Therefore, it is difficult to use an exciplex model to explain the intermolecular triplet energy transfer processes in the gas phase as presently discussed.

Future Studies

The exchange interaction mechanism has given the most satisfactory account of most of the observed rate data and the spectral data for the intermolecular triplet energy transfer processes in the gas phase. In order to test this mechanism more thoroughly, however, more precise and extensive rate measurements must be carried out and a consistent and precise set of the electron energy-loss cross section measurements for all of the acceptor molecules concerned must be obtained. Particularly, isotopic substitution studies would be extremely valuable. It would also be useful to study the temperature effects on rates, provided that the necessary lifetime data for the excited donor molecules at varying temperatures are available.

Acknowledgment. The financial support for this research by the Petroleum Research Fund, administered by the American Chemical Society through Grant No. 3852-A5, is greatly appreciated.

Intramolecular Excimer Formation and Fluorescence Quenching in Dinaphthylalkanes[1]

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Abstract: The fluorescence spectra of various dinaphthylalkanes have been studied over the temperature range −100–100°. Strong intramolecular excimer formation is found only in the two symmetrical 1,3-dinaphthylpropanes, which implies that the stable excimer configuration is the symmetrical sandwich arrangement. Thermally activated self-quenching of fluorescence is important only in the two species which form stable excimers. The quenching path probably does not involve intersystem crossing to a triplet state and transient photodimer formation is suggested.

The question of the geometry of an excimer consisting of two identical (or nearly so) aromatic hydrocarbon nuclei has been discussed in the literature but has been largely unapproached from an experimental viewpoint. A sandwich configuration with an interplanar spacing less than the normal graphite distance of 3.5 Å was suggested by Ferguson[2] in his study of the pyrene crystal fluorescence. However there has been little work done to determine if there is a preference for a particular orientation of the two hydrocarbon nuclei with respect to each other and what such a preference might be. Various theoretical treatments[3–5] of the excimer pair have favored the symmetrical sandwich configuration which gives the largest exciton splitting. However Birks has suggested[6] that the preferred orientation might have one molecule displaced considerably (*ca.* 1.4 Å) from the other, along one of the molecular axes, so as to minimize van der Waals repulsion between corresponding carbon atoms in the two molecules.

The geometry of the excimer pair in the crystal is not necessarily that which would be favored in solution because of the constraints imposed by the lattice. Similarly, the geometries of the various ground state anthracene pairs in rigid glasses do not fix the geometries of the excimers although one can make some qualitative statements regarding the latter. Thus the anthracene pair, produced by the photolytic dissociation of dianthracene in a rigid glass, is known to have the symmetrical (long and short axes parallel) sandwich arrangement in the ground state.[7,8] It is unlikely that there could be any large rotation about the axis perpendicular to both rings during the lifetime of the excited state, simply because of the high viscosity of the surrounding medium. However one cannot preclude the possibility of small rotations and/or translations during conversion to the excimer. In this case the lifetime[9] (about 20 times the monomer lifetime) of the excimer indicates that the molecular axes must be essentially parallel. This is in accord with the prediction of the simple exciton model where the transition from the lower lying level to the ground state has no transition moment and is forbidden. A small rotation would increase the transition moment, as has been suggested by Chandra and Lim.[3]

The ground state sandwich dimer of 9,10-dichloroanthracene in a rigid matrix at low temperature is rather different from that of anthracene; here the molecular axes are angled at 60°.[8] This is presumably a reflection of van der Waals repulsion between adjacent chlorine atoms. These interactions would be even

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[1] Presented in part at the 156th National Meeting of the American Chemical Society, Division of Physical Chemistry, Atlantic City, N. J., Sept 1968.

[2] J. Ferguson, *J. Chem. Phys.*, 28, 765 (1958).

[3] A. K. Chandra and E. C. Lim, *ibid.*, 49, 5066 (1968).

[4] J. N. Murrell and J. Tanaka, *Mol. Phys.*, 4, 363 (1964).

[5] F. J. Smith, A. T. Armstrong, and S. P. McGlynn, *J. Chem. Phys.*, 44, 442 (1966), and preceding papers.

[6] J. B. Birks, *Nature*, 214, 1187 (1967).

[7] E. A. Chandross, E. G. MacRae, and J. Ferguson, *J. Chem. Phys.*, 45, 3546 (1966).

[8] E. A. Chandross and J. Ferguson, *ibid.*, 45, 3554 (1966).

[9] N. Mataga, Y. Torihashi, and Y. Ota, *Chem. Phys. Lett.*, 1, 385 (1967).

larger in the excited state where the intermolecular spacing is less and it is quite likely that this excimer is angled rather than symmetrical.

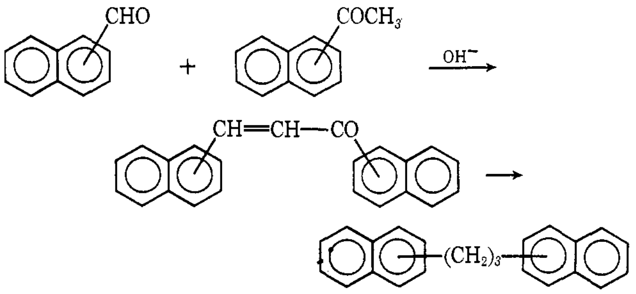
There has been little work done on the geometry of the excimer state in fluid solution. The only approach to this problem that we know of is through a study of intramolecular excimer formation in suitably chosen species. It has been known for a few years that both polystyrene and polyvinylnaphthalene exhibit excimer fluorescence in fluid solution.[10] Further, Hirