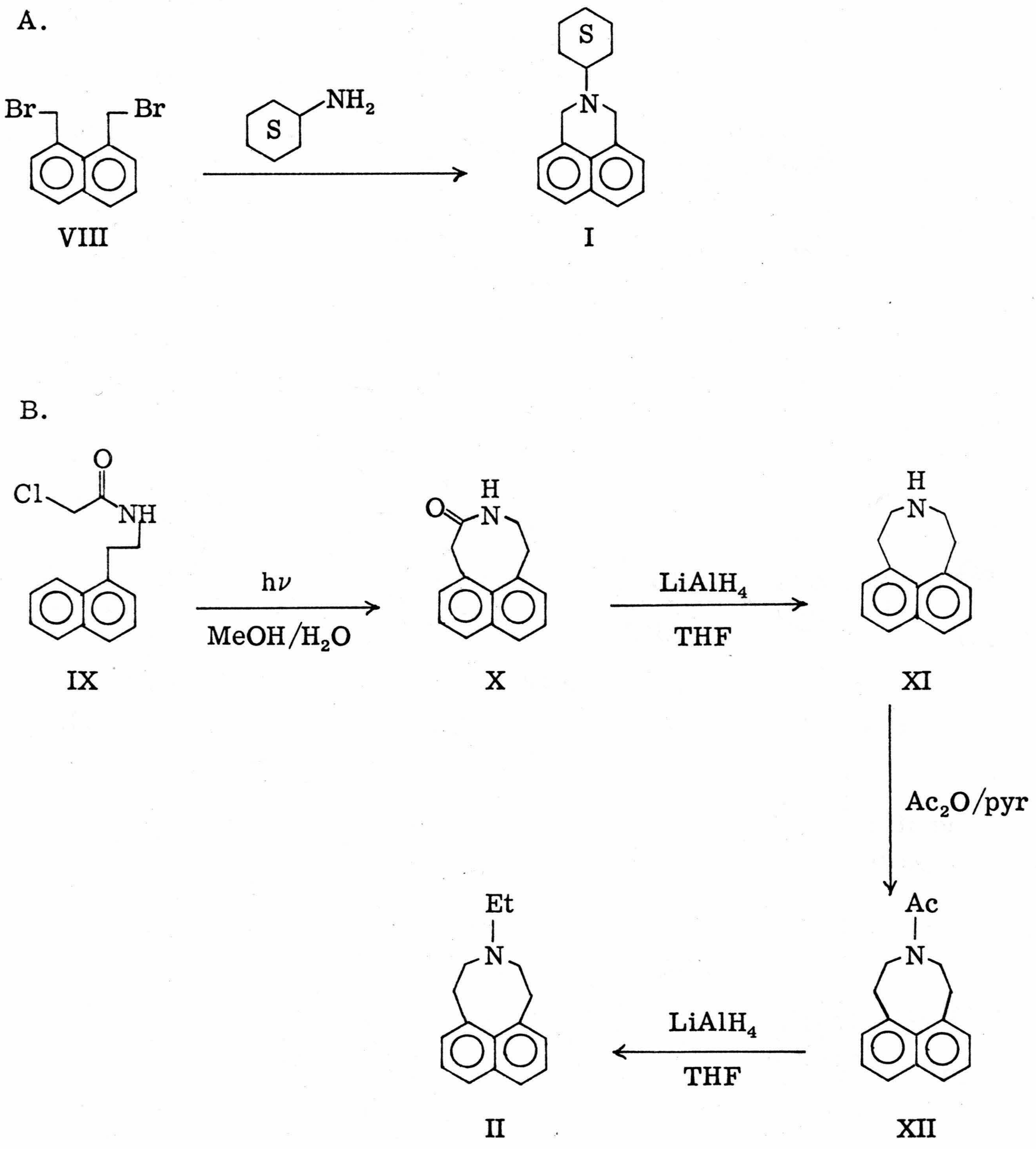
Any study of this type requires substantial synthetic endeavor. A number of synthetic approaches either failed or gave products which could not be sufficiently purified for the fluorescence experiments. The synthetic routes used in the preparation of the cyclic naphthyl-amine bichromophores are outlined in Scheme 1. Compound I[8] and derivatives of III[9] were known and their preparation straightforward. The purification of III, however, required additional effort. Although the N-carbomethoxy analog of IV was known,[10] the procedure was not adaptable to the preparation of IV. The unexceptional approach in Scheme 1 proved adequate for the preparation of this compound. At the beginning of this study, derivatives of II were unknown. Attempts to enter this ring system by the procedure for IV failed at the stage of the dibromide VIII. Attempts at displacement of bromide by cyanide in this compound were invariably unsuccessful. Reports of the novel cyclization of IX to X,[11,12] however, provided a simple method for generating this ring system. Since no simple method for the introduction of an N-cyclohexyl group could be conceived, the N-ethyl derivative II was prepared *via* the known[11] amide XII.

The syntheses of the acyclic systems V-VII were straightforward (Scheme 2) and similar to other procedures in the literature.[13]

Absorption Spectra

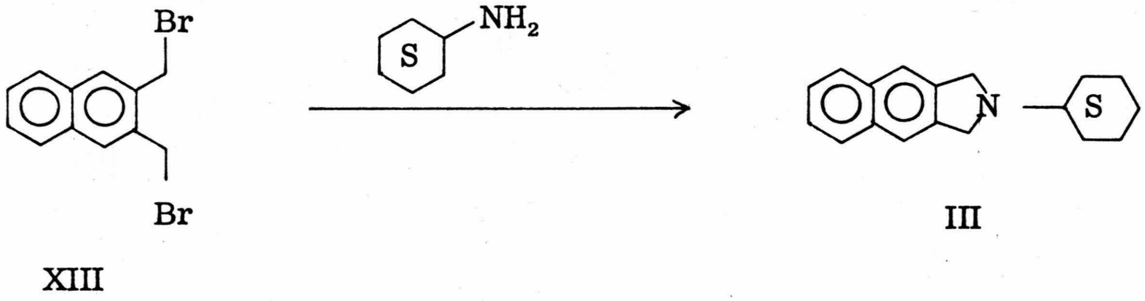
The absorption spectra of the naphthyl-amine bichromophores I-V are consistent with expectations based upon the nature and degree of

Scheme 1. Syntheses of Bichromophores I-IV.

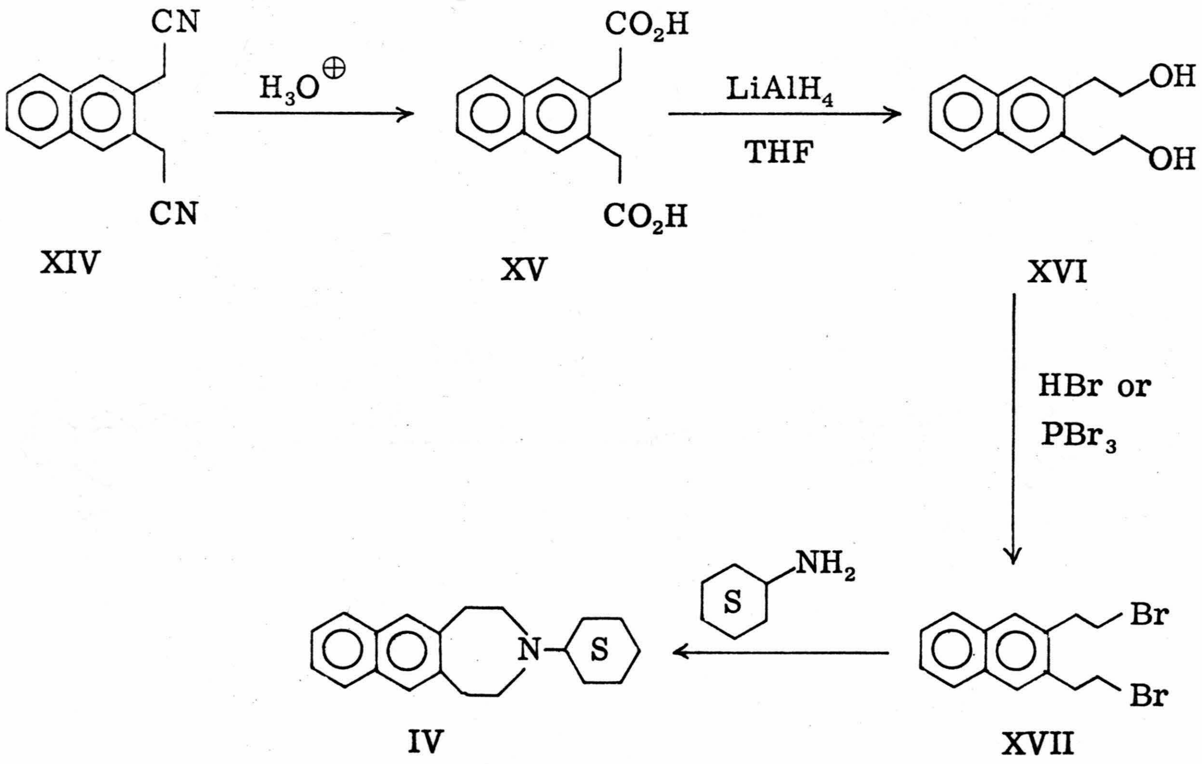


Scheme 1. (Continued)

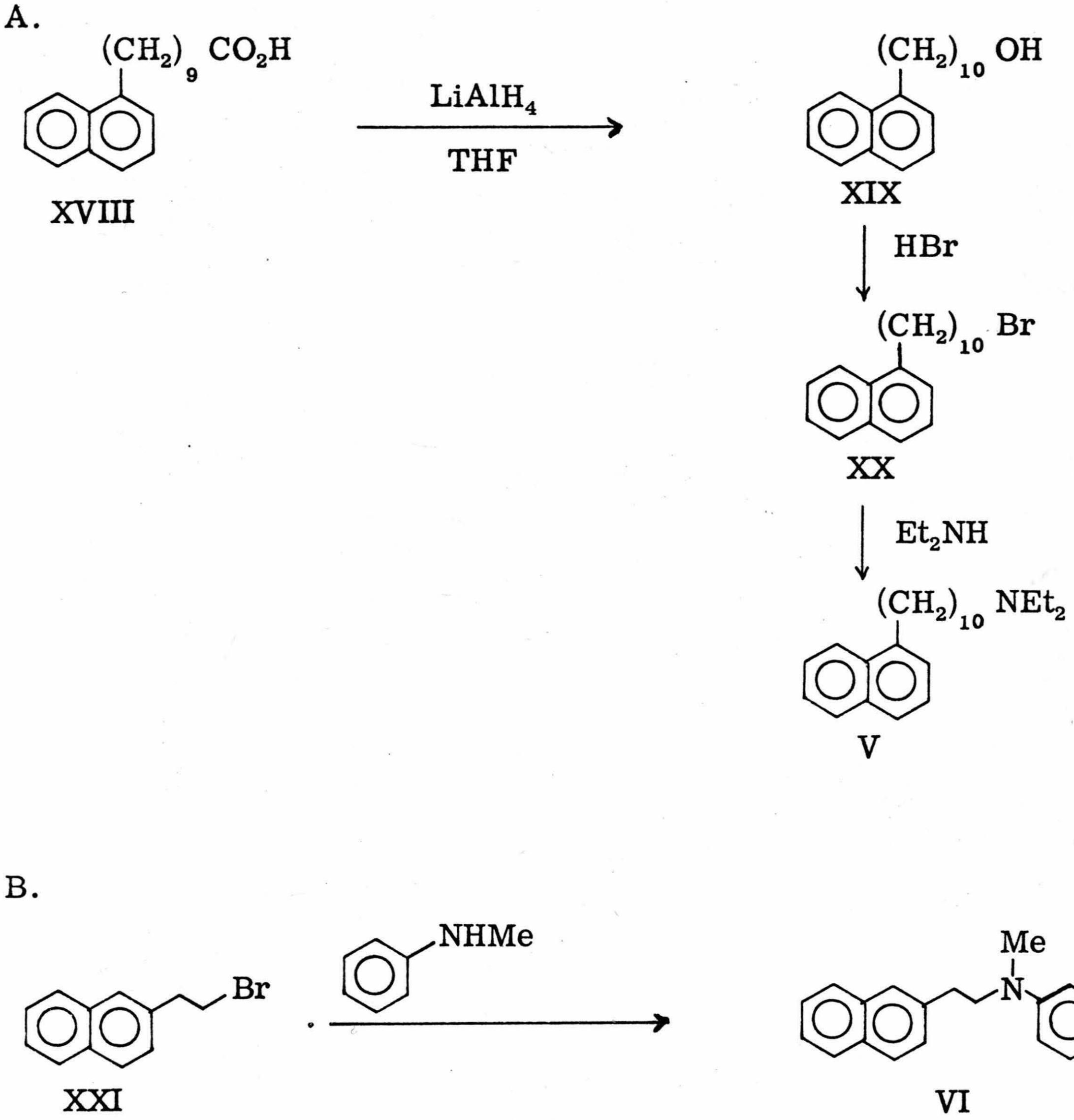
C.



D.

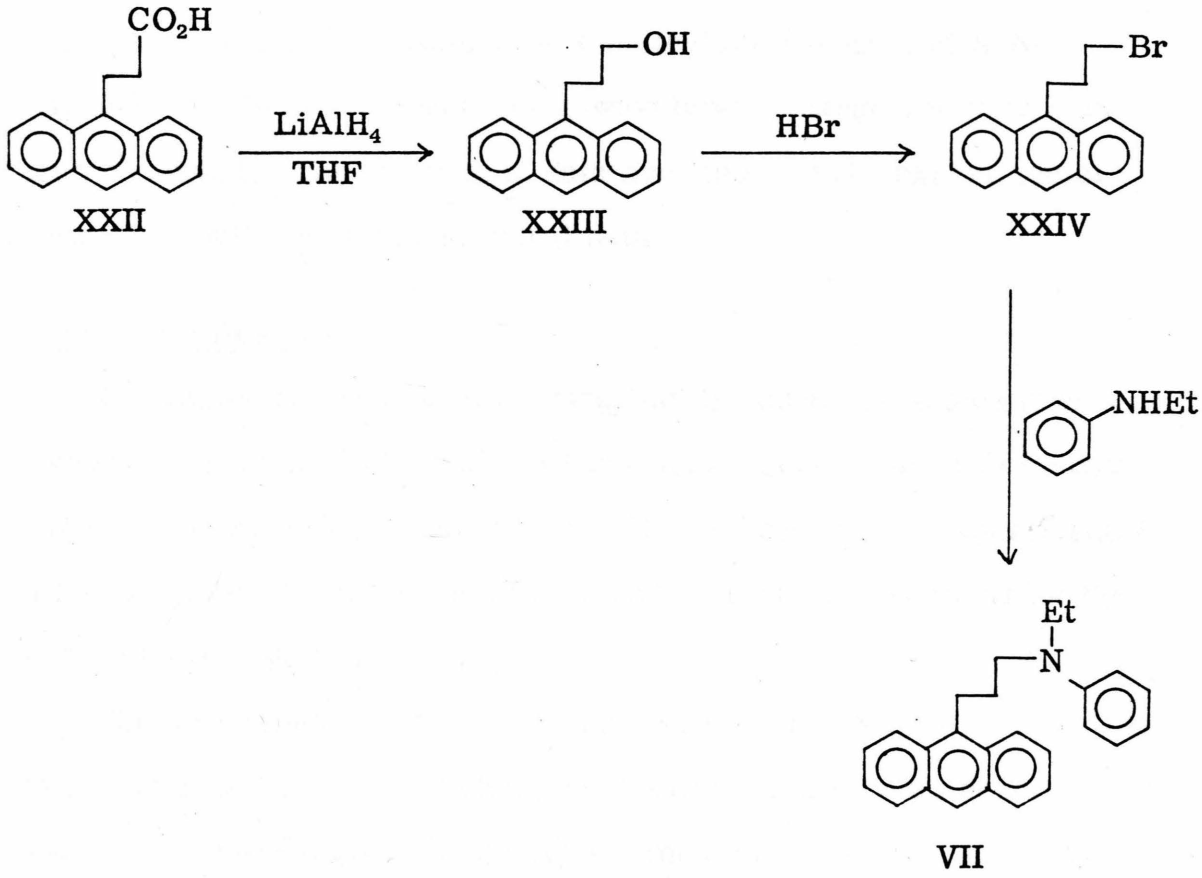


Scheme 2. Syntheses of Bichromophores V-VII.



Scheme 2. (Continued)

C.



substitution of the naphthalene nucleus.[14] The absorption spectrum of VI is similar to but not identical to the sum of spectra of 2-ethylnaphthalene and N,N-diethylaniline. The maxima of the anthracene moiety of VII are red shifted about 2 nm and are slightly enhanced relative to an equimolar mixture of 9-methylanthracene and N,N-diethylaniline. In no case were long-wavelength charge transfer transitions observed. The absorption data are listed in the experimental section along with the other spectral data.

Fluorescence Results

Corrected fluorescence spectra for the amine bichromophores are shown in Figures 1-9. Table I lists fluorescence and lifetime data for some reference compounds. Table II summarizes the experimental results for the cyclic bichromophores and Tables III-V summarize the results for the acyclic systems.

Dipole moments of the "exciplex" state were calculated from the solvent shifts of the long-wavelength emission maximum as described by Weller.[15] These values, along with assumed values of the interaction radii ($\underset{\sim}{a}$), are listed in Table VI.

Recent Advances in the Understanding of Amine Quenching

Our initial fluorescence results were quite puzzling within the context of our preliminary expectations. Since separation into radical ions represents a quite endothermic process in the cyclic bichromophores, the persistence of the intensity-lifetime discrepancy was not anticipated on the basis of the simple Weller formulation [eq. (1)]. The alternative Mataga formulation was unattractive because the discrepancy was quite

Figure 1

Fluorescence of I in Various Solvents

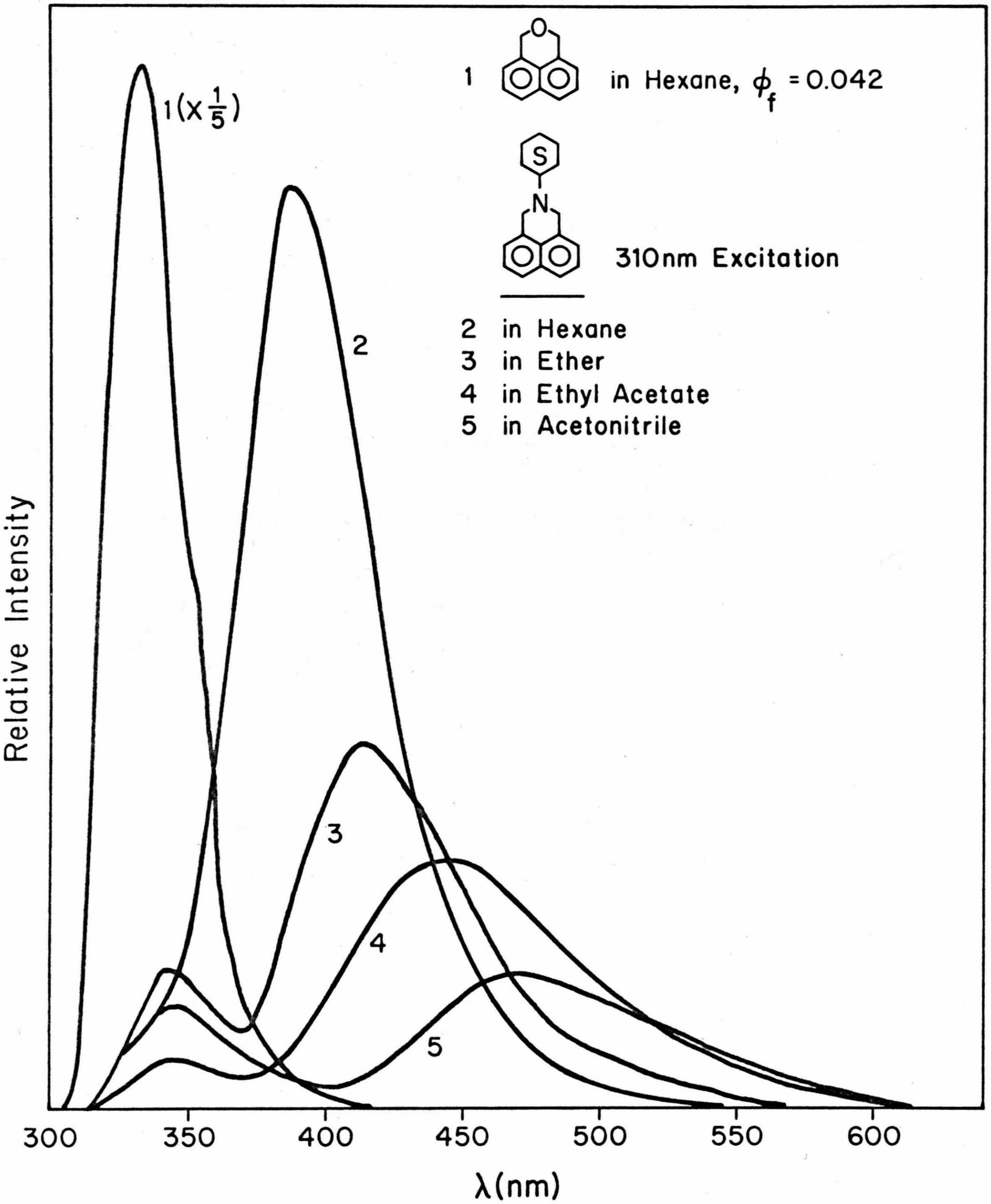

1(X 1/5)
1
in Hexane, ϕ_f = 0.042
S
N
310nm Excitation
2 in Hexane
3 in Ether
4 in Ethyl Acetate
5 in Acetonitrile
2
3
4
5
Relative Intensity
300
350
400
450
500
550
600
λ(nm)

Figure 2

Fluorescence of II in Various Solvents

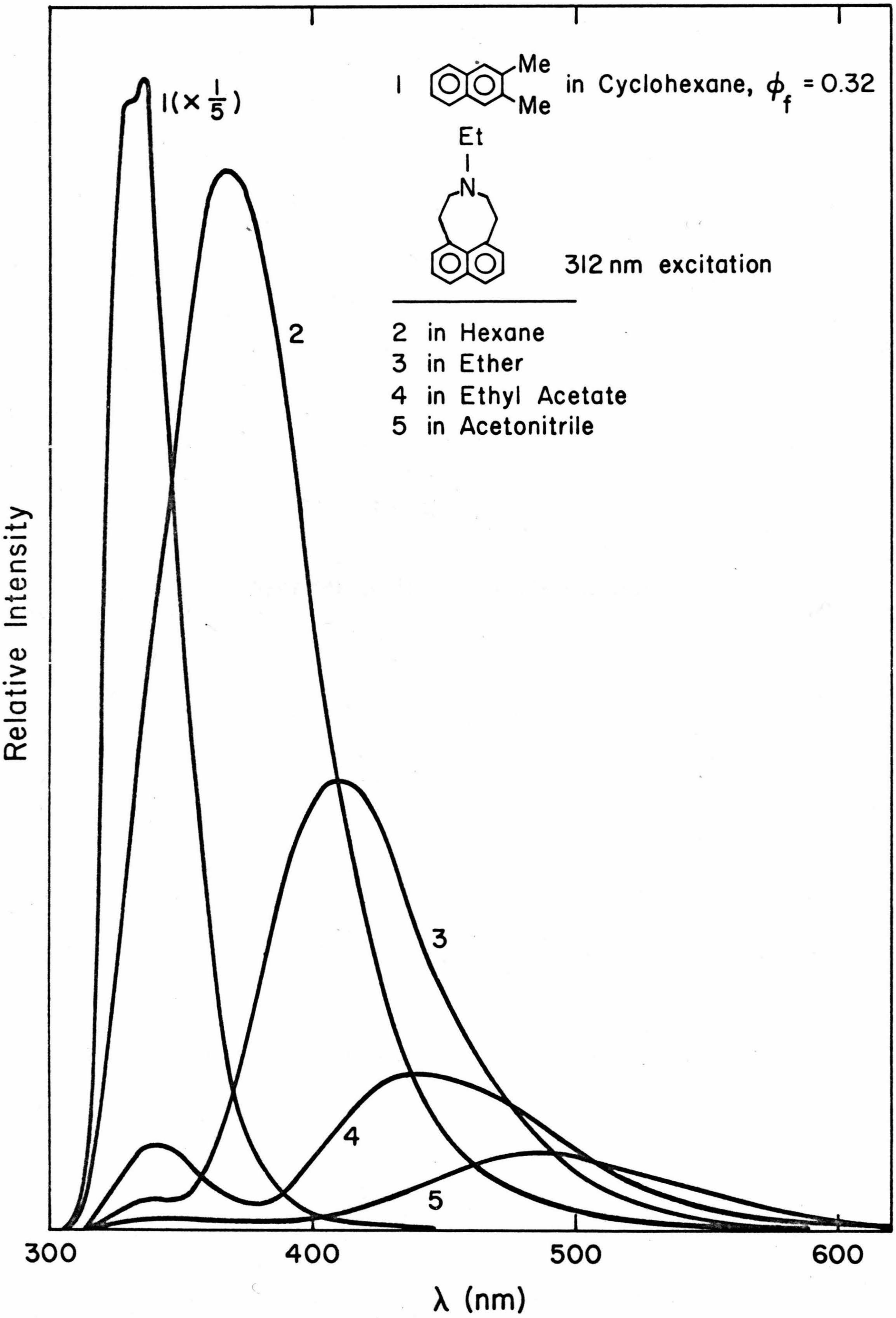

1(× 1/5)
2
3
4
5
1
Me
Me
in Cyclohexane, ϕ_f = 0.32
Et
N
312 nm excitation
2 in Hexane
3 in Ether
4 in Ethyl Acetate
5 in Acetonitrile
Relative Intensity
300
400
500
600
λ (nm)

Figure 3

Fluorescence of III in Various Solvents

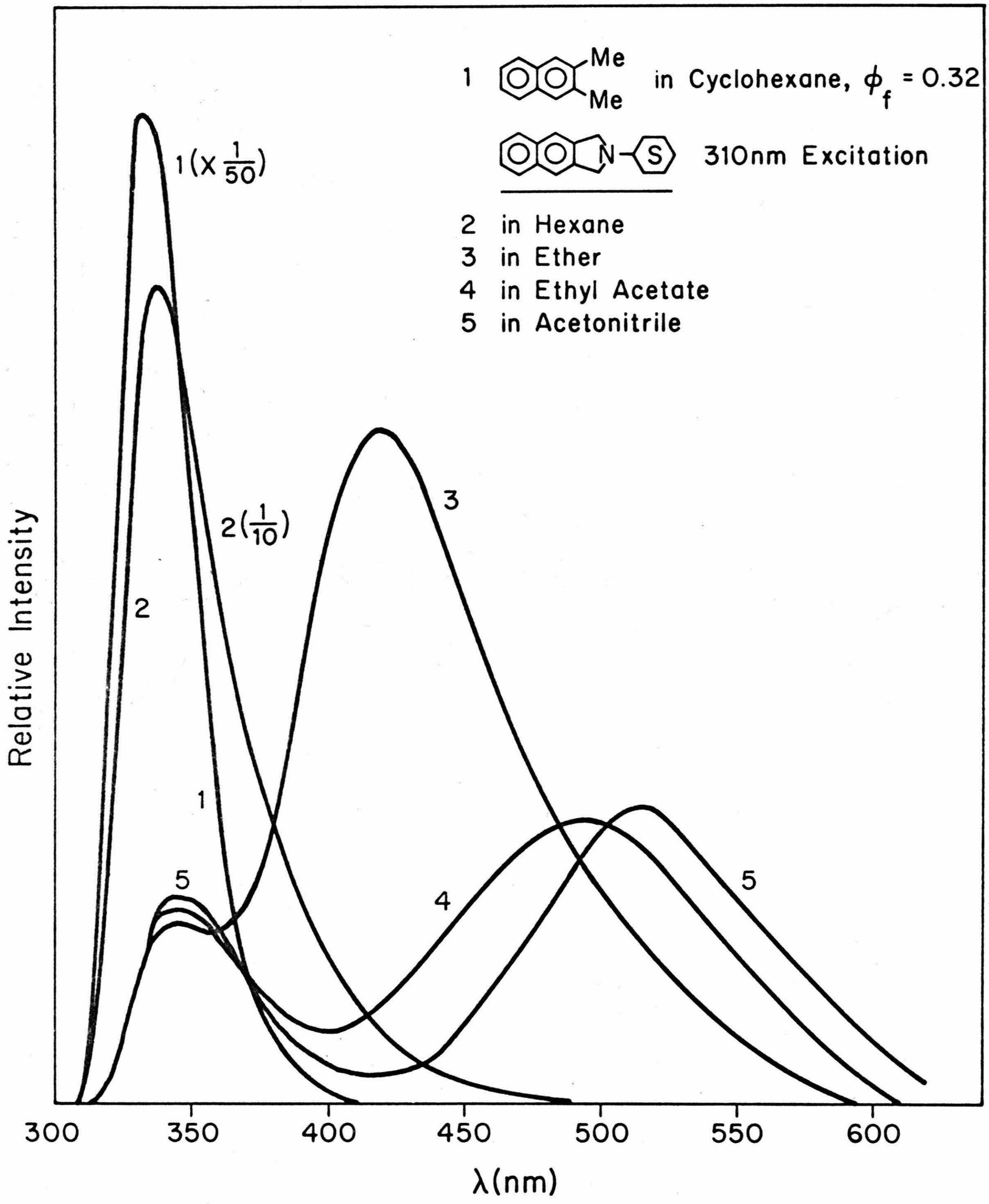

1
Me
Me
in Cyclohexane, ϕ_f = 0.32
N
S
310nm Excitation
2 in Hexane
3 in Ether
4 in Ethyl Acetate
5 in Acetonitrile
1(X $\frac{1}{50}$)
2($\frac{1}{10}$)
2
1
5
3
4
5
Relative Intensity
300
350
400
450
500
550
600
λ(nm)

Figure 4

Fluorescence of IV in Various Solvents

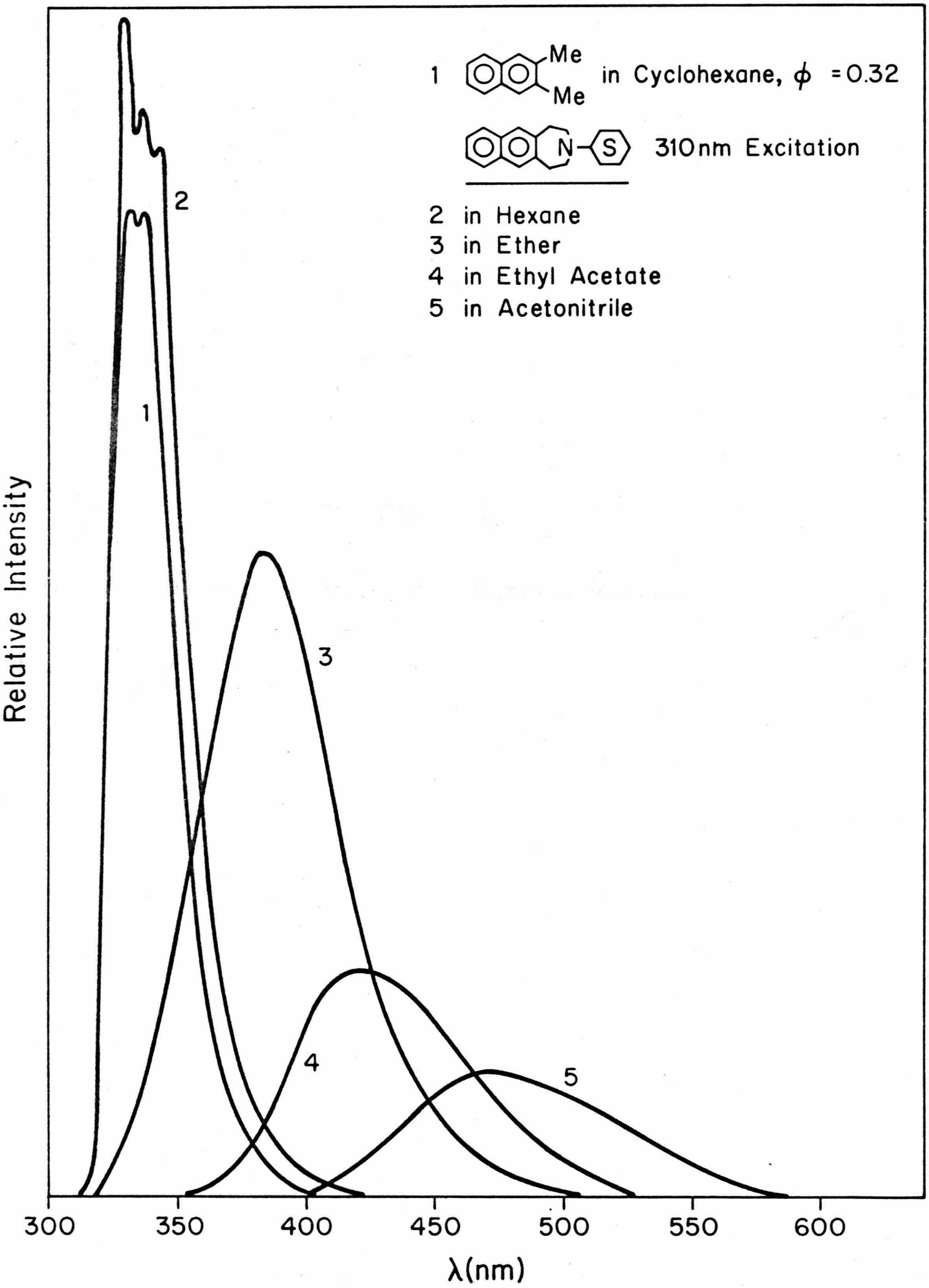

1
Me
Me
in Cyclohexane, φ = 0.32
N
S
310nm Excitation
2 in Hexane
3 in Ether
4 in Ethyl Acetate
5 in Acetonitrile
Relative Intensity
300
350
400
450
500
550
600
λ(nm)
1
2
3
4
5

Figure 5

Fluorescence of V in Various Solvents

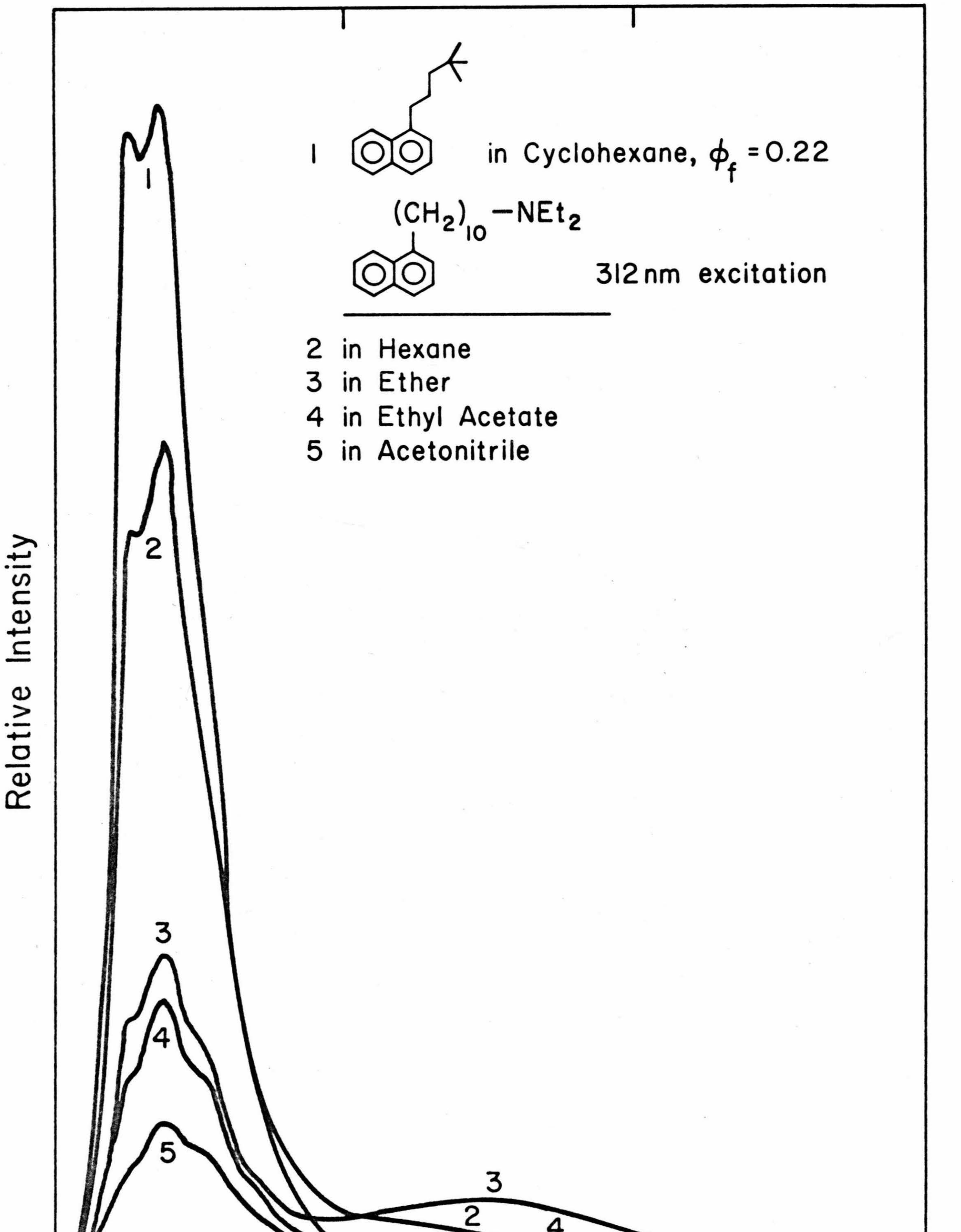

1
in Cyclohexane, $\phi_f = 0.22$
$(CH_2)_{10}-NEt_2$
312 nm excitation
2 in Hexane
3 in Ether
4 in Ethyl Acetate
5 in Acetonitrile
1
2
3
4
5
3
2
4
Relative Intensity
300
400
500
600
λ (nm)

Figure 6

Fluorescence of VI in Various Solvents

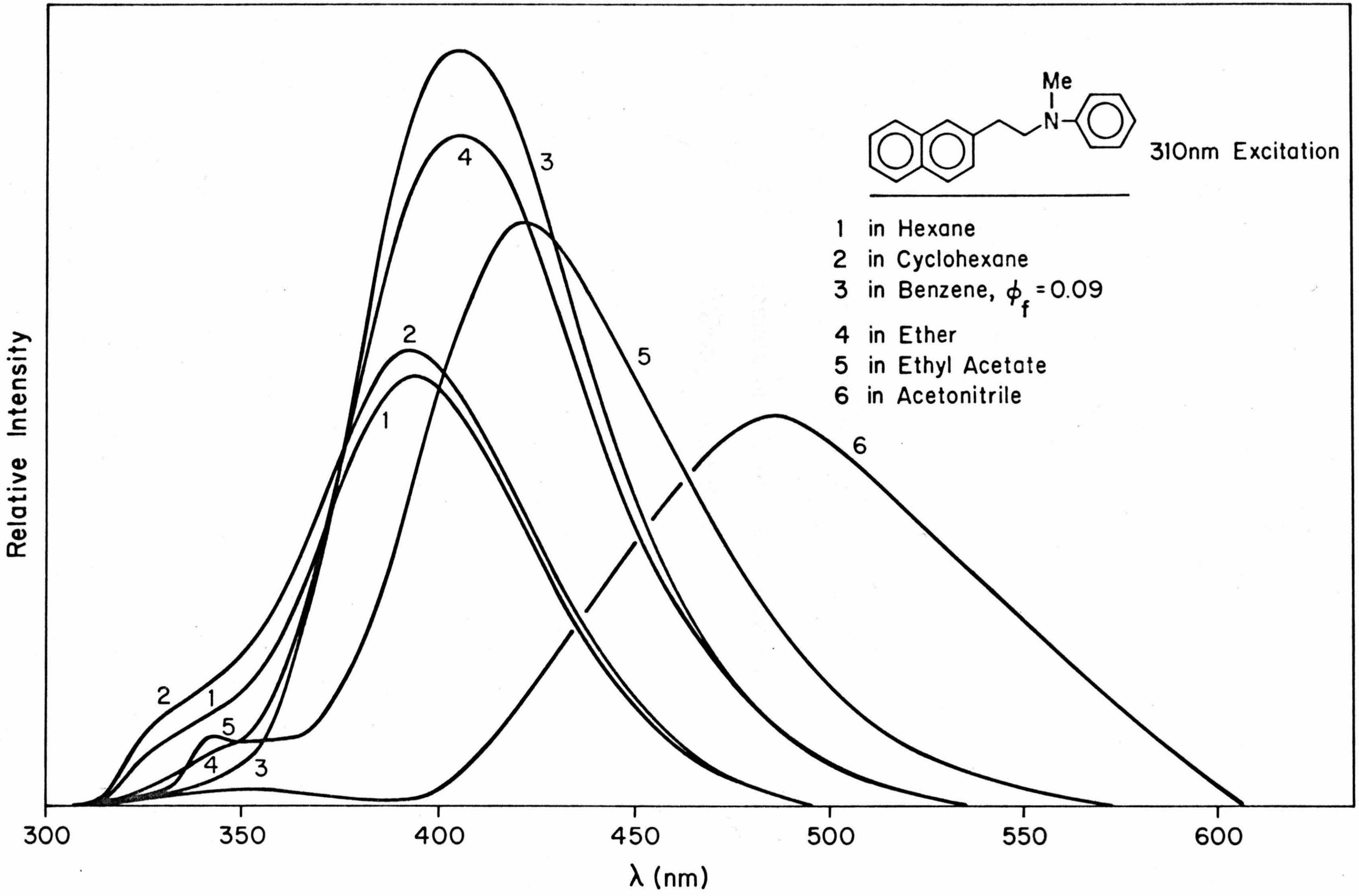

Me
N
310nm Excitation
1 in Hexane
2 in Cyclohexane
3 in Benzene, $\phi_f = 0.09$
4 in Ether
5 in Ethyl Acetate
6 in Acetonitrile
1
2
3
4
5
6
Relative Intensity
300
350
400
450
500
550
600
λ (nm)

Figure 7

Fluorescence of VII in Non-polar and Weakly Polar Solvents

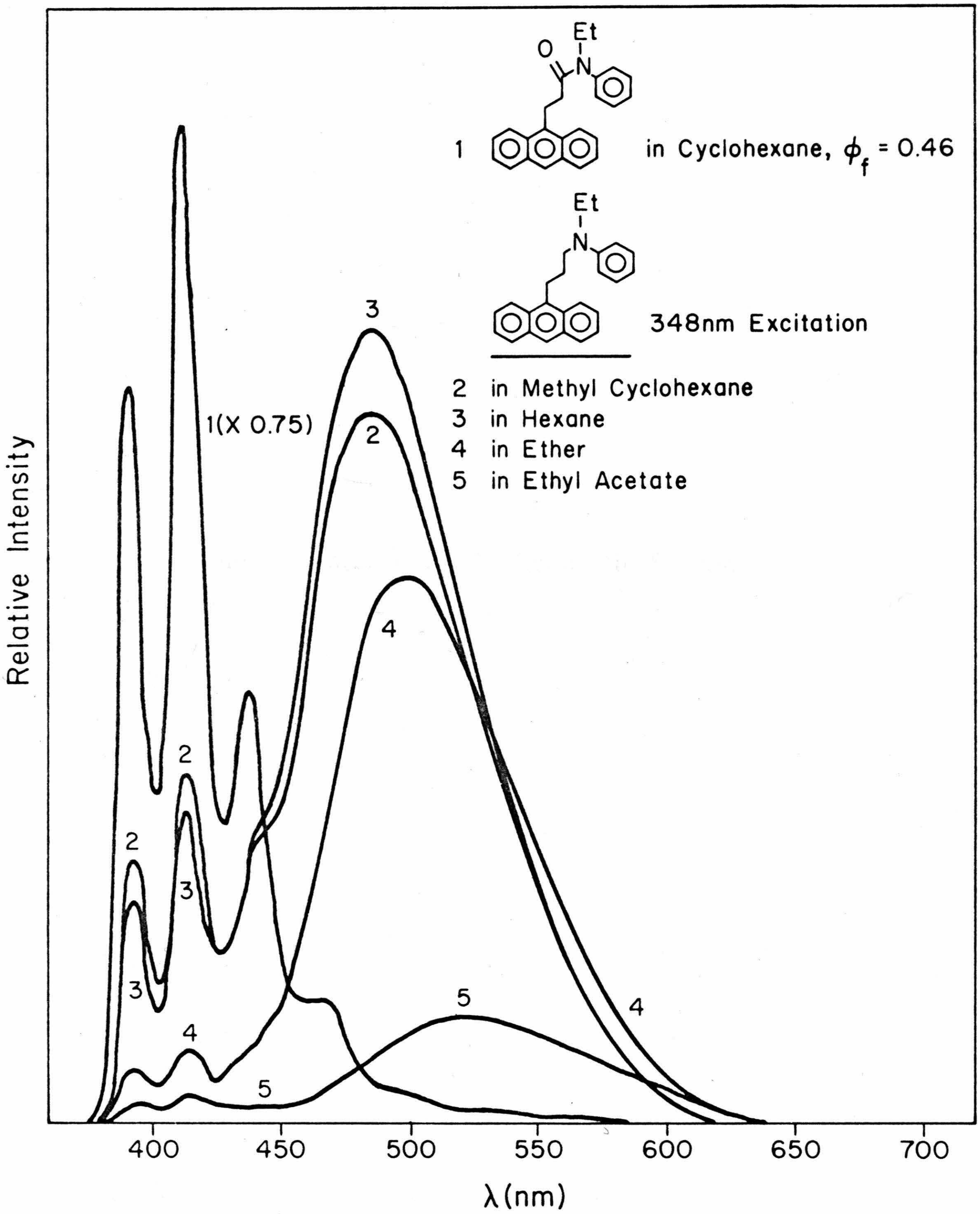

Et
O
N
1
in Cyclohexane, ϕ_f = 0.46
Et
N
348nm Excitation
2 in Methyl Cyclohexane
3 in Hexane
4 in Ether
5 in Ethyl Acetate
1(X 0.75)
Relative Intensity
λ (nm)
400
450
500
550
600
650
700
2
3
4
5

Figure 8

'Fluorescence of VII in Aromatic Solvents

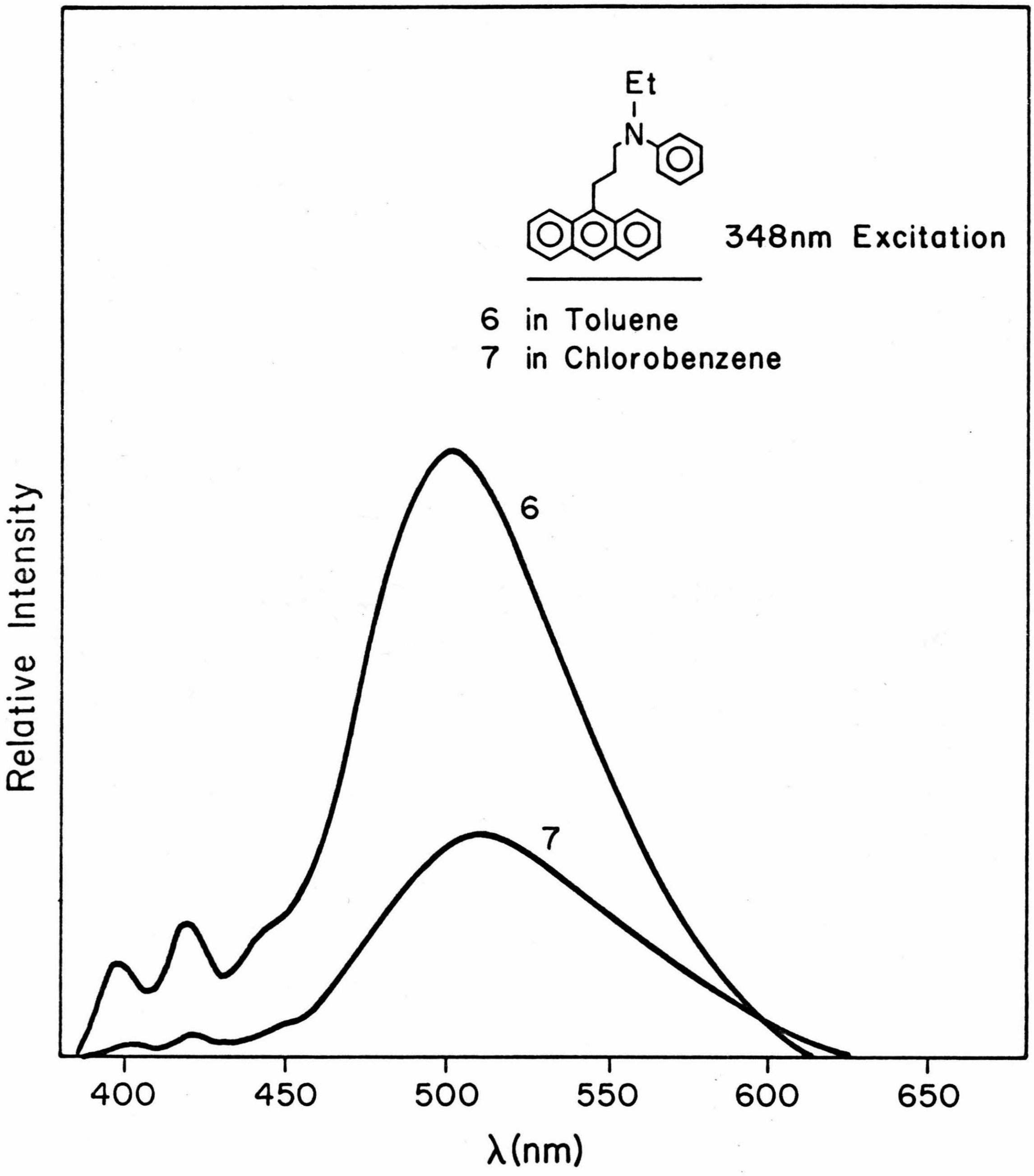

Et
N
348nm Excitation
6 in Toluene
7 in Chlorobenzene
6
7
Relative Intensity
400
450
500
550
600
650
λ(nm)

Figure 9

Fluorescence of VII in Polar Solvents

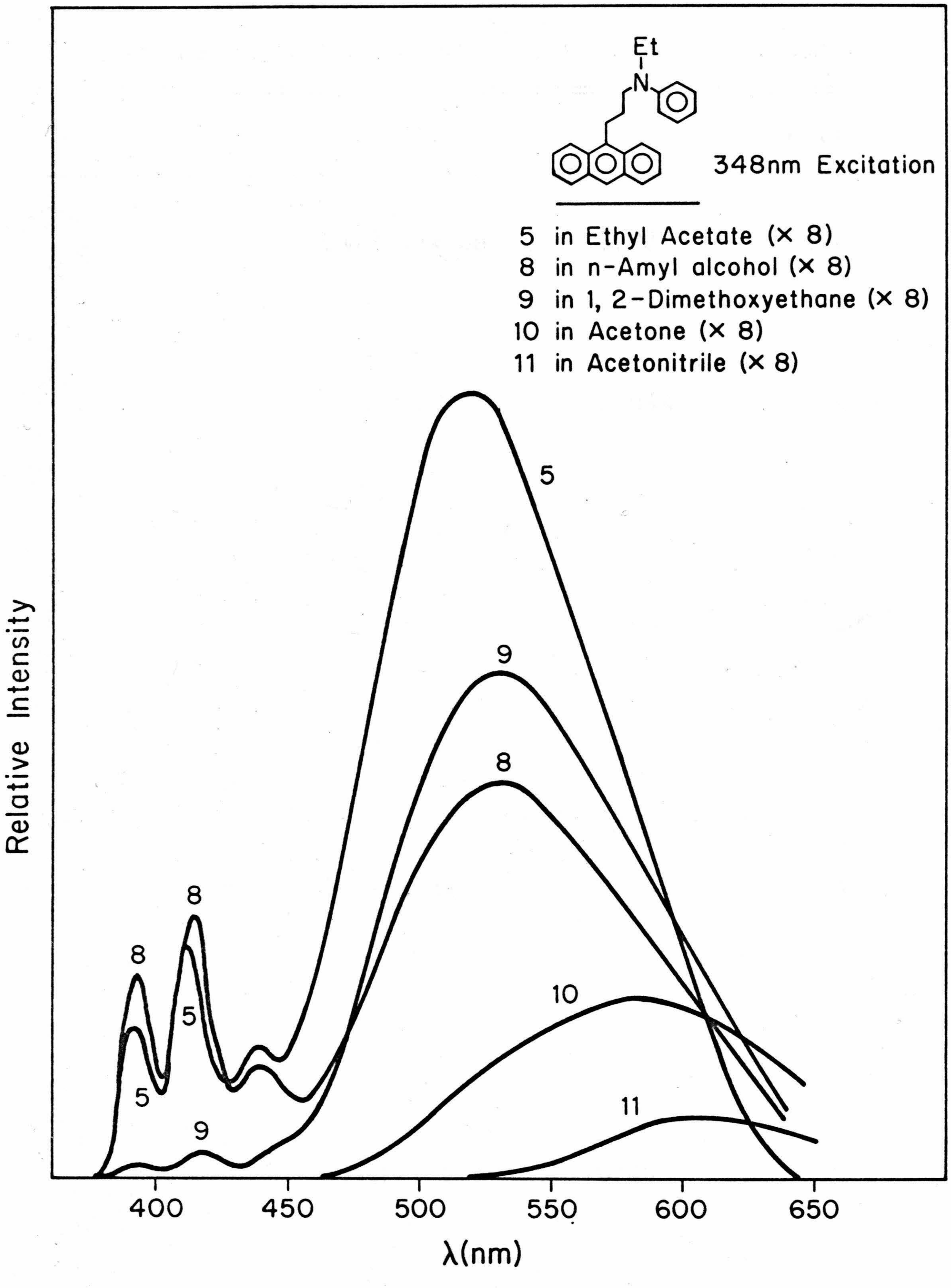

Et
N
348nm Excitation
5 in Ethyl Acetate (× 8)
8 in n-Amyl alcohol (× 8)
9 in 1, 2-Dimethoxyethane (× 8)
10 in Acetone (× 8)
11 in Acetonitrile (× 8)
5
9
8
8
8
5
5
9
10
11
Relative Intensity
400
450
500
550
600
650
λ(nm)

Table I

Fluorescence and lifetime data for some reference compounds.

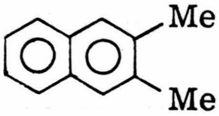
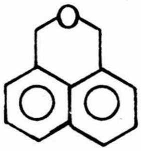
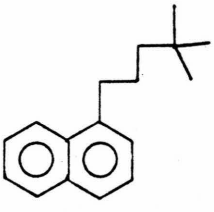
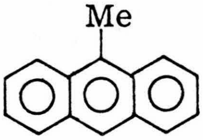
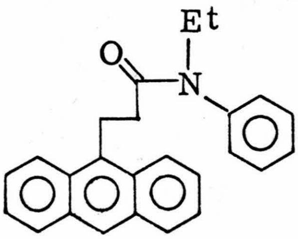
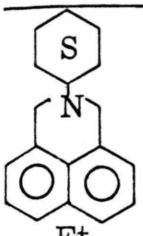
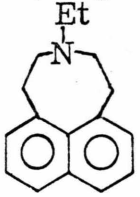
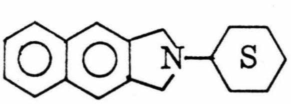
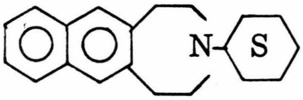
Compound	Solvent	ϕ_f	τ_f (± 1 nsec)
	Cyclohexane	0.32	78
 XXV	Hexane	0.042	10.5
 XXVI	Cyclohexane	0.22	56
	Cyclohexane	0.29	4.5
 XXVII	Cyclohexane	0.46	7.2

Table II

Fluorescence and lifetime data for the cyclic naphthalene-teritary aliphatic amine bichromophores I-IV.

Compound	Solvent	ϕ_f^{Ar}[a]	ϕ_f^{CT}[a]	τ_f^{Ar}[b] (nsec)	τ_f^{CT}[b] (nsec)	λ_{max}^{CT}[c] (nm)
	Hexane	5×10^{-4}	0.013	--	4	387
	Ether	10^{-3}	0.006	--	<4	414
	Ethyl Acetate	4×10^{-4}	0.006	--	<4	445
	1,2-Dimethoxyethane	10^{-3}	0.006	--	<4	447
	Acetonitrile	10^{-3}	0.003	--	<4	470
	Hexane	--	0.12	--	27.5	368
	Ether	1.4×10^{-4}	0.052	--	20	411
	Ethyl Acetate	5×10^{-3}	0.025	--	13	443
	1,2-Dimethoxyethane	5×10^{-4}	0.024	--	12	448
	Acetonitrile	5×10^{-4}	0.013	--	6.5	486
	Hexane	0.073		25	--	--
	Ether	2×10^{-3}	0.011	--	14	419
	Ethyl Acetate	2×10^{-3}	0.006	--	12	492
	1,2-Dimethoxyethane	2×10^{-3}	0.006	--	12	485
	Acetonitrile	2×10^{-3}	0.005	--	12	515
	Hexane	0.40	--	52	--	--
	Ether	10^{-2}	0.42	--	19	384
	Ethyl Acetate	--	0.18	--	12	422
	1,2-Dimethoxyethane	--	0.16	--	12	426
	Acetonitrile	--	0.11	--	17	473

[a] ± 20%. Superscript "Ar" refers to the hydrocarbon-like emission; superscript "CT" refers to the exciplex-like long-wavelength emission.

[b] ± 1 ns.

[c] ± 3 nm. Maximum from plots of quanta/sec/unit wavelength interval *versus* wavelength.

Table III[a]

Fluorescence and lifetime data for V.

Solvent	ϕ_f^{Ar}	ϕ_f^{CT}	τ_f^{Ar} (nsec)	τ_f^{CT} (nsec)	λ_{max}^{CT} (nm)	$(\phi_f^{CT})^o$[b]
Hexane	0.14	0.020	44	30	416	0.055
Ether	0.054	0.030	17.5	27	444	0.040
Ethyl Acetate	0.047	0.015	13	20	482	0.020
1,2-Dimethoxyethane	0.044	0.017	12	21	486	0.020
Acetonitrile	0.024	~0	--	--	--	~0

[a] See footnotes of Table II for explanation of symbols.

[b] Emission quantum yield of the exciplex state corrected for the amount of singlet quenching relative to XXVI. Calculated assuming that $(\phi_f^{CT})^o = \phi_f^{CT}[\phi_f^{XXVI}/(\phi_f^{XXVI} - \phi_f^{Ar})]$.

Table IV[a]

Fluorescence and lifetime data for VI.

Solvent	ϕ_f^{CT}	τ_f^{CT}	λ_{max}^{CT} (nm)	$\bar{\nu}_{max}^{CT}$ [b] ($cm^{-1} \times 10^{-3}$)
Cyclohexane	0.049	16.2	393	25.3
Hexane	0.041	15.5	395	25.2
Benzene	0.090	24.8	405	24.4
Ether	0.065	24	406	24.3
Ethyl Acetate	0.066	23.1	422	23.5
Acetonitrile	0.055	29	485	20.4

[a] See footnotes of Table II for explanation of symbols.

[b] ± 0.1 kk. Maximum from plots of quanta/sec/unit wavenumber interval *versus* wavenumber.

Table V[a]

Fluorescence and lifetime data for VII.

Solvent	ϕ_f^{Ar}	ϕ_f^{CT}	τ_f^{Ar} (nsec)	τ_f^{CT} (nsec)	λ_{max}^{CT}	$\bar{\nu}_{max}^{CT}$ ($cm^{-1} \times 10^{-3}$)
Hexane	0.10	0.59	3.5	70	487	20.3
Methylcyclohexane	0.12	0.57	4	68	486	20.3
Toluene	0.04_1	0.41	--	55	501	19.8
Ether	0.02_4	0.41	--	70	499	19.8
Chlorobenzene	0.009_2	0.18	--	30	510	19.4
Ethyl Acetate	0.009	0.091	--	23.5	519	19.0
1,2-Dimethoxyethane	0.001	0.06_2	--	18.7	530	18.7
<u>n</u>-Amyl alcohol	0.01_2	0.05_2	--	15.7	531	18.7
Acetone	<0.001	0.02_4	--	14.4	585	16.8
Acetonitrile	<0.001	0.006	--	6.0	610	15.9

[a] For explanation of symbols, see footnotes of Table IV.

Table VI

Calculated dipole moments of the aromatic hydrocarbon-tertiary amine bichromophores.

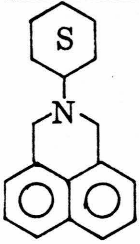
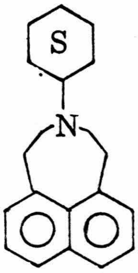
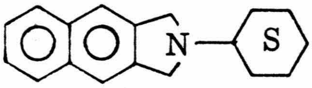
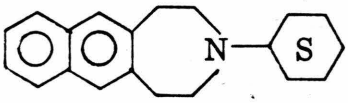
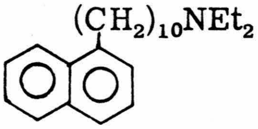
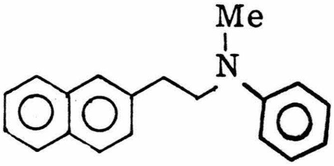
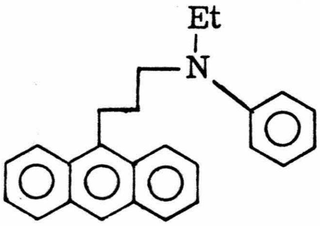
Compound		a (Å)^a	μ (Debye)^b	$\mu^{o\,c}$
		3.5	7.2	16.8
		3.5	8.6	16.8
		4.5	15	21.6
	(XXX)	4.5	15	21.6
	(XXIX)	5+	>18	>24
		4.5	11	21.6
		4.5	8.2	21.6
		5	8.7	24

Table VI (Continued)

[a] Assumed interaction radius. For the cyclic systems I-IV, this represents the distance from the nitrogen to the center of the 9,10-bond of the naphthalene nucleus, as measured from models. For the acyclic systems V-VII, generally employed literature values[2,15,20] were used.

[b] Dipole moments calculated from solvent-dependent shifts of the maximum of the exciplex-like fluorescence.[15]

[c] Dipole moment calculated assuming complete electron transfer.

large even over a small range of solvent polarity (e.g., from ether to 1,2-dimethoxyethane).

Nanosecond time-resolved laser flash studies reported during the course of this investigation have led to a much more detailed understanding of the amine quenching and have resolved much of the mechanistic controversy. Direct evidence for the presence of an intervening state (Weller model) was obtained by Mataga.[16] The rise time of the photocurrent in the pyrene-N,N-dimethylaniline-pyridine system was found to be much shorter than the decay time of the fluorescent exciplex, indicating that ionic dissociation occurred primarily from an intervening state. A small component of the photocurrent with rise time similar to the exciplex fluorescence lifetime was, however, observed at longer times. Similar time dependences for triplet formation were observed by Ottolenghi[17] in the anthracene-N,N-diethylaniline system. Fast intersystem crossing from the intervening state was shown to be a major decay route in both polar and non-polar solvents.

These groups have proposed that the initial interaction between the amine and the excited aromatic hydrocarbon produces a non-relaxed or "Franck-Condon" exciplex. Fast intersystem crossing and ionic dissociation processes compete with the relaxation of this species to the fluorescent exciplex. The intensity-lifetime discrepancy may be attributed to the solvent dependence of these rates. Slow intersystem crossing and ionic dissociation processes which occur from the relaxed fluorescent exciplex are responsible for variations of the exciplex fluorescence lifetime with solvent. This mechanistic formulation is outlined in eq. (2). Kinetic expressions for the exciplex fluorescence

$$\begin{tikzcd}
\mathrm{Ar}^{*(1)} + \mathrm{Q} \arrow[r, "k_1"] & {[(\mathrm{Ar}\ \mathrm{Q})^{*(1)}]_{\text{F-C}}} \arrow[dl, "k_{ion}"'] \arrow[dr, "k_{isc}"] \arrow[dd, squiggly, "k_{rlxn}"] & \\
\mathrm{Ar}^{-} + \mathrm{Q}^{+} & & \mathrm{Ar}^{*(3)} + \mathrm{Q} \\
 & {[(\mathrm{ArQ})^{*(1)}]_{\text{Equil}}} \arrow[ul, "k'_{ion}"] \arrow[ur, "k'_{isc}"'] \arrow[d, "k'_f"] & \\
 & \mathrm{Ar} + \mathrm{Q} + h\nu' &
\end{tikzcd} \tag{2}$$

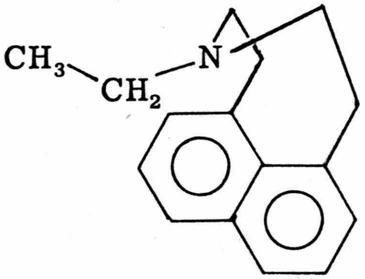
quantum yield and lifetime are given in eqs. (3) and (4), respectively.

$$\phi_f^{CT} = \frac{k_{rlxn}}{k_{rlxn} + k_{ion} + k_{isc}} \; \frac{k'_f}{k'_f + k'_{isc} + k'_{ion}} = \phi_{rlxn}(\phi_f^{CT})_0 \tag{3}$$

$$\tau_f^{CT} = \frac{1}{k'_f + k'_{isc} + k'_{ion}} \tag{4}$$

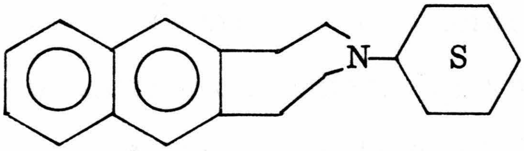
The Naphthalene-Tertiary Aliphatic Amine Bichromophores (I-V)

Any bichromophoric study should make use of reasonable estimates regarding the relative configurations available to the component chromophores. For I and III, conformational mobility should be quite restricted and the variety of accessible configurations rather small. NMR data imply that XXVIII is probably an important conformation for II. The broad, non-first-order character of the methylene hydrogen resonances of the ring are suggestive of slow ring inversion on the NMR time scale. The upfield position of the methyl hydrogen resonance (0.76δ)

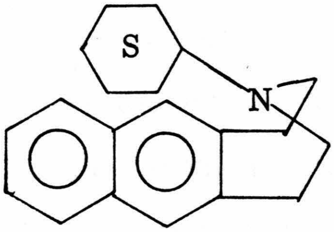


XXVIII

suggests that the ethyl group is positioned over the aromatic ring system. An analogous conformation has been postulated for XII by Foltz[11] on the basis of similar considerations. Conformational studies of cycloheptene and benzocycloheptene derivatives[18] implicate the chair (XXIX) and boat (XXX) forms as potentially significant conformers of IV. The



XXIX



XXX

energy barrier separating these two forms is unknown, but is probably somewhat less than 10 kcal/mole. The high polarity of the exciplex might be expected to favor the boat conformer in order to minimize Coulombic energies. The decamethylene chain of V is expected to be conformationally flexible, permitting a range of configurations similar to that encountered in the bimolecular system.

The acyclic bichromophore V indeed exhibits fluorescence behavior typical of the bimolecular system.[1,2] The increase of the quenching rate with increasing solvent dielectric constant is exemplified by a decrease in the yield and lifetime of the naphthalene emission. The intensity-lifetime discrepancy is similar to that observed in the bimolecular systems. The yield of emission from the "exciplex" state, corrected for the amount of singlet quenching relative to XXVI, decreases rapidly with increasing solvent polarity and is zero in acetonitrile. Only modest changes in the lifetime of this emission are observed, however. Finally, the emission maxima (and calculated dipole moment of 11 D) are quite similar to those observed for the naphthalene-triethylamine[1,2] and 1-methylnaphthalene-triethylamine[2] exciplexes. Thus, the decamethylene chain seems to operate primarily as an entropic factor, allowing V to act as a bimolecular mimic in its fluorescence properties.

The cyclic bichromophores I-IV exhibit rather different fluorescence behavior. In general, only a small amount of naphthalene-like fluorescence remains. This implies that the initial interaction between the aromatic and the amine has little or no configurational requirements. Since III exhibits moderate and IV intense naphthalene-like emission in hexane, it is tempting to postulate a minimum interaction radius of about 4.5-5 Å in hexane. Extrapolation of the dipole moment plot for IV also predicts that formation of the fluorescent exciplex-like state should be slightly endothermic in hexane. A more rigorous study would be required to substantiate this postulate.

Having seen that formation of the intervening state is essentially complete (except for III and IV in hexane as noted above), we can attribute differences in fluorescence properties of I-IV to differences in the relaxation modes of the intervening state and to variations in the relaxed emitting state. In both the bimolecular and bichromophoric cases, all the interactive configurations we know about are very polar. This includes both the intervening non-relaxed precursors to ions and triplets (which might well be the same) and the relaxed, delocalized emitting state. In the bimolecular case, dissociation into ions represents a significant decay route in polar solvents. The presence of exciplex-like emission in I-IV, even in acetonitrile, implies that in the bichromophores the emissive state is of energy lower than or comparable to the state corresponding to separated ion radicals. The persistence of the intensity-lifetime discrepancy (although greatly attenuated relative to the bimolecular case) bespeaks the presence of other slightly solvent dependent processes competitive with relaxation of the initial interactive species.

The most probable candidate for a process competitive with relaxation is intersystem crossing. Its importance in the bimolecular system has been demonstrated in the laser flash studies.[17] In addition, triplet counting experiments on the naphthalene-triethylamine exciplex in benzene indicate a triplet yield of about 0.85.[19] No definitive data exist for the role of processes which lead directly to ground states; however, the sum of approximate yields of ions, triplets, and fluorescence in general approaches unity, indicating that other non-radiative routes are of much lesser importance in the bimolecular systems for which these yields have been measured.

The emitting exciplex-like states of II-IV exhibit similar fluorescence lifetimes in the same solvents. This may indicate that these emissive states, although of very different relative configuration, decay via similar routes with similar rates. In the absence of any estimate of the inherent emission efficiency, $(\phi_f^{CT})_0$, of these states, it is unknown whether the lifetime is dominated by radiative or by non-radiative decay rates. The fluorescence lifetimes of I are much shorter than those of II-IV, indicating that I may represent a configuration in which non-radiative decay is accelerated. The lifetimes of I-IV are rather different from those observed for V (the lifetimes of V being comparable to those observed for bimolecular analogs). In V (and bimolecular analogs), the amine presumably occupies a central position above the naphthalene π-plane (to minimize Coulombic forces). In I-IV, the amine is restricted to a peripheral position. It is interesting that the lifetime data are not incompatible with a model in which displacement of the amine from a central to a peripheral position changes the decay rates of the emitting state rather uniformly over a variety of positions on the periphery.

The most apparent feature of the fluorescence results is that the "exciplex" fluorescence yields of II are substantially larger than those of I and the yields of IV are much larger than those of III. Accepting the premise that the inherent emission properties of the exciplex-like states are not drastically different, there appears to be a large effect of configuration on the efficiency of relaxation of the "Franck-Condon" species to the emissive species. This effect may be related to the degree of conformational flexibility inherent in the ring systems. In I and III, the non-relaxed precursor to triplets and the relaxed emissive state are required by the ring system to be of the same or very similar geometry. II and IV have a much larger range of conformations available to them and, in particular, have readily accessible conformations which elevate the amine above the plane of the naphthalene π-system, permitting much better overlap of the amine orbital with the naphthalene π-system.

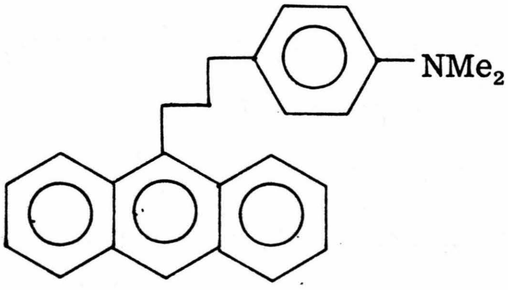
The Anthracene-Aniline and Naphthalene-Aniline Systems

The naphthalene-aniline bichromophore VI is somewhat unique among the systems studied in that it exhibits little or no intensity-lifetime discrepancy. Only in acetonitrile is any significant deviation apparent. The reasons for this unique behavior are not compellingly obvious. No data exist for the effects of solvent on the bimolecular system; therefore, this feature might be related to inherent properties of this hydrocarbon-amine pair. It may also be related in some way to the conformational properties of the methylene chain. No matter what the reason, both the efficiency of relaxation to the emissive state and the radiative rate constant of this state are relatively unaffected by solvent. Solvent-specific variations in the emission lifetime are very nicely compensated for by changes in the emission yield. These features make this chromophore pair an attractive one for further study, especially when incorporated into ring systems similar to those of I-IV.

In contrast, the anthracene-aniline bichromophore VII exhibits a substantial intensity-lifetime discrepancy. This discrepancy is, however, significantly smaller than that observed in the bimolecular system, for which extensive data exist.[4,15] The observed solvent dependence for VII is not unlike that which would be expected if ionic dissociation pathways were eliminated in the bimolecular system. As discussed in the previous section, ion formation should be of negligible importance and the most significant non-radiative decay path competitive with relaxation to the emissive species is probably intersystem crossing.

One of the most interesting features of the fluorescence of VII is that the lifetime of the residual anthracene-like emission is not much shorter (if any) than that of 9-methylanthracene. Because of the weakness of the anthracene-like emission in the other solvents, this measurement was feasible only for the hydrocarbon solvents hexane and methylcyclohexane. If the reasonable association with static quenching phenomena is made, then it is apparent that there must be configurations of VII which are non-interacting and which persist for a time longer than the anthracene fluorescence lifetime (4-5 nsec). Simple considerations of internal rotational barriers and rates would predict much more rapid conformational equilibration. The rates of getting out of non-interacting configurations and into interactive ones are probably governed by some kind of solvent relaxation times.

Shortly after the completion of experimental studies on VII, Mataga[20] reported fluorescence results for a similar anthracene-aniline bichromophore XXXI. In addition to an intensity-lifetime discrepancy similar to that of VII, the residual anthracene-like fluorescence of XXXI has a lifetime comparable to that of 9-methylanthracene



XXXI

throughout the solvent range. The aniline chromophores of VII and XXXI have quite different donor properties; however, bimolecular studies have been carried out for both systems. By comparison of bichromophoric data with bimolecular data, it is possible to gain some insight into the preferred bimolecular configuration. The fluorescence lifetimes and maxima and the calculated dipole moment for the exciplex-like fluorescence of XXXI were shown to agree quite well with those for the anthracene-N, N-dimethyl-p-toluidine and 9-methylanthracene-N, N-dimethyl-p-toluidine exciplexes.[20] Agreement of similar data for VII with that of the anthracene-N, N-diethylaniline exciplex[4,15] is much less satisfactory. In addition to further emphasizing the fact that a number of interactive configurations can produce emissive species, these comparisons suggest that the interaction of anilines with excited anthracenes may occur preferentially through the aniline ring (XXXI) rather than directly with the aniline nitrogen (VII).

Further Studies

The measurement of triplet yields for these and other amine bichromophores constitutes an important extension of this work. Intersystem crossing data would allow quantitative evaluation of the nature and importance of the various non-radiative decay pathways utilized in the bichromophores.

The nature of the factors which give rise to non-interactive configurations in IV (hexane), VII and XXXI should be subjected to further scrutiny. In this context, the apparent unimportance of such conformations in V is of significance. The potential existence of non-interactive conformations is a factor which should be considered in studies of bichromophoric systems, particularly those in which the component chromophores possess short emission lifetimes.

EXPERIMENTAL

Apparatus and general techniques are described in Part I. Washing the Pyrex test tubes with 6 M NH_4OH before drying had no observable effect on the fluorescence spectra. Appropriate filters were used to isolate the emission from scattered excitation in the fluorescence lifetime measurements.

Solvents and Materials

Cyclohexane (Matheson Coleman and Bell (MCB) Spectroquality), hexane (Phillips pure grade), and methylcyclohexane (MCB) were purified by the method of Murray and Keller[21] and distilled (center cut). Toluene (MCB Spectroquality), benzene (MCB Spectroquality), ethyl acetate (Aldrich Spectrophotometric grade), and acetone (MCB Spectroquality) were used as received. Ether (Mallinckrodt anhydrous) and 1,2-dimethoxyethane (MCB) were distilled from $LiAlH_4$ under N_2 immediately prior to use. Chlorobenzene (MCB) was distilled from anhydrous K_2CO_3. Acetonitrile (MCB Spectroquality) was distilled from P_2O_5 and then from anhydrous K_2CO_3. n-Amyl alcohol had been previously purified by J. W. Meyer. Triethyl amine was purified by distillation from $LiAlH_4$.

Quantum Yield Standards

2,3-Dimethylnaphthalene had been purified by D. A. Labianca for an earlier study.[22] 9-Methylanthracene (1.0 gm, Aldrich) was purified by chromatography on silica gel (220 gm, solvent Phillips hexane previously passed through 100 gm of grade I alumina), recrystallization from methanol (MCB Spectroquality), and sublimation (77°/0.05 torr). M.P. 79-80° (literature[23], M.P. 80-81°). The preparation and purification of 4,4-dimethyl-1-(1-naphthyl)-pentane (XXVI) is described in Part I.

Fluorescence Quantum Yields

Fluorescence quantum yields were determined as follows: Solutions of the compound of unknown yield and the standard were adjusted to equal absorbance at the desired excitation wavelength. Solutions were degassed and relative fluorescence spectra recorded. Spectra recorded on the Aminco-Bowman Spectrophotofluorometer were corrected manually for detector response and replotted. The excitation intensity as a function of wavelength was determined using rhodamine B and quinine sulfate quantum counters. The emission correction factors were then determined by reflecting the excitation beam from a surface coated with Eastman white reflectance paint into the emission monochromator of the Aminco. Correction factors determined in this manner agreed well with those determined by correction of the fluorescence spectrum of quinine sulfate.[24] Emission wavelengths were calibrated relative to the mercury lines. Corrected spectra were recorded directly on the Perkin-Elmer Spectrometer in the corrected emission mode. Corrected spectra were expressed as relative quanta per second per unit wavelength interval *versus* wavelength. Quantum yields were corrected for index of refraction according to equation (1), where A_f is the integrated

$$\phi_f = \phi_f^0 \frac{A_f (n)^2}{A_f^0 (n^0)^2} \tag{1}$$

area under the fluorescence curve (relative areas were determined by cutting and weighing corrected relative fluorescence spectra), ϕ_f is the fluorescence quantum yield, n is the index of refraction of the solvent (values of n_D were used since the variation of n with wavelength is not large), and superscript "o" refers to the standard. Cyclohexane was the solvent for the fluorescence standards and values of ϕ_f^o , taken from the data of Berlman[25] as corrected by Birks,[26] were: 2,3-dimethylnaphthalene, 0.32; 9-methylanthracene, 0.29.

Synthetic

Naphthalan (XXV) was prepared by the procedure of Hauser[27] and purified by recrystallization from hexane and sublimation (70°/0.05 torr); two fusions with $LiAlH_4$, followed by sublimation, provided material of M.P. 82-83° (literature,[27] M.P. 83-83.5°). UV (hexane): 320 nm (ϵ 400), 316 (460), 310 (460), 305 (900), 296 (4150), 291 (4500), 284 (6250), 274 (5300).

2-Cyclohexyl-2-aza-perinaphthindane (I) was prepared by the procedure of Reid and Grabosch.[8] The sample used in the fluorescence experiments was recrystallized twice from aqueous methanol and sublimed twice (60-65°/0.02 torr) and had M.P. 71-72° (literature,[8] M.P. 71-72°).

NMR ($CDCl_3$): 0.09-2.8δ (m, 11H), 4.11δ (s, 4H), 7.05-7.85δ (m, 6H). UV (hexane): 321 nm (ϵ 570), 317 (645), 305 (1620), 297 (4500), 286 (6600), 277 (5700). UV (ethyl acetate): 321 (695), 317 (700), 307 (1850), 298sh (4600), 287 (6700), 278 (5770). UV (acetonitrile): 321 (775), 316 (725), 306sh (1850), 298sh (4400), 287 (6300), 277 (5500).

2-Oxo-2,3,4,5-tetrahydro-1H-naphth[1,8-de]azocine (X). 1.0 gm of N-chloroacetyl-2-(1-naphthyl)-ethyl amine (IX) was dissolved in 400 ml of reagent methanol and diluted to 800 ml with water. This solution was irradiated (with stirring) for 1.5 hrs with a 450W Hanova high-pressure lamp (679A-36) using a quartz immersion well and a Vycor filter sleeve. 7.0 ml of 5% $NaHCO_3$ were added and the photolyzed solution evaporated to dryness in vacuo. 100 ml of 95% ethanol and 200 ml of ether were added to the residue and the solution allowed to stand overnight. After filtering, the solution was concentrated to 50 ml and cooled. Filtration gave 0.5 gm of tan product, M. P. 265-270°. Recrystallization from methanol (charcoal) raised the melting point to 271-274° (literature,[11,12] M.P. 276-279°, 284-286°).

2,3,4,5-Tetrahydro-1H-naphth[1,8-de]azocine (XI). A solution of 0.90 gm (0.0043 mole) of X in 900 ml of dry THF (freshly distilled from $LiAlH_4$) was added rapidly to a suspension of 1.04 gm (0.027 mole) of $LiAlH_4$ in 100 ml of dry THF. The yellow-green solution was refluxed gently overnight, cooled, and decomposed by dropwise addition of 1.1 ml of water, 1.1 ml of 15% NaOH, and 3.3 ml of water. The resultant mixture was refluxed for 2 hrs, cooled, and filtered to remove the aluminum salts. Removal of the THF in vacuo and sublimation (68°/0.05 torr) of the residue gave 0.71 gm (85%) of product, M. P. 107-111° (literature,[11] M. P. 111-114°).

N-Acetyl-2,3,4,5-tetrahydro-1H-naphth[1,8-de]azocine (XII). To 0.70 gm (0.0036 mole) of XI in 10 ml of dry pyridine was added 4 ml of acetic anhydride. After stirring for 22 hrs at room temperature, this solution was diluted to 80 ml with water, scratched to induce crystallization, and allowed to stand. The deposited crystals were filtered, washed with water, and air dried (0.31 gm, M.P. 134-135°). The filtrate was extracted with ether (3 × 60 ml). The ether extracts were washed with 4 M HCl (2 × 75 ml), water (1 × 75 ml), saturated $NaHCO_3$ (1 × 75 ml), and saturated NaCl (1 × 75 ml) and dried ($MgSO_4$). Removal of the ether gave a yellow oil (0.3 gm) which solidified upon standing. Chromatography of this material on silica gel (spectroquality methanol solvent) gave 0.13 gm of product of M.P. 133-135°. The HCl, H_2O, and $NaHCO_3$ washes were combined, basified with KOH, and allowed to stand overnight. Filtration gave an additional 0.13 gm of product, M.P. 133-135°. Total yield 0.57 gm (66%). The literature melting point is 133-135°.[11]

N-Ethyl-2,3,4,5-tetrahydro-1*H*-naphth[1,8-*de*]azocine (II). A solution of 0.13 gm (0.00054 mole) of XII in 10 ml of THF was added dropwise to 0.15 gm (0.0025 mole) of $LiAlH_4$ in 10 ml of THF. The mixture was refluxed 24 hrs, cooled, and decomposed by dropwise addition of 0.15 ml water, 0.15 ml 15% NaOH, and 0.45 ml water. The mixture was heated at reflux for 30 min and filtered to remove the precipitated aluminum salts. The THF was removed *in vacuo* and the oily residue taken up in hexane (10 ml) and filtered. Removal of the hexane left a crystalline residue which was recrystallized from 2 ml of hexane at low temperature and sublimed (70°/0.05 torr) to give 0.040 gm of M.P. 73.5-75.5°. This material was used for the fluorescence measurements, analysis, and UV spectra. Removal of the hexane from the filtrate above and sublimation of the residue gave an additional 0.045 gm of M.P. 72-75°.

Analysis. Calculated for $C_{16}H_{19}N$: 85.28% C, 8.50% H, 6.22% N

Found: 85.38% C, 8.50% H, 6.13% N

NMR ($CDCl_3$): 0.76δ (tr, 3H, J = 7 Hz), 2.36δ (q, 2H, J ≈ 7 Hz), 2.83δ (broad tr, 4H, J ≈ 7 Hz), 3.1-4.0δ (broad, unresolved peak, 4H), 7.20δ (d of d, 2H, $J_{ab} \approx 7$ Hz, $J_{ax} \approx 2$ Hz), 7.37δ (tr, 2H, $J_{ab} \approx 7$ Hz, $J_{bx} \approx 7$ Hz), 7.74δ (d of d, 2H, $J_{ax} \approx 2$ Hz, $J_{bx} \approx 7$ Hz). UV (hexane): 321 nm (ϵ 445), 317 (550), 311 (625), 306 (1150), 297 (5700), 292 (5750), 285 (8250), 274 (6750). UV (ethyl acetate): 321 (565), 317 (585), 306 (1350), 297 (5300), 285 (7650), 275 (6350). UV (acetonitrile): 321 (700), 316 (660), 306sh (1600), 297 (5300), 286 (7650), 276 (6400). Mass spectrum: m/e 225 (M+, 25%), 210 (25), 169 (8), 168 (46), 167 (19), 166 (8), 165 (24), 155 (16), 154 (22), 153 (100), 152 (32), 151 (8), 84 (10), 56 (10).

2-Cyclohexyl-1,3-dihydro-benz[*f*]isoindoline (III) was prepared by the method of Wenner.[9] The synthetic amine was contaminated by a yellow-green fluorescent impurity which could not be removed by chromatography (alumina or silica gel), recrystallization, sublimation, or careful purification of the starting materials. The same type of impurity was obtained in preparations of the 2-ethyl-, 2-butyl-, 2-isopropyl-, and 2-*tert*-butyl-derivatives. The fluorescence of the impurity in the 2-*tert*-butyl-derivative had an excitation maximum of 435 nm in hexane and exhibited a structured fluorescence with maxima at 460, 485, and 515 nm. This data suggested that the impurities were the corresponding 2-alkyl-benz[*f*]isoindoles formed by oxidation of the dihydro-derivative. The following procedure was found to effectively eliminate this impurity. 5.0 gm (0.015 mole) of 2,3-*bis*-(bromomethyl)-naphthalene and 4.8 gm (0.048 mole) of cyclohexyl amine were dissolved in 100 ml of benzene and allowed to stand overnight. The precipitate of cyclohexyl amine hydrobromide was removed by filtration and the benzene removed in vacuo. The yellow-green fluorescent residue was treated with 150 ml of boiling hexane and filtered hot. Cooling the filtrate deposited the product as yellow-green fluorescent plates. This material was dissolved in 100 ml of hot methanol and treated with 100-200 mg of $NaBH_4$. Decolorization of the yellow-green solution was immediate. The product crystallized as white plates upon cooling. Freshly recrystallized white product was sublimed (90-95°/0.02 torr) overnight in the dark and the fresh sublimate, M. P. 180-181°, used in the fluorescence experiments.

Analysis. Calculated for $C_{18}N_{21}N$: 86.00% C, 8.42% H

Found: 86.06% C, 8.22% H

NMR ($CDCl_3$): 1.1-2.6δ (broad m, 11H), 4.07δ (broad s, 4H), 7.25-7.88δ (both halves of an A_2B_2 pattern centered at 7.55δ, 4H), 7.60δ (broad s, 2H). UV (hexane): 321 nm (1270), 313 (610), 307 (955), 289 (4000), 278 (6150), 268 (5800), 259 (4600). UV (ethyl acetate): 321 (1100), 313 (585), 307 (875), 289 (4050), 278 (6150), 269 (5850), 260 (4650). UV (acetonitrile): 321 (910), 312sh (510), 307 (740), 288 (3500), 278 (5300), 268 (5150), 259 (4150).

2,3-Naphthalene diacetic acid (XV). A mixture of 25.0 gm (0.121 mole) of 2,3-naphthalene diacetonitrile (XIV),[28] 100 ml of concentrated sulfuric acid, 200 ml of water, and 28 ml of glacial acetic acid was refluxed 3 hrs and allowed to cool to room temperature. 250 ml of water were added and the precipitated solid collected by filtration and washed with several portions of water. This material was dissolved in 1000 ml of 1 M Na_2CO_3, filtered, and the filtrate acidified with H_2SO_4. The precipitated diacid was collected by filtration, washed thoroughly with water, and air-dried. After drying 24 hrs in a vacuum dessicator, the product weighed 24.7 gm (83%) and had M. P. 228-230°. The analytical sample was recrystallized three times from 95% ethanol and had M. P. 228-230°.

Analysis. Calculated for $C_{14}H_{12}O_4$: 68.84% C, 4.95% H
Found: 68.65% C, 5.15% H

The NMR spectrum was not obtained because the diacid failed to dissolve in either $CDCl_3$ or acetone-d_6. Mass spectrum: m/e 244 (M+, 74%), 226 (22), 200 (62), 182 (22), 180 (62), 171 (23), 155 (100), 154 (46), 152 (38), 152 (45), 143 (29), 141 (28), 128 (58), 127 (19), 115 (19), 76 (21).

2,3-Naphthalene diethanol (XVI). 20.0 gm (0.082 mole) of the diacid XV in 400 ml of THF were added dropwise to a slurry of 9.0 gm (0.24 mole) of $LiAlH_4$ in 100 ml of THF. The mixture was refluxed overnight and the product isolated according to the general procedure of Part I. The crude product was recrystallized from $CHCl_3$ to give 13.3 gm (75%) of M. P. 143-145°. The analytical sample was sublimed (100°/0.02 torr) and had M. P. 145-146°.

Analysis. Calculated for $C_{14}H_{16}O_2$: 77.75% C, 7.46% H
Found: 77.92% C, 7.28% H

NMR ($CDCl_3$, saturated): 1.60δ (broad s, 2H), 3.11δ (tr, 4H, J=6.5-7 Hz), 3.98δ (tr, 4H, J=6.5-7 Hz), 7.25-8.0δ (both halves of an A_2B_2 pattern, 4H), 7.73δ (broad s, 2H). Mass spectrum: m/e 216 (M+, 65%), 198 (20), 186 (67), 169 (39), 168 (30), 167 (100), 165 (20), 156 (23), 155 (86), 154 (24), 153 (32), 152 (36), 144 (28), 143 (45), 142 (41), 128 (22), 115 (22).

2,3-bis-(2-bromoethyl)-naphthalene (XVII). This compound was prepared by two different methods. In the first method, 1.0 gm (0.0046 mole) of diol XVI, 3.9 ml of 48% HBr, and 0.015 gm of red phosphorus were refluxed for 18 hrs. The product (1.2 gm) was isolated as described in the general procedure of Part I and chromatographed on silica gel (20 gm, benzene solvent, 25 ml fractions). Fractions 2 and 3 were combined and evaporated to dryness *in vacuo*. The residue was dissolved in 25 ml of hot $CHCl_3$, treated with charcoal, and filtered. Removal of the $CHCl_3$ from the filtrate gave 0.76 gm (60%) of pale yellow product. Sublimation of 0.11 gm of this material from a melt (105°/0.05 torr) gave 0.10 gm of white crystals, M. P. 55.5-56.5°. This material provided the analytical sample.

Analysis. Calculated for $C_{14}H_{14}Br_2$: 49.16% C, 4.13% H
Found: 49.21% C, 4.01% H

In the second procedure, 9.7 gm (0.045 mole) of diol XVI were suspended in 275 ml of dry ether containing 2.0 ml of dry pyridine. A solution of 17.5 gm (0.064 mole) of PBr_3 in 150 ml of dry ether was added dropwise with stirring. The solution was stirred 48 hrs and poured into 400 ml of water. The layers were separated and the aqueous phase extracted with ether (2 × 200 ml). The ether extracts were combined, washed with saturated $NaHCO_3$ (1 × 200 ml) and saturated NaCl (1 × 200 ml), and dried ($MgSO_4$). Removal of the ether *in vacuo* and sublimation (50°/0.05 torr) of the residue gave 5.4 gm (35%) of dibromide XVII, of M. P. 55-56.5°.

NMR ($CDCl_3$): 3.0-4.0δ (both halves of an A_2B_2 pattern centered at 3.50δ, 8H), 7.3-8.0δ (both halves of an A_2B_2 pattern, 4H), 7.72δ (broad s, 2H).

Mass spectrum: m/e 344 (M+, $Br^{81}Br^{81}$, 51%), 342 (M+, $Br^{79}Br^{81}$, 100), 340 (M+, $Br^{79}Br^{79}$, 53), 263 (22), 261 (21), 181 (24), 169 (21), 168 (52), 167 (82), 166 (25), 165 (44), 154 (22), 153 (27), 152 (38), 141 (15), 115 (12), 89 (22).

N-Cyclohexyl-2,3,6,7-tetrahydro-naphth[2,3-*d*]azepine (IV). All samples of this compound contained a small amount of an impurity with similar fluorescence behavior, but with an excitation maximum of about 340 nm in polar solvents. Recrystallization, sublimation, chromatography, and treatment with $NaBH_4$ or $LiAlH_4$ were ineffective in eliminating this impurity. The amount of this impurity could be minimized by the synthetic procedure below; its effect on the fluorescence of IV was then negligible when dilute solutions of this material ($\sim 6 \times 10^{-4}$ *M*) and 310 nm excitation were employed. 0.78 gm (0.0023 mole) of freshly sublimed dibromide XVII and 0.70 gm (0.0071 mole) of cyclohexyl amine were dissolved in 13 ml of spectroquality benzene and the solution refluxed gently in a N_2 atmosphere for 9 days. The mixture was cooled, filtered to remove the precipitated cyclohexyl amine hydrobromide, and the solvent removed *in vacuo*. Recrystallization of the residue from spectroquality methanol gave 0.375 gm (59%) of the desired amine. This material was dissolved in 30 ml of hot spectroquality methanol. Slow cooling deposited large white plates which were collected by filtration at room temperature, washed with methanol, and air dried. Residual solvent was removed by pumping overnight at 0.02 torr and room temperature to give 0.213 gm of amine, M. P. 135-136°. This material was used in the fluorescence experiments. The analytical sample (M. P. 135-136°) was from an earlier preparation in which the crude amine was recrystallized twice from 95% ethanol and sublimed (105-110°/0.02 torr).

Analysis. Calculated for $C_{20}H_{25}N$: 85.95% C, 9.02% H
Found: 86.03% C, 8.97% H

NMR ($CDCl_3$): 0.9-2.6δ (broad m, 11H), 2.65-3.25δ (both halves of an A_2B_2 pattern centered at 2.94δ, 8H), 7.25-7.90δ (both halves of an A_2B_2 pattern centered at 7.56δ, 4H), 7.55δ (broad s, 2H). UV (hexane): 320 nm (ϵ 460), 315 (280), 306 (515), 302 (350), 289 (3400), 278 (5670), 268 (5760), 259 (4700), 251 (3640). UV (ethyl acetate): 320 (450), 315 (290), 306 (525), 302 (390), 289 (3550), 278 (5850), 269 (5900), 260 (4750). UV (acetonitrile): 320 (435), 316 (300), 306 (525), 302sh (420), 289 (3600), 278 (5950), 269 (6100), 260 (5000), 251sh (3900). Mass spectrum: m/e 279 (M+, 38%), 236 (100), 167 (15), 155 (23), 154 (80), 142 (27), 141 (44), 115 (15).

<u>1-(N, N-Diethylamino)-10-(1-naphthyl)-decane (V)</u> was prepared by Dr. M. T. McCall. A solution of 2.0 gm of 10-(1-naphthyl)-decanoic acid (XVIII)[29] in 30 ml of dry ether was added to a slurry of 0.25 gm of $LiAlH_4$ in 10 ml of ether. After stirring 1.5 hrs at room temperature, the excess $LiAlH_4$ was destroyed by addition of ethyl acetate. Sufficient 10% HCl was added to dissolve the aluminum salts and the layers separated. The ether layer was washed with water and saturated NaCl and dried ($MgSO_4$). Removal of the ether gave a yellow oil which was chromatographed on grade III alumina (2.5 × 12 cm column, ether solvent) to give 1.4 gm of 10-(1-naphthyl)-1-decanol (XIX). 1.3 gm of this alcohol, 10 ml of 48% HBr, and 5-10 mg of red phosphorus were refluxed overnight and the product isolated as described in the general procedure of Part I. The crude product was chromatographed on grade III

alumina (2.5 × 15 cm column, benzene solvent) to give 1.5 gm of 1-bromo-10-(1-naphthyl)-decane (XX). 1.4 gm of this bromide were stirred with 20 ml of diethyl amine for 5 days. The mixture was poured into dilute NaOH and extracted with ether. The ether extracts were dried and the ether removed in vacuo. Residual bromide was removed by chromatography on alumina (benzene) and the desired amine (V) purified by vacuum transfer from $LiAlH_4$. The amine was repurified by kugelrohr distillation (195°/0.05 torr) immediately prior to the fluorescence experiments. The pure amine was a colorless oil.

Analysis. Calculated for $C_{27}H_{37}N$: 84.89% C, 10.99% H, 4.13% N
Found: 84.92% C, 11.12% H, 4.12% N

NMR ($CDCl_3$): 0.96δ (tr, 6H, J = 7 Hz), 0.7-2.0δ (broad pattern with a broad methylene "s" at 1.25δ, 16H). 2.44δ (q, 4H, J = 7 Hz), 2.1-2.6δ (broad pattern unresolved from q at 2.44δ, 2H), 2.75-3.25δ (broad tr centered at 3.00δ, 2H), 7.0-8.2δ (m, 7H).

N-Methyl-N-[2-(2-naphthyl)-ethyl]-aniline (VI) was prepared by Dr. M. T. McCall using the following procedure. 0.5 gm of 1-(2-bromoethyl)-naphthalene (XXI) and 1.0 gm of N-methyl-aniline were heated at 150° for 2 hrs. The black solution was poured into 10% Na_2CO_3 and the precipitated product filtered, washed with water, dried, recrystallized from hexane (twice), and sublimed (90°/0.5 torr). The product was resublimed (90°/0.05 torr) prior to the fluorescence measurements and had M. P. 101.8-102.8°.

Analysis. Calculated for $C_{19}H_{19}N$: 87.31% C, 7.33% H
Found: 87.28% C, 7.21% H

NMR ($CDCl_3$): 2.77δ (s, 3H), 2.6-3.8δ (both halves of an A_2B_2 pattern centered at 3.24δ, 4H), 6.5-7.0δ (m, 3H), 7.0-7.95δ (m, 9H). UV (cyclohexane): 320 nm (ϵ 850), 255 (26,000). Mass spectrum: m/e 261 (M+, 6%), 141 (3), 121 (10), 120 (100), 115 (3), 106 (8), 105 (6), 104 (4), 77 (9).

N-Ethyl-N-phenyl-9-anthracenepropyl amine (VII). 5.0 gm (0.02 mole) of 9-anthracenepropionic acid (XXII)[30] in THF (100 ml) was added dropwise to 0.05 gm (0.013 mole) of $LiAlH_4$ in THF (30 ml). The solution was stirred at reflux for 5 hrs and the product isolated by the general procedure of Part I. The yield of crude 9-anthracenepropanol (XXIII) was 4.8 gm (100%).

The crude alcohol (4.8 gm), 20 ml of 48% hydrobromic acid, and 0.05 gm of red phosphorus were stirred at reflux for 40 hrs and the product isolated by methylene chloride extraction as described in the general procedure of Part I. The crude product was chromatographed on silica gel (225 gm, benzene solvent) to give 5.1 gm (85%) of 9-anthracenepropyl bromide (XXIV). The analytical sample was sublimed three times from a melt (90-95°, 0.05 torr) and had M. P. 86-87°.

Analysis. Calculated for $C_{17}H_{15}Br$: 68.24% C, 5.05% H
Found: 68.15% C, 5.12% H

NMR ($CDCl_3$): 1.9-2.6δ (m, 2H), 3.2-4.0δ (m, 4H), 7.15-8.4δ (m, 9H).

0.62 gm (0.0021 mole) of chromatographed bromide and 1.0 gm (0.0083 mole) of freshly distilled N-ethyl aniline (Calbiochem) were heated at 150° for 2.5 hrs. After cooling, the dark mixture was poured into 10% Na_2CO_3 (25 ml) and extracted with ether (2 × 25 ml). Addition of 10% HCl (100 ml) to the ether extracts precipitated the oily amine hydrochloride. The ether was removed by decantation and the hydrochloride extracted into CH_2Cl_2 (3 × 25 ml). The CH_2Cl_2 extracts were washed with water (2 × 50 ml), shaken with 10% Na_2CO_3 (2 × 50 ml) to regenerate the free amine, and dried ($MgSO_4$). Removal of the CH_2Cl_2 left a residue which was recrystallized from hexane and sublimed twice from a melt (120-130°/0.05 torr and 100-105°/0.05 torr). Yield 0.20 gm (28%), M. P. 75.8-76.5°.

Analysis. Calculated for $C_{25}H_{25}N$: 88.45% C, 7.42% H, 4.10% N

Found: 88.40% C, 7.48% H, 4.13% N

NMR ($CDCl_3$): 1.15δ (tr, 3H, J = 7 Hz), 1.8-2.4δ (m, 2H), 3.15-4.85δ (m, 6H), 6.6-8.4δ (m, 14H). UV (hexane): 388 nm (ε 11,400), 368 (11,350), 349 (6,750), 333 (3,100), 314 (2,300), 304 (2,550), 257 (201,000), 249 (118,000). UV (ethyl acetate): 389 (10,500), 369 (10,800), 350 (6,470), 334 (3,070), 314sh (2,600), 306 (2,750), 257 (183,000). UV (acetonitrile): 389 (9,570), 368 (9,960), 350 (6,050), 333 (2,900), 313 (2,700), 307 (2,710), 257 (165,000), 250 (114,000). Mass spectrum: m/e 339 (M+, 22%), 191 (15), 161 (28), 160 (100), 146 (12), 134 (70), 106 (39).

Absorption of equimolar mixtures of 9-methylanthracene and N-ethyl aniline. UV (hexane): 386 nm (ε 10,000), 366 (9800), 347 (5900), 330 (2700), 313 (2500), 303 (2700), 256 (212,000), 248 (101,000). UV (ethyl acetate): 387 (9000), 367 (9300), 348 (5700), 331 (2700), 313 (2660), 305 (2700), 256 (210,000). UV (acetonitrile): 387 (8100), 367 (8500), 349 (5260), 332 (2620), 313 (2800), 307sh (2700), 255 (180,000), 249sh (108,000).

N-Ethyl-N-phenyl-9-anthracenepropionamide (XXVII). 5.2 gm (0.021 mole) of 9-anthracenepropionic acid and 6.5 gm (0.032 mole) of

PCl_5 (Baker) in 50 ml of reagent benzene were stirred at 5-10 °C for 2 hrs.[31] 10 gm (0.08 mole) of N-ethyl aniline in 20 ml of benzene were added dropwise over a period of 20 min. After stirring 5 hrs at room temperature, the precipitated solid was collected by filtration, washed repeatedly with 10% HCl and 10% NaOH, rinsed with water, and air dried. Two recrystallizations from methanol gave 3.0 gm (42%), M. P. 133-134.5°.

Analysis. Calculated for $C_{25}H_{23}NO$: 84.95% C, 6.56% H
Found: 84.76% C, 6.58% H

NMR ($CDCl_3$): 1.05δ (tr, J = 7 Hz, 3H), 2.3-2.8δ (m, 2H), 3.5-4.15δ (m, 4H), 6.7-8.4δ (m, 14H). UV (cyclohexane): 388 nm (10,000), 368 (9900), 349 (5650), 333 (2600), 318 (1000), 257 (170,000), 250 (81,000).

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PART III

INTERSYSTEM CROSSING IN THE METHYL BENZENES

INTRODUCTION

Despite their importance in understanding excited state decay processes in solution, very few intersystem crossing quantum yields (ϕ_{isc}) have been measured for substituted benzenes. This is in part due to the lack of a simple, generally applicable method for determining ϕ_{isc}. Although the method of Sandros[1] (sensitized biacetyl phosphorescence) gives satisfying results for a wide variety of benzene derivatives, it requires an elaborate procedure and kinetic analysis. The Lamola-Hammond method[2] (sensitized piperylene isomerization) suffers a multitude of debilitating experimental corrections, as discussed by Morrison.[3] Application of the Cundall method[4] (2-butene isomerization) to substituted benzenes requires assumptions which, while not unreasonable, are not readily subject to experimental verification. Since many substituted benzenes have triplet energies comparable to those of the isomeric 2-butenes, uncertainties regarding the nature of the isomerization process[5] and the role of energy wasting steps inevitably arise.

Recently, Dr. Carroll and I developed a new method designed primarily for the determination of intersystem crossing yields of substituted benzenes in solution.[6] This portion of the thesis describes the application of this method to a structure-reactivity study of intersystem crossing in the methyl benzenes.

DESCRIPTION OF THE METHOD

The method is a combination of the "triplet counting" techniques[2,4] and the flash spectroscopic method of Wilkinson and co-workers.[7] A "triplet counter" ($\underset{\frown}{C}$) is used instead of flash spectroscopy to monitor the increase in triplet state population of the aromatic ($\underset{\frown}{A}$) with increasing concentration of heavy atom fluorescence quencher ($\underset{\frown}{H}$). The processes of interest are shown in the kinetic scheme below.

$$\underset{\frown}{A}_0 \xrightarrow{h\nu} \underset{\frown}{A}^{*(1)} \tag{1}$$

$$\underset{\frown}{A}^{*(1)} \xrightarrow{k_2} \underset{\frown}{A}_0 + h\nu' \tag{2}$$

$$\underset{\frown}{A}^{*(1)} \xrightarrow{k_3} \underset{\frown}{A}_0 \tag{3}$$

$$\underset{\frown}{A}^{*(1)} + \underset{\frown}{C} \xrightarrow{k_4} \underset{\frown}{A}_0 + \underset{\frown}{C} \tag{4}$$

$$\underset{\frown}{A}^{*(1)} \xrightarrow{k_5} \underset{\frown}{A}^{*(3)} \tag{5}$$

$$\underset{\frown}{A}^{*(1)} + \underset{\frown}{H} \xrightarrow{k_6} \underset{\frown}{A}^{*(3)} + \underset{\frown}{H} \tag{6}$$

$$\underset{\frown}{A}^{*(3)} \xrightarrow{k_7} \underset{\frown}{A}_0 \tag{7}$$

$$\underset{\frown}{A}^{*(3)} + \underset{\frown}{C} \xrightarrow{k_8} \underset{\frown}{A}_0 + \underset{\frown}{C}^{*(3)} \tag{8}$$

$$\underset{\frown}{A}^{*(3)} + \underset{\frown}{C} \xrightarrow{k_9} \underset{\frown}{A}_0 + \underset{\frown}{C} \tag{9}$$

$$\underset{\frown}{C}^{*(3)} \xrightarrow{k_{10}} \underset{\frown}{C} \tag{10}$$

$$\underset{\frown}{C}^{*(3)} \xrightarrow{k_{11}} \underset{\frown}{T} \tag{11}$$

Although eqs. (8-11) describe a sensitized isomerization, it should be noted that any sensitized reaction may be employed as the triplet counter.

In the following derivation, F' and F^0 represent the fluorescence intensities of A with and without C present; τ_f' and τ_f^0 represent the corresponding singlet lifetimes. Y_T' is the yield of T in the absence of H. F, τ_f, and Y_T refer to quantities with both C and H present. The effect of fluorescence quenching by C in the absence of H is given by eq. (12). For

$$F^0/F' = \tau_f^0/\tau_f' = 1 + k_4\,\tau_f^0[C] \qquad (12)$$

solutions containing constant concentrations of A and C, but varying concentrations of H, the relative fluorescence intensities are given by eq. (13). The ratio of yields for the appearance of

$$F'/F = \tau_f'/\tau_f = 1 + k_6\,\tau_f'[H] \qquad (13)$$

T in the presence of H to that without H, at constant light dose, is given by eq. (14). Since the second term in both numerator and denominator is

$$Y_T/Y_T' = \frac{(k_5 + k_6[H])\tau_f \cdot \left(\dfrac{k_8[C]}{k_7 + k_8[C] + k_9[C]}\,\dfrac{k_{11}}{k_{10} + k_{11}}\right)}{k_5\tau_f' \cdot \left(\dfrac{k_8[C]}{k_7 + k_8[C] + k_9[C]}\,\dfrac{k_{11}}{k_{10} + k_{11}}\right)} \qquad (14)$$

unaffected by xenon, the ratio of these terms is unity. Combining eqs. (12-14) gives eq. (15), which predicts that

$$\frac{F^0}{F'}\left(\frac{F'}{F} - 1\right) = \Phi_{isc}\left(\frac{Y_T}{Y_T'}\,\frac{F'}{F} - 1\right) \qquad (15)$$

a plot of $(F^0/F')(F'/F - 1)$ vs $(Y_T/Y_T')(F'/F) - 1$ should be linear with slope ϕ_{isc}.

An important advantage of the present method over previous methods employing sensitized isomerization[2,4] is that neither the efficiency of energy transfer nor the triplet counter decay ratio need be known. In addition, only relative measurements with the same sensitizer are required and actinometry is unnecessary if all samples are irradiated under identical conditions. Unlike the Wilkinson method,[7] this method is not limited by the lifetime or spectral characteristics of the aromatic triplet state.

RESULTS AND DISCUSSION

The impetus for this study was a report by Reiser and Leyshon[8] of the fluorescence quantum yields (ϕ_f) of the methyl benzenes in degassed cyclohexane solution. The variation of the radiative rate constants ($k_f = k_2$) was shown to be related to the symmetry of the substitution pattern (vide infra). Except for pentamethyl- and hexamethylbenzene, the total nonradiative decay rates of the methyl benzenes were found to be quite similar. Since energy gaps are only slightly affected by methyl substitution, these authors tentatively concluded that the rates of intersystem crossing ($k_{isc} = k_5$) and internal conversion ($k_d = k_3$) were insensitive to methyl substitution in these compounds. Because the available intersystem crossing data for these compounds[1,6] did not appear to support this conclusion, a systematic study of intersystem crossing in the methyl benzenes was undertaken.

Intersystem Crossing Quantum Yields and Calculation of Rates

As before,[6] cis-2-pentene (0.05 M) was employed as the triplet counter ($\underset{\frown}{C}$) and xenon as the heavy atom fluorescence quencher ($\underset{\frown}{H}$). The solvent was cyclohexane and concentrations of the methyl benzenes varied from 0.008 M to 0.02 M. Excimer interactions are relatively unimportant at these concentrations. Table I contains the experimental data and Figures 1 and 2 show plots of this data according to eq. (15). Tables II and III summarize the experimental results and relevant literature data.

We were unable to detect isomerization of <u>cis</u>-2-pentene in experiments with hexamethylbenzene as sensitizer. Since the triplet energy of hexamethylbenzene is only slightly lower than that of pentamethylbenzene at 77 °K (79.2 <u>versus</u> 79.3 kcal), this failure cannot be attributed entirely to a change in energetics. A short triplet lifetime and/or a very low intersystem crossing yield would account for the absence of energy transfer.

Rate constants for deactivation of the first excited singlet state of the methyl benzenes, calculated according to eq. (16), are given in

$$k_x = \phi_x/\tau_f^0 \qquad (16)$$

Table III. The use of this equation implicitly assumes that vibrational relaxation in S_1 is rapid relative to k_x. In support of this assumption, Lipsky[9] has found that the fluorescence quantum yields of a number of these compounds in solution are independent of excitation wavelength throughout the region of interest ($\lambda > 240$ nm). Furthermore, the quantum yield for formation of benzvalene from excited benzene is reported to be constant over this wavelength range.[10] Rate data for hexamethylbenzene is taken from Ref. 8, with the assumption that k_{isc} is approximately equal to the total nonradiative decay rate at 77 °K.

Table I

Experimental data for the effect of xenon on fluorescence and sensitized cis-trans isomerization.

Sensitizer ($\underset{\sim}{A}$)	$[\underset{\sim}{A}_0]$ ($\underline{M} \times 10^2$)	F^0/F' [a]	F'/F	Y_T/Y_T'
Benzene	1.08	1.10	1.00	1.00
			1.09	1.38
			1.24	1.76
			1.40	1.99
			1.55	2.16
Toluene	1.09	1.08	1.00	1.00
			1.38	1.32
			2.49	1.60
			2.74	1.75
o-xylene	1.25	1.03	1.00	1.00
			1.35	1.17
			1.60	1.29
			1.04	1.37
			2.29	1.46
m-xylene	1.47	1.00	1.00	1.00
			1.46	1.16
			1.92	1.30
			2.04	1.40
			2.58	1.44
p-xylene	1.11	1.04	1.00	1.00
			1.65	1.24
			2.36	1.37
			3.40	1.43
			3.81	1.49
1,2,3-Trimethylbenzene (hemimellitene)	1.52	1.00	1.00	1.00
			1.04	1.26
			1.26	1.40
			1.34	1.56
			1.53	1.82

Table I (Continued)

Sensitizer (A)	$[A_0]$ ($M \times 10^2$)	F^o/F'^a	F'/F	Y_T/Y_T'
1,2,4-Trimethylbenzene (pseudocumene)	0.84	1.00	1.00	1.00
			1.38	1.16
			1.61	1.30
			2.09	1.45
			2.36	1.48
Mesitylene (1,3,5-trimethylbenzene)	2.27	1.00	1.00	1.00
			1.08	1.10
			1.50	1.27
			1.81	1.41
			2.04	1.41
1,2,4,5-Tetramethylbenzene (durene)	1.24	1.00	1.00	1.00
			1.23	1.13
			1.73	1.26
			2.06	1.35
1,2,3,5-Tetramethylbenzene (isodurene)	2.02	1.00	1.00	1.00
			1.16	1.29
			1.36	1.35
			1.75	1.55
			1.74	1.54
1,2,3,4-Tetramethylbenzene (prehnitene)	1.69	1.00	1.00	1.00
			1.16	1.28
			1.27	1.41
			1.36	1.49
			1.47	1.61
Pentamethylbenzene	0.87	1.00	1.00	1.00
			1.04	1.21
			1.09	1.46
			1.18	1.74
			1.24	1.92

[a] Initial *cis*-2-pentene concentration of 0.05 M.

Table II

Intersystem crossing yields and fluorescence lifetimes of the methyl benzenes in degassed cyclohexane solution at room temperature.

Sensitizer	ϕ_{isc}[a,b]	ϕ_{isc}(lit.)	τ_f^0[a] (±2 ns)	τ_f(lit.)[c] (ns)
Benzene	0.25 ± 0.02	0.25 (1)[d,e]	28	28[f] 29
Toluene	0.51 ± 0.03	0.53 (1) 0.52 ± 0.03 (6)	34	34
o-Xylene	0.58 ± 0.03	0.28[f]	32	32.2
m-Xylene	0.58 ± 0.03		31	30.8
p-Xylene	0.64 ± 0.03	0.63 (1)	30	30
1,2,3-Trimethylbenzene	0.31 ± 0.02		35	
1,2,4-Trimethylbenzene	0.55 ± 0.03		28	27.2
Mesitylene	0.55 ± 0.03	0.60 ± 0.03 (6)	36.5	36.5
1,2,4,5-Tetramethylbenzene	0.60 ± 0.03		26.5	
1,2,3,5-Tetramethylbenzene	0.44 ± 0.02		31	
1,2,3,4-Tetramethylbenzene	0.35 ± 0.02		27	
Pentamethylbenzene	0.17 ± 0.01		15	
Hexamethylbenzene	---	---	--	4 (8) 6[h]

[a] This work.

[b] Obtained from the slopes in Figures 1 and 2.

[c] Data of Berlman[38] unless otherwise noted.

Table II (Continued)

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[d] S. Sato, H. Kobayashi, and K. Fukano, *Kogyo Kagaku Zasshi*, **72**, 209 (1969).

[e] In methylcyclohexane solution. R. B. Cundall, L. C. Pereira, and D. A. Robinson, *Chem. Phys. Letters*, **13**, 253 (1972).

[f] W. P. Helman, *J. Chem. Phys.*, **51**, 354 (1969).

[g] In methylcyclohexane solution. R. B. Cundall and A. J. R. Voss, *Chem. Commun.*, 116 (1969).

[h] T. V. Ivanova, P. I. Kudryashov, and B. Ya. Sveshnikov, *Soviet Phys. Doklady*, **6**, 407 (1961).

Table III

Fluorescence quantum yields and rate constants for deactivation of S_1 of the methyl benzenes in degassed cyclohexane solution at room temperature.

Sensitizer	ϕ_f	ϕ_d[a]	k_f[b]	k_{isc}[b]	kd[b]
			($sec^{-1} \times 10^{-6}$)		
Benzene	0.063 (8) 0.058[c] 0.06 (27) 0.061 (18)	0.69	2.2	8.9	25
Toluene	0.14[c] (8)	0.35	4.1	15	10
o-Xylene	0.16[c]	0.26	5.0	18	8.1
m-Xylene	0.14[c]	0.28	4.5	19	9.0
p-Xylene	0.34 (8) 0.33[c]	(0.02)	11	21	(0.7)
1,2,3-Trimethylbenzene	0.15 (8)	0.54	4.3	8.9	15
1,2,4-Trimethylbenzene	0.34[c]	0.11	12	20	3.9
1,3,5-Trimethylbenzene	0.14[c]	0.31	3.8	15	8.5
1,2,4,5-Tetramethylbenzene	0.25 (8)	0.15	9.4	23	5.7
1,2,3,5-Tetramethylbenzene	0.16 (8)	0.40	5.2	14	13
1,2,3,4-Tetramethylbenzene	0.12 (8)	0.53	4.4	13	20
Pentamethylbenzene	0.08 (8)	0.75	5.3	11	50
Hexamethylbenzene	0.015 (8) 0.02[d]	(0.95)[e]	3.8	(10)[e]	(240)[e]

[a] Calculated from $\phi_d = 1 - (\phi_f + \phi_{isc})$.

[b] ± 15-20% calculated from eq. (17).

Table III (Continued)

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[c] Data of Berlman[38] as corrected by Birks (reference 23, p. 122).

[d] See footnote h of Table II.

[e] Estimated assuming that k_{isc} is equal to the nonradiative decay rate at 100 °K (8).

Figure 1

Plots of Experimental Data According to Equation 15 for the Methyl Benzenes

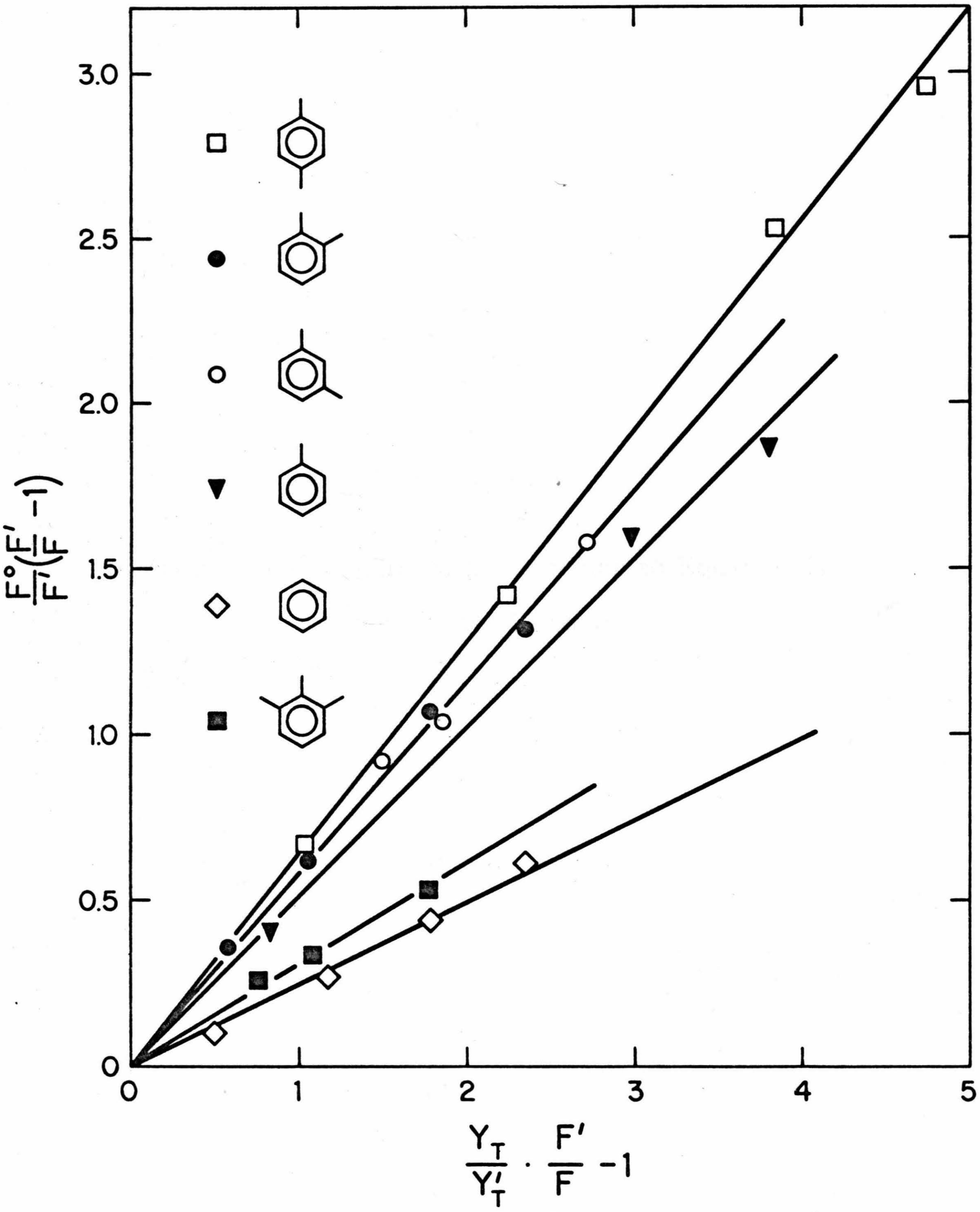
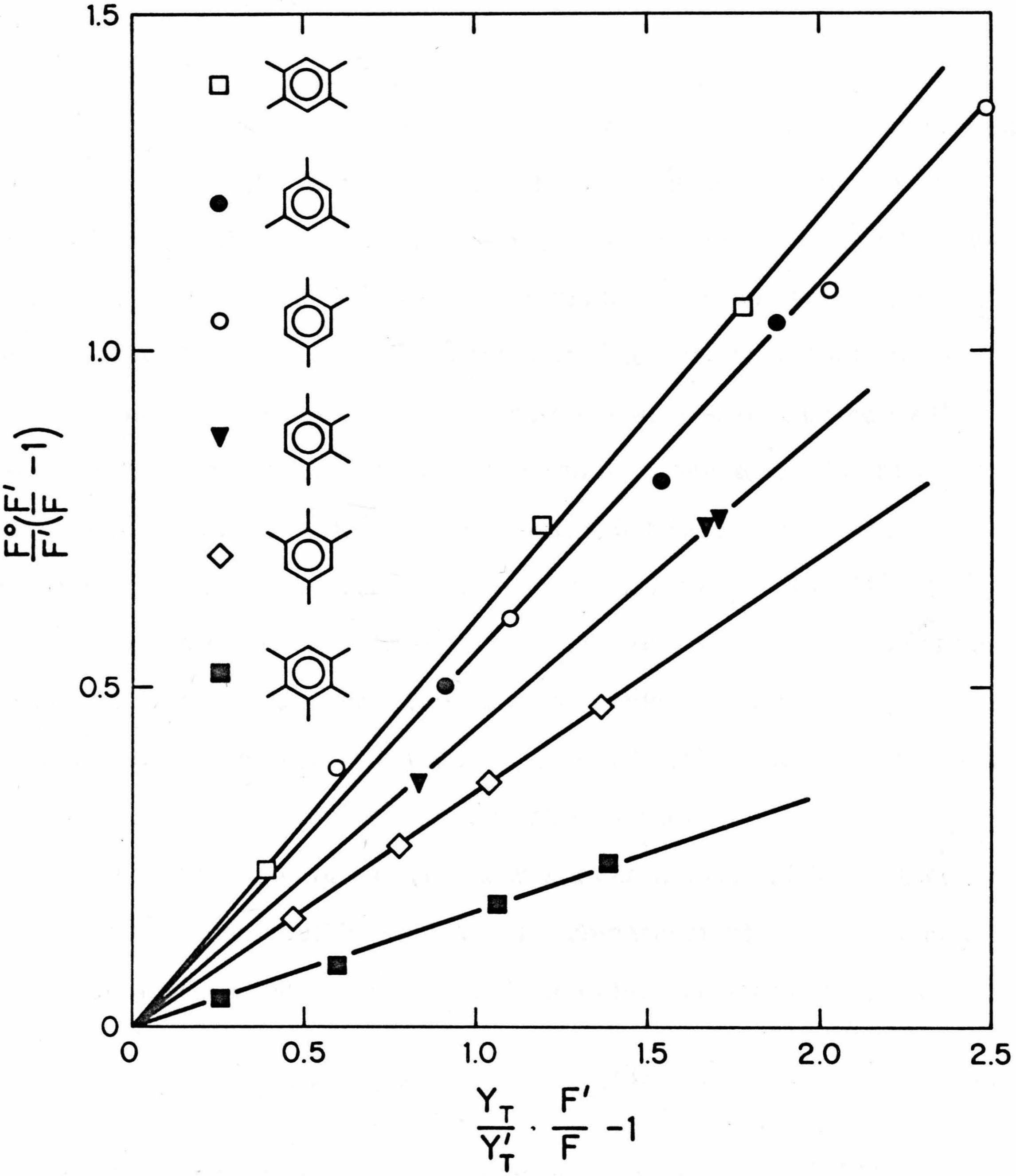

3.0
2.5
2.0
1.5
1.0
0.5
0
0
1
2
3
4
5
$\frac{F°}{F'}(\frac{F'}{F}-1)$
$\frac{Y_T}{Y'_T} \cdot \frac{F'}{F} -1$

Figure 2

Plots of Experimental Data According to Equation 15 for the Methyl Benzenes


1.5
1.0
0.5
0
0
0.5
1.0
1.5
2.0
2.5
$\frac{F°}{F'}(\frac{F'}{F} - 1)$
$\frac{Y_T}{Y'_T} \cdot \frac{F'}{F} - 1$

Figures 3 and 4 display the rate data graphically.

Singlet Quenching by the 2-Pentenes

The nature of the singlet quenching by the 2-pentenes is uncertain. Cundall[11] reports that "pure olefins, free from dienes and oxidation products" quench the fluorescence of benzene and toluene with rate constants of the order of 10^5 M^{-1} sec^{-1}. Morrison,[12] however, obtained a k_q of 1.5×10^7 M^{-1} sec^{-1} for the quenching of toluene fluorescence by trans-2-heptene. We have found that rates of singlet quenching by the 2-pentenes are comparable to that reported by Morrison. The absence of significant amounts of diene impurities ($< 0.01\%$ by glpc), the efficiency of the process (a quenching impurity with $k_q = 10^{10}$ M^{-1} sec^{-1} would have to be present to the extent of 0.6% in order to quench benzene fluorescence at the observed rate), and the unusual ordering of the quenching rates[6] (anisole > benzene > toluene > other methyl benzenes) argue for a process involving pentene rather than impurities.

In the derivation of eq. (15) it was assumed that singlet quenching by 2-pentene is described by eq. (4). If aromatic triplets are produced in the quenching act [eq. (17)], ϕ_{isc} values obtained from the slopes in

$$\underset{\wedge}{A}^{*(1)} + \underset{\wedge}{C} \xrightarrow{k_{17}} \underset{\wedge}{A}^{*(3)} + \underset{\wedge}{C} \qquad (17)$$

Figures 1 and 2 are in error by the factor in brackets in eq. (18).

$$\frac{F^0}{F'}\left(\frac{F'}{F} - 1\right) = \left[\left(\frac{F^0}{F'} - 1\right)\frac{k_{17}}{k_4 + k_{17}} + \phi_{isc}\right]\left(\frac{Y_T}{Y'_T}\frac{F'}{F} - 1\right) \quad . \qquad (18)$$

For $F^0/F' = 1$ or for $k_4 \gg k_{17}$, eq. (18) reduces to eq. (15). At the

Figure 3

Fluorescence and Intersystem Crossing Rates
of the Methyl Benzenes

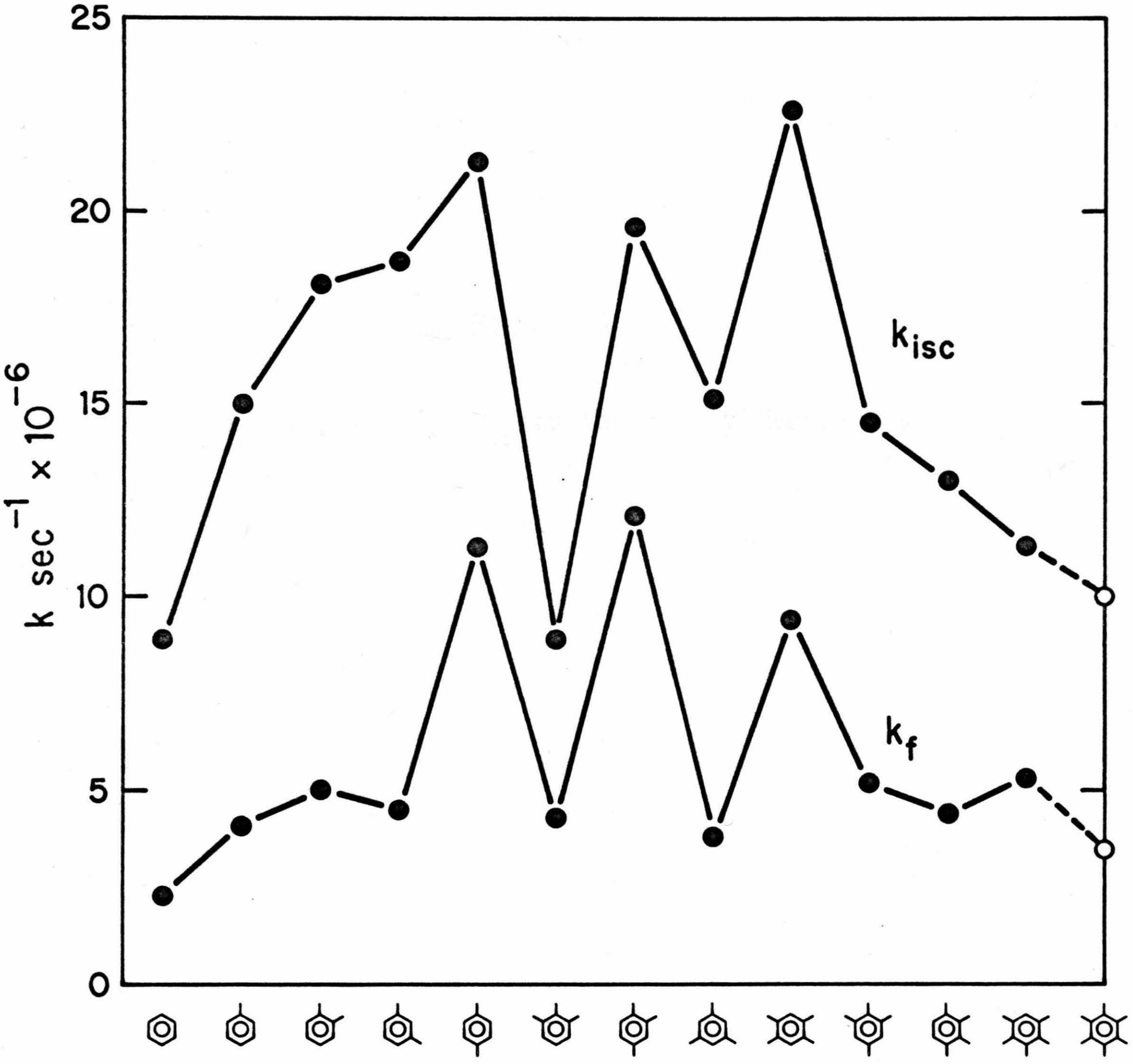
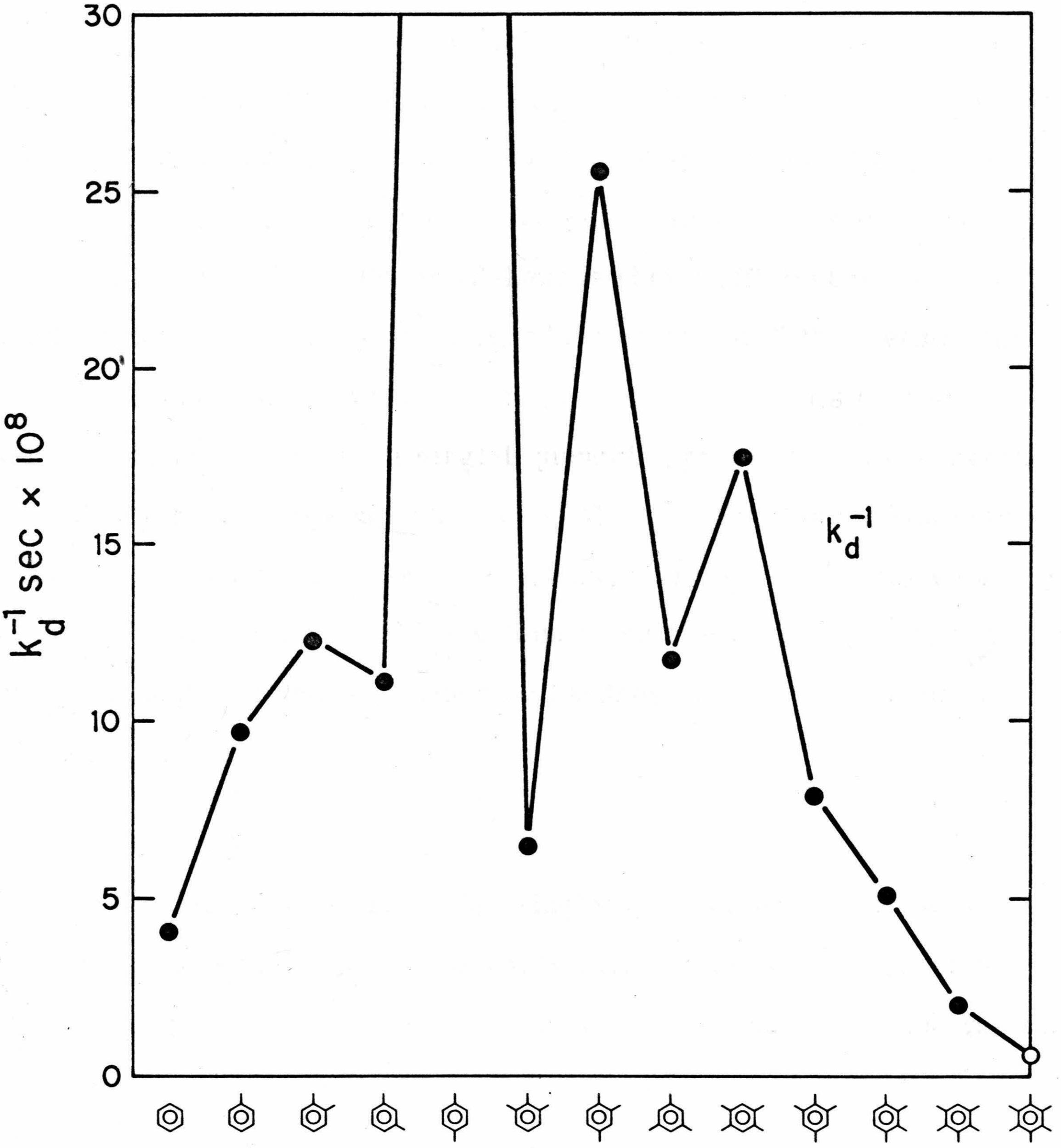

25
20
15
10
5
0
k sec^{-1} x 10^{-6}
k$_{isc}$
k$_f$

Figure 4

The Reciprocal of k_d for the Methyl Benzenes


30
25
20
15
10
5
0
k_d^{-1} sec × 10^8
k_d^{-1}

experimental pentene concentration of 0.05 M, only benzene, toluene, p-xylene, and o-xylene exhibit measurable singlet quenching. In order to significantly affect the validity of ϕ_{isc} values for these compounds, the singlet quenching process would have to lead to efficient triplet production ($k_{17} \approx k_4$). The justification for our original assumption that $k_4 \gg k_{17}$ is twofold: (a) 6-Phenyl-2-hexene shows efficient intramolecular singlet quenching, but very inefficient isomerization of the olefinic unit. Because intramolecular cyclization is also efficient in this system, Morrison[3] has associated the singlet quenching process with the formation of 1,3-adducts between benzene and olefins. Similar explanations of olefin singlet quenching have been advanced by others.[13] (b) Values of ϕ_{isc} for benzene, toluene, and p-xylene calculated from eq. (15) are in good agreement with those obtained by Sandros[1] using an independent technique.

Quenching by Xenon

In the derivation of eq. (15), singlet quenching by xenon was assumed to result entirely from enhancement of intersystem crossing [eq. (6)]. Acceleration of internal conversion by xenon [eq. (19)] was thus

$$\underset{\wedge}{A}^{*(1)} + \underset{\wedge}{H} \xrightarrow{k_{19}} \underset{\wedge}{A}_0 + \underset{\wedge}{H} \qquad (19)$$

presumed to be unimportant. Inclusion of eq. (19) in the derivation of the method gives eq. (20), from which it is apparent that measured

$$\frac{F^0}{F'}\left(\frac{F'}{F} - 1\right) = \left(1 + \frac{k_{19}}{k_6}\right)\phi_{isc}\left(\frac{Y_T}{Y_T'}\frac{F'}{F} - 1\right) \qquad (20)$$

values of ϕ_{isc} are potentially too large by the factor $(1 + k_{19}/k_6)$.

The evidence for the neglect of k_{19} relative to k_6 has been presented by Horrocks and Wilkinson.[7] The good agreement of ϕ_{isc} values calculated from eq. (15) with those obtained by Sandros[1] further implies that the process in eq. (19) may be neglected. As a further independent check on this assumption, initial quantum yields for sensitized isomerization of the 2-pentenes (ϕ_{c-t} and ϕ_{t-c}) were measured at an initial olefin concentration of 0.05 M. If this concentration of olefin were sufficient to scavenge most of the aromatic triplets and energy wasting steps [eq. (9)] were unimportant, then the sum of isomerization quantum yields should approach ϕ_{isc}. (This amounts to a crude application of the Cundall method for the determination of ϕ_{isc}.[4]) The data in Table IV indicate that the sum of isomerization quantum yields does indeed approach ϕ_{isc} for most of the methyl benzenes. The differences are probably due to inefficient scavenging or a systematic experimental error (in the actinometry, for example). Benzene and 1,2,3,4-tetramethylbenzene, however, exhibit markedly inefficient energy transfer to the 2-pentenes. Inefficient energy transfer from benzene to the 2-butenes has been observed by Cundall.[14] Although Cundall has interpreted this inefficiency in terms of a short benzene triplet lifetime, this is clearly in conflict with the lifetime of 2×10^{-6} sec estimated from sensitized biacetyl phosphorescence data.[1] Our data are insufficient to resolve this question.

Table IV

Cis to trans and trans to cis quantum yields for isomerization of the 2-pentenes.

Sensitizer	$\phi_{c\to t}^{a}$ ± 10%	$(F^{o}/F')_{T}^{b}$	$\phi_{t\to c}^{b}$ ± 10%	$\phi_{c\to t} + \phi_{t\to c}$ ± 10%
Benzene	0.093	1.07	0.091	0.18_4
Toluene	0.23	1.07	0.21	0.44
o-Xylene	0.26	1.00	0.25	0.51
m-Xylene	0.26	1.00	0.24	0.50
p-Xylene	0.29	1.00	0.28	0.57
1,2,3-Trimethylbenzene	0.13	1.00	0.13	0.26
1,2,4-Trimethylbenzene	0.27	1.00	0.27	0.54
Mesitylene	0.26	1.00	0.23	0.49
1,2,4,5-Tetramethylbenzene	0.28	1.00	0.24	0.52
1,2,3,5-Tetramethylbenzene	0.19	1.00	0.19	0.38
1,2,3,4-Tetramethylbenzene	0.13	1.00	0.11	0.24
Pentamethylbenzene	0.075	1.00	0.085	0.16
Hexamethylbenzene	<0.01			

[a] Initial *cis*-2-pentene concentration 0.05 M. Conversions of C to T were less than 3%.

[b] Initial *trans*-2-pentene concentration 0.05 M. Conversions of T to C were less than 3%.

That the processes involving quenching of triplets by xenon [eqs. (21-23)] are unimportant is evidenced by the absence of significant

$$\underset{\wedge}{A}^{*(3)} + \underset{\wedge}{H} \xrightarrow{k_{21}} \underset{\wedge}{A}_0 + \underset{\wedge}{H} \tag{21}$$

$$\underset{\wedge}{C}^{*(3)} + \underset{\wedge}{H} \xrightarrow{k_{22}} \underset{\wedge}{C} + \underset{\wedge}{H} \tag{22}$$

$$\underset{\wedge}{C}^{*(3)} + \underset{\wedge}{H} \xrightarrow{k_{23}} \underset{\wedge}{T} + \underset{\wedge}{H} \tag{23}$$

curvature in the plots of eq. (15) (Figures 1 and 2). Processes in eqs. (21) and (22) predict upward curvature and that in eq. (23) downward curvature with increasing xenon concentration.

Fluorescence Rate Constants

Reiser and Leyshon[8] have discussed the correlation of the radiative rate constants ($k_f = k_2$) of the methyl benzenes with the symmetry of the substitution pattern. As pointed out by these authors, the treatment of extinction coefficients by Petruska[15] and by Murrell[16] provides an explanation for this correlation. Perturbations of E_{2g} symmetry (in D_{6h}) mix the $^1B_{2u}$ and $^1E_{1u}$ singlet states of benzene, allowing the symmetry forbidden $^1B_{2u} \leftarrow {}^1A_{1g}$ ($S_1 \leftarrow S_0$) absorption to gain intensity from the allowed $^1E_{1u} \leftarrow {}^1A_{1g}$ ($S_3 \leftarrow S_0$) transition. In benzene, this perturbation is vibronic in nature. Treating the substituents as perturbations on the π-electron symmetry of the $^1B_{2u}$ state of benzene, Petruska and Murrell demonstrated that the absorption intensities of homo-substituted benzenes may be described by an equation of the form [eq. (24)]:

$$I_{tot} = I_{vib} + \alpha I_{subst}(\text{toluene}) \tag{24}$$

The total intensity is the sum of a "vibronic" intensity and a substituent induced "electronic" intensity; α is a parameter whose magnitude is related to the relative content of E_{2g} symmetry in a given substituent pattern. Values of α (relative to toluene) are listed and experimental and calculated values of $(I_{tot} - I_{vib})$ are compared in Table V.

That the fluorescence rates will be affected in a similar manner is suggested by theoretical expressions, such as the Strickler-Berg equation,[17] which relate k_f to the absorption intensity. Quantitative correlation of this model with the fluorescence rates cannot be expected because (a) the relationship between k_f and absorption intensities is nontrivial,[17] (b) differences in ground-state and excited-state geometry are not accounted for, and (c) the presence of solvent induced "electronic" intensity[18] has been ignored. As can be seen from Figure 5, the correlation is qualitative, but reasonable.

Intersystem Crossing Rates

The development of general theoretical models for the description and discussion of radiationless transitions in aromatic hydrocarbons has been of great interest for more than a decade. For experimental and theoretical reasons, most of the activity has concentrated on $T_1 \rightsquigarrow S_0$ radiationless decay. Although a comprehensive treatment of intersystem crossing in aromatic hydrocarbons has recently appeared[19,20,21], the discussion of $S_1 \rightsquigarrow T_x$ intersystem crossing in benzene is inadequate for our purposes. Indeed, since the discussion by Robinson and Frosch,[22] there has been relatively little progress in the description of intersystem crossing from S_1 in benzene.

Table V

Comparison of experimental and calculated changes in the oscillator strength of the $S_0 \rightarrow S_1$ absorption of the methyl benzenes.[a]

Sensitizer	α	$(I_{tot} - I_{vib}) \times 10^4$ Calculated	$(I_{tot} - I_{vib}) \times 10^4$ Experimental
Benzene	0	0	0
Toluene	1	10	10
o-Xylene	1	10	11
m-Xylene	1	10	12
p-Xylene	1	40	34
1,2,3-Trimethylbenzene	0	0	0
1,2,4-Trimethylbenzene	3	30	30
Mesitylene	0	0	0
1,2,4,5-Tetramethylbenzene	4	40	50
1,2,3,5-Tetramethylbenzene	1	10	10
1,2,3,4-Tetramethylbenzene	1	10	13
Pentamethylbenzene	1	10	10
Hexamethylbenzene	0	0	0

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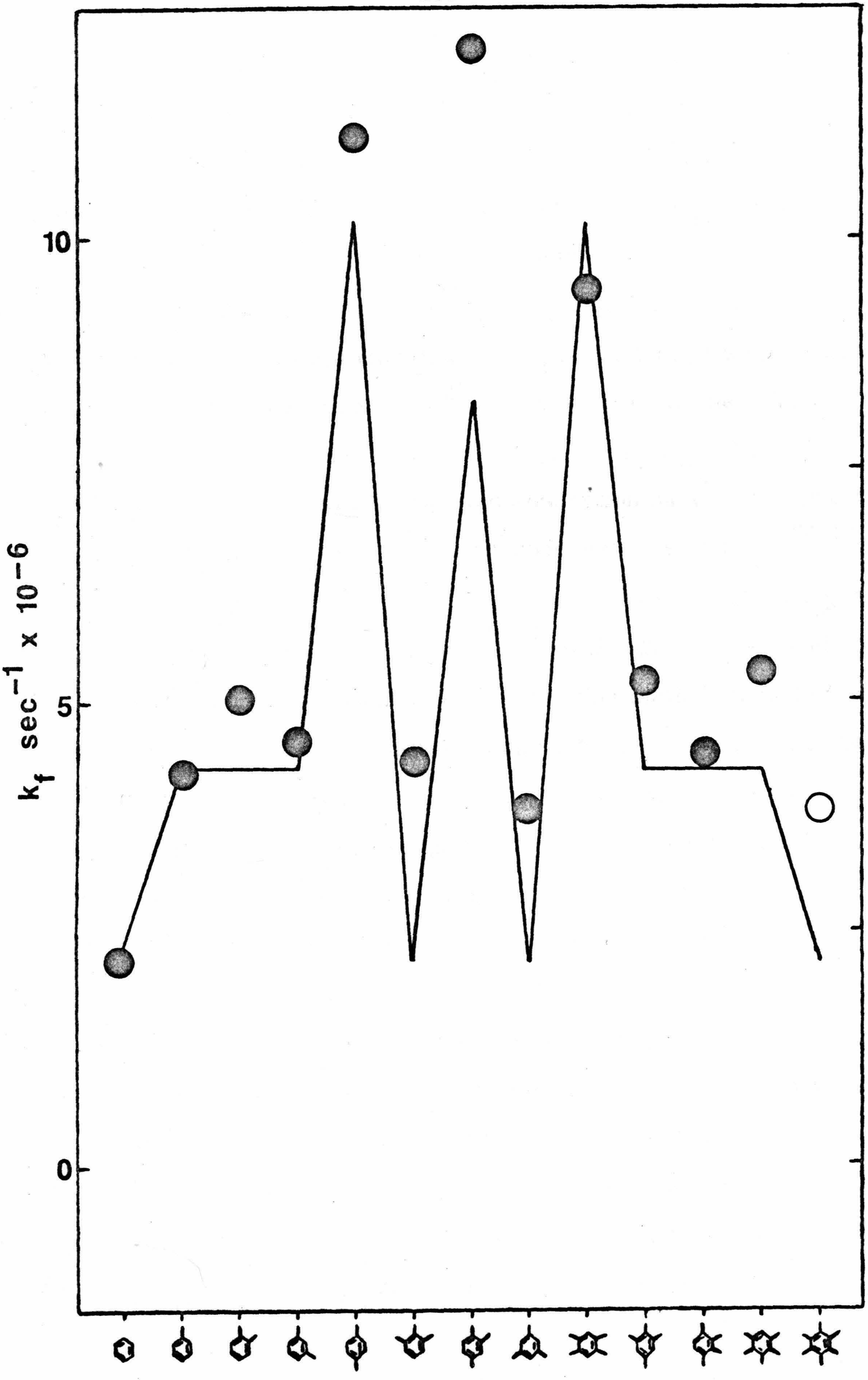
[a] Isoöctane solution. Data of reference 15.

Figure 5

Correlation of the Fluorescence Rates with the Predictions of Symmetry for the Methyl Benzenes


k_f sec^{-1} x 10^{-6}
10
5
0

It is evident from Figure 3 that the effects of methyl substitution on k_f and the intersystem crossing rates ($k_{isc} = k_5$) are qualitatively similar. The data in Table VI further indicate that the strength of the substituent perturbation plays a role; thus, both k_f and k_{isc} for anisole and fluorobenzene are enhanced relative to toluene.

Symmetry-dependent changes in energy gaps appear to be too small to explain the observed variation of k_{isc}. An energy level diagram for benzene is shown in Figure 6.[15,23] Figure 7 depicts the effects of methyl substitution on the energies of S_1 (^1L_b), S_2 (^1L_a), S_3 (^1B), and T_1 (^3L_a). Singlet energies are taken from absorption data[15] and lowest triplet energies from low-temperature phosphorescence data.[23,24,25] Changes in the energies of these states are small and are largely determined by the number of methyl groups.[15,24] Although the S_1-S_3 and S_1-S_2 energy gaps decrease slightly with increasing methyl substitution, the S_1-T_1 energy gap remains relatively constant. No experimental data exist for the effect of methylation on T_2 ($^3E_{1u}$ in benzene); if, by analogy the T_1-T_2 energy gap decreases slightly with increasing methyl substitution, an increase in the S_1-T_2 energy gap is predicted.

The effects of temperature and perdeuteration on k_{isc} are small. Sandros[26] has shown that k_{isc} (benzene-h_6)/k_{isc} (benzene-d_6) = 1.16 in cyclohexane solution. An activation energy of 0.097 eV and a pre-exponential factor of 3.2×10^8 sec^{-1} have been reported for benzene intersystem crossing (cyclohexane solution) by Cundall.[14] For toluene and tetralin (methylcyclohexane solution), k_{isc} is insensitive to temperature within experimental error.[27] It is therefore concluded that the observed variations of k_{isc} are not attributable to an activated process.

Figure 6

Energy Levels of Benzene

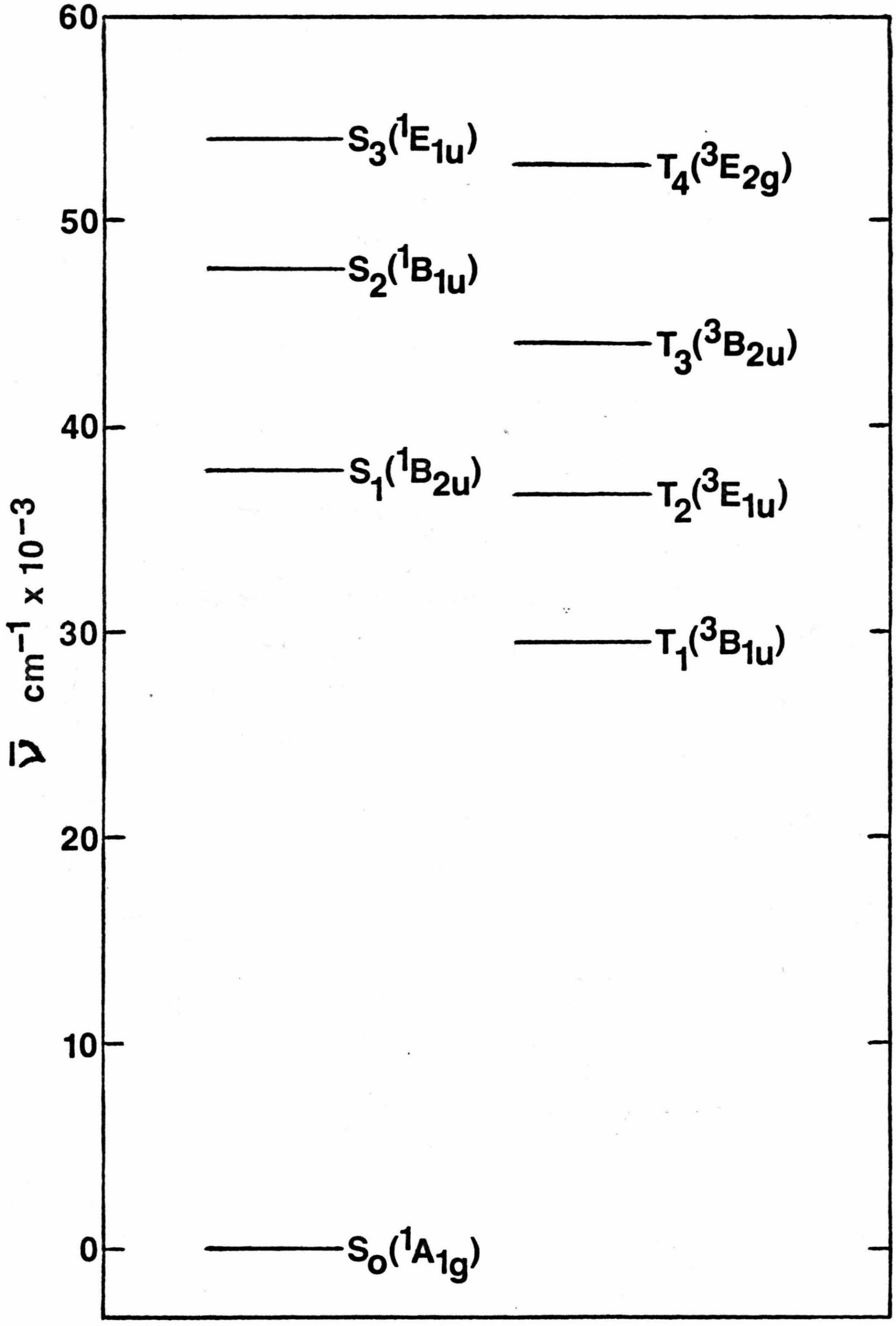
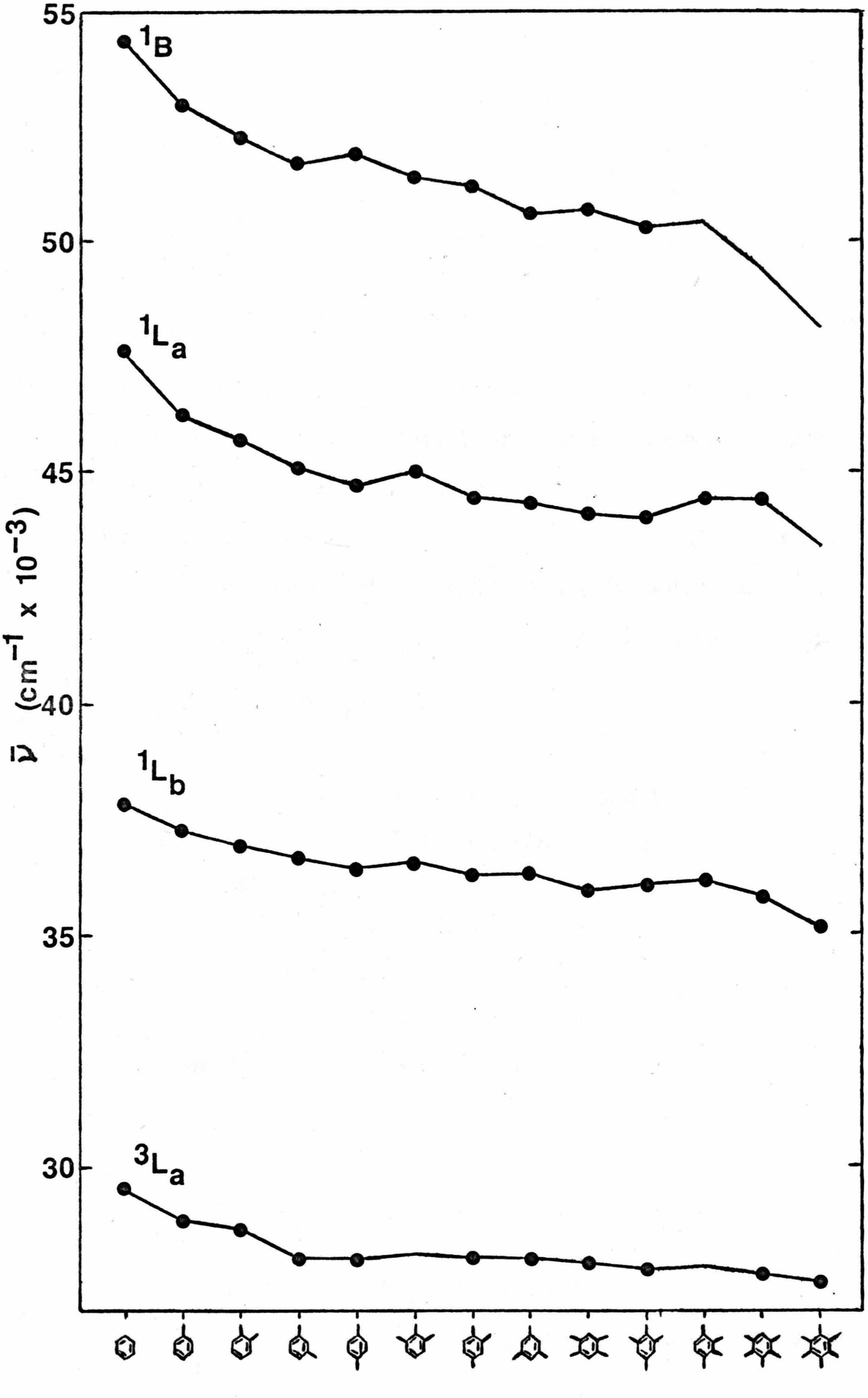

60
50
40
30
20
10
0
$\bar{\nu}$ cm^{-1} x 10^{-3}
$S_3(^1E_{1u})$
$S_2(^1B_{1u})$
$S_1(^1B_{2u})$
$S_o(^1A_{1g})$
$T_4(^3E_{2g})$
$T_3(^3B_{2u})$
$T_2(^3E_{1u})$
$T_1(^3B_{1u})$

Figure 7

Energy Levels of the Methyl Benzenes


^1B
^1L_a
^1L_b
^3L_a
$\bar{\nu}$ (cm^{-1} x 10^{-3})
55
50
45
40
35
30

Using the perturbation treatments of the radiative transitions[15,24] and Robinson-Frosch theory,[22] mechanisms compatible with our data may be formulated. The overall rate of intersystem crossing from S_1 (k_{isc}) is given by eq. (25),[28] where β represents the electronic factor

$$k_{isc} = k_{isc}(S_2 \rightarrow T_1) + k_{isc}(S_1 \rightarrow T_2) = k_1F_1(\beta_1)^2 + k_2F_2(\beta_2)^2 \qquad (25)$$

and F the Franck-Condon factor. Although the observed variation in k_{isc} could arise from variations in either F or β, the correlation with k_f favors a mechanism involving the latter.

Treating the methyl groups as perturbations on the benzene states, S_1 for the methyl benzenes is described by eq. (26), where the ψ^0 are unperturbed benzene states and λ_v and λ_s denote mixing due to vibronic

$$\psi_{S_1} = \psi^0_{{}^1B_{2u}} + (\lambda_v + \lambda_s)\psi^0_{{}^1E_{1u}} \qquad (26)$$

and substituent perturbations, respectively. T_1 and T_2 may be represented in a similar fashion [eqs. (27) and (28)]. Coupling S_1 and T_1 via

$$\psi_{T_1} = \psi^0_{{}^3B_{1u}} + (\lambda'_v + \lambda'_s)\psi^0_{{}^1E_{1u}} \qquad (27)$$

$$\psi_{T_2} = \psi^0_{{}^3E_{1u}} + (\lambda''_v + \lambda''_s)\psi^0_{{}^3B_{1u}} \qquad (28)$$

the spin-orbit operator (H_{so}) gives eq. (29). Since ${}^1B_{2u} \rightarrow {}^3B_{1u}$

$$\langle\psi_{T_1}|H_{so}|\psi_{S_1}\rangle$$

$$= \langle\psi^0_{{}^3B_{1u}}|H_{so}|\psi^0_{{}^1B_{2u}}\rangle + (\lambda_v + \lambda_s)(\lambda'_v + \lambda'_s)\,\langle\psi^0_{{}^3E_{1u}}|H_{so}|\psi^0_{{}^1E_{1u}}\rangle \qquad (29)$$

intersystem crossing is orbitally allowed, the first term in eq. (29) should dominate.[25] Since the S_1-T_1 energy gap is relatively constant, large variations in F_1 would not be expected. Therefore, $k_{isc}(S_1 \rightarrow T_1)$ should be relatively insensitive to methyl substitution and be given by eq. (30).

$$k_{isc}(S_1 \rightarrow T_1) \approx k_1(\langle \psi^0_{3_{B_{1u}}} | H_{so} | \psi^0_{1_{B_{2u}}} \rangle)^2 \quad . \tag{30}$$

Coupling S_1 and T_2 via H_{so} [eq. (31)] provides two terms

$$\begin{aligned}\langle T_2 | H_{so} | S_1 \rangle &= (\lambda_v + \lambda_s) \langle \psi^0_{3_{E_{1u}}} | H_{so} | \psi^0_{1_{E_{1u}}} \rangle \\ &\quad + (\lambda''_v + \lambda''_s) \langle \psi^0_{3_{B_{1u}}} | H_{so} | \psi^0_{1_{B_{2u}}} \rangle \quad .\end{aligned} \tag{31}$$

Since $(\lambda_s)^2$ is related to α^{15} [eq. (32)],

$$\frac{(\lambda_s)^2}{(\lambda_s(\text{toluene}))^2} = \alpha \frac{\Delta E_{T_1-T_2}(\text{toluene})}{\Delta E_{T_1-T_2}} \tag{32}$$

either or both of these terms could contribute to the observed variation of k_{isc} [eq. (33)].

$$\begin{aligned}k_{isc} &= k_{isc}(S_1 \rightarrow T_1) + k_2[(\lambda_v + \lambda_s) \langle \psi^0_{3_{E_{1u}}} | H_{so} | \psi^0_{1_{E_{1u}}} \rangle \\ &\quad + (\lambda''_v + \lambda''_s) \langle \psi^0_{3_{B_{1u}}} | H_{so} | \psi^0_{1_{B_{2u}}} \rangle]^2 \quad .\end{aligned} \tag{33}$$

Since the matrix elements for $^1B_{2u}$ - $^3B_{1u}$ and $^1E_{1u}$ - $^3E_{1u}$ spin-orbit coupling have been evaluated,^{29} eq. (33) may be reduced somewhat [eq. (34)]. If the variation of the T_1 - T_2 energy gap with methyl

$$k_{isc} = k_1F_1(0.11) + k_2F_2[(\lambda_v + \lambda_s)(0.41) + (\lambda''_v + \lambda''_s)(0.33)]^2 \tag{34}$$

substitution were known and if reliable estimates of the Franck-Condon factors were available, further quantification of eq. (34) might be profitable. An additional complication is the absence of any experimental data regarding the relative contributions of $S_1 \rightarrow T_1$ and $S_1 \rightarrow T_2$ intersystem crossing in benzene itself. However, noting [eq. (33)] that $k_{isc}(S_1 \rightarrow T_1) \leqslant k_{isc}(\text{benzene})$, this treatment implies that (with the possible exception of 1,2,3-trimethylbenzene) $S_1 \rightarrow T_2$ intersystem crossing is a significant process in the methyl benzenes. For durene, 1,2,4-trimethylbenzene, and the isomeric xylenes this route is predicted to be dominant.

Internal Conversion Rates

The efficient internal conversion in benzene has been the subject of a number of reviews.[30,31,32] There is general agreement that the process is dominated by crossing to isomeric potential surfaces and that vibrational deformations of the planar ring structure are involved. Small yields of products have been observed.

Birks[32] has presented an interesting analysis of the effects of medium, temperature, and excitation wavelength on the internal conversion process. For $\lambda_{ex} \geqslant 250$ nm and $p \geqslant 10$ torr in the gas phase, ϕ_f is relatively constant for benzene and the sum of ϕ_f and ϕ_{isc} is about 0.9. At shorter wavelengths, ϕ_f decreases and is negligible for $\lambda_{ex} \leqslant 240$ nm. For benzene in a rigid glass at 77°K,[33] the ratio of ϕ_f and ϕ_{isc} is independent of excitation wavelength. ϕ_f is constant for longer excitation wavelengths, but decreases for $\lambda_{ex} \leqslant 243$ nm, reaching a minimum at 210 nm. The sum of ϕ_f and ϕ_{isc} is about 0.9 for $\lambda_{ex} > 250$ nm.[34] For cyclohexane solution at room temperature, ϕ_f is independent of excitation wavelength for $\lambda_{ex} \geqslant 225$ nm, but decreases rapidly at shorter wavelengths.[9] The internal conversion process has an activation energy (E_a) of 0.325 eV and a pre-expenential factor of 7.9×10^{12} sec^{-1}.[14] Association of the decrease in ϕ_f for $\lambda_{ex} < 245$ nm in the gas phase and in a rigid glass with the onset of the internal conversion process is consistent with the observed activation energy in solution ($E_{S_1} + E_a$ = 40,500 cm^{-1} = 247 nm). Competitive vibrational relaxation in solution accounts for the constancy of ϕ_f for $\lambda_{ex} \geqslant 225$ nm. Collisional activation contributes to the greater yield of internal conversion in solution.

The internal conversion rates ($k_d = k_3$) are plotted as their reciprocals in Figure 4 in order to make the symmetry correlation more apparent. Two other trends are of interest: (a) k_d generally increases with increasing methyl substitution; (b) the data in Table VI demonstrate that k_d is relatively insensitive to the magnitude of k_f. In terms of the theory of radiationless transitions, these data implicate changes in the Franck-Condon factors as the source of the inverse symmetry dependence.

Concluding Remarks

This study represents the first systematic study of intersystem crossing from S_1 of benzene derivatives. It is hoped that these results will contribute to theoretical discussion of intersystem crossing and to a better understanding of the non-radiative decay of benzene derivatives.

Table VI

Quantum yields and decay rates for deactivation of S_1 of monosubstituted benzenes.

Aromatic	ϕ_f	ϕ_{isc}	ϕ_d[a]	T_f (ns)	k_f[b]	k_{isc}[b]	kd[b]
					(sec^{-1} × 10^{-6})		
Toluene[c]	0.14	0.51	0.35	34	4.1	15	10
Fluorobenzene	0.11[d]	0.80 (1)	0.09	8 (38)	14	100	11
Anisole	0.24 (6)	0.74 (6)	(0.02)	8.3 (38)	30	90	2

[a] Calculated from $\phi_d = 1 - (\phi_f + \phi_{isc})$.

[b] ± 15-20%. Calculated from eq. (17).

[c] This work.

[d] Data of Berlman[38] as corrected by Birks (reference 23, p. 122).

EXPERIMENTAL SECTION

Materials

Cyclohexane (Matheson Coleman and Bell (MCB), Spectroquality) was purified by the method of Murray and Keller,[35] followed by careful distillation through an 80 cm spinning band column to remove saturated impurities which interfered with the analysis of the pentenes. Distillation of two liters of cyclohexane required two to three weeks and yielded 700-1000 ml of usable material. n-Pentane (Phillips, 99%) was purified by the method of Murray and Keller,[35] followed by distillation from lithium aluminum hydride. Cis-2-pentene (Phillips, 99.9%) and trans-2-pentene (Chemical Samples Co. (CS), 99.9%) were distilled from lithium aluminum hydride and stored at < 0° until use. No diene impurities (< 0.01%) could be detected by gas chromatography (glpc). Xenon (Airco analyzed reagent grade) was used as received; the lot analysis supplied indicated 12 ppm krypton as the only mass spectral impurity.

Sensitizers

Benzene (MCB, Spectroquality) was purified by the Saltiel-Metts photochlorination technique[36] and distilled from sodium prior to use. Mesitylene (Aldrich Gold Label, 99+%) was distilled from sodium. The other methyl benzenes were used as received: compound (supplier, stated purity); toluene (Harleco, Fluorimetric Grade); o-xylene (James Hinton (JH), 99.85%); m-xylene (JH, 99.7%); p-xylene (CS, 99.6%); 1,2,4,5-tetramethylbenzene (Aldrich, zone refined, 99.9+%); 1,2,3,5-tetramethylbenzene (CS, 99.5%); 1,2,3,4-tetramethylbenzene (CS, 99%);

pentamethylbenzene (Aldrich, 99%); hexamethylbenzene (Aldrich, 99+%).

Apparatus

Absorption spectra were determined with a Cary Model 14 spectrophotometer. Relative fluorescence intensities were determined with a Hitachi-Perkin Elmer MPF-3 fluorescence spectrophotometer. Fluorescence lifetimes were measured with a TRW Model 31A nanosecond spectral source (D_2 lamp) coupled to a Tektronix Type 556 dual-beam oscilliscope. Glpc analyses were performed with a Hewlett-Packard Model 700 gas chromatograph (flame-ionization detector); peak integrals were measured by means of a Hewlett-Packard Model 3307B electronic integrator.

Procedure for Determination of ϕ_{isc}

A cyclohexane stock solution of the aromatic sensitizer with an optical density of about 11 at 254 nm[37] was prepared (solution I). ϵ_{254} was either taken from the data of Berlman[38] or determined from the absorption spectrum. A 2.00 ml aliquot of solution I was diluted to 10.0 ml with cyclohexane (solution II). A 5.00 ml aliquot of solution I, 5.0 μl of n-pentane (internal standard), and 140 μl of <u>cis</u>-2-pentene (0.05 M) were diluted to 25.0 ml with cyclohexane (solution III). A set of matched 13 mm quartz tubes (tubes A-H) with graded glass seals, Pyrex constrictions, grease seals, and ground glass joints was used for each determination. 4.0 ml aliquots of solution II were added by syringe to tubes A and B; 4.0 ml aliquots of solution III were similarly added to tubes C-H. The remaining portion of solution III served as the blank for the glpc analysis. The tubes were degassed on a mercury-free vacuum line by two freeze-pump-thaw cycles at 2×10^{-4} torr and two cycles with an oil diffusion pump at $< 5 \times 10^{-6}$ torr. The xenon flask was connected to the vacuum line via a short glass tube of known volume (2.5 ml) between two stopcocks. After the fourth degassing cycle, the tubes and the xenon flask were isolated from the remainder of the vacuum line. By alternately opening and closing the stopcocks to the xenon bulb, any number of 2.5 ml aliquots of xenon could be distilled into a selected tube. In this manner, increasing amounts of xenon were added to tubes E-H. All eight tubes were then sealed without being reopened to the vacuum line.

All measurements were carried out at room temperature (24 ± 1°). After equilibrating for several hours in the dark, relative fluorescence spectra (254 nm excitation) were recorded. F^0, F', and F were obtained from peak intensities for tubes A-B, C-D, and E-H, respectively. Tubes C-H were then irradiated simultaneously at 254 nm in a mery-go-round apparatus.[39] Light intensities were monitored by potassium ferrioxalate actinometry;[40] the quantum yield for ferrous ion production at 254 nm was taken to be 1.25. Conversions of cis-2-pentene to trans-2-pentene were low (< 5%) in all cases. Trans-2-pentene analyses were performed by glpc on a tandem column consisting of 7 in × 1/8 in of 10% UCW-98, 22 ft × 1/8 in of 25% β,β'-oxydipropionitrile ($\beta\beta'$), and 15 ft × 1/8 in of 25% $\beta\beta'$ plus 5% $AgNO_3$, all on Chromosorb W, operated at room temperature. Peak areas of trans-2-pentene relative to n-pentane gave Y_T' (tubes C-D) and Y_T (tubes E-H). Data were treated graphically according to eq. (15) to obtain ϕ_{isc}.

Determination of Isomerization Quantum Yields

Cis to trans and trans to cis initial quantum yields ($\phi_{c\rightarrow t}$ and $\phi_{t\rightarrow c}$) were measured at an initial olefin concentration of 0.05 M. Values of $\phi_{c\rightarrow t}$ were determined from Y_T' and the measured light intensity, correcting for singlet quenching and gc detector response. Values of $\phi_{t\rightarrow c}$ were obtained in the following manner.[41] A cyclohexane stock solution of the sensitizer with an optical density of about 5.5 at 254 nm was prepared (solution IV). 4.00 ml of solution IV were diluted to 10.0 ml with cyclohexane (solution V). 4.00 ml of solution IV, 2.0 μl of n-pentane, and 56 μl of trans-2-pentene were diluted to 10.0 ml (solution VI). Duplicate 4.0 ml aliquots of solutions V and VI were added by syringe to matched 13 mm quartz tubes. The solutions were degassed by two freeze-pump-thaw cycles at 2×10^{-4} torr and one cycle with the diffusion pump and the tubes sealed under a final pressure of $< 5 \times 10^{-6}$ torr. Fluorescence spectra (254 nm excitation) were recorded and the tubes containing solution VI irradiated at 254 nm. Conversions were about 2%. For the cis-2-pentene analyses, the 15 ft × 1/8 in ββ′-$AgNO_3$ portion of the tandem column above was replaced by 20 ft × 1/8 in of 25% ββ′ plus 5% $AgNO_3$ on Chromosorb P. An unirradiated portion of solution VI served as the blank for the glpc analysis. Values of $\phi_{t\rightarrow c}$ were determined from the peak areas for cis-2-pentene relative to n-pentane and the measured light intensity, correcting for singlet quenching and gc detector response.

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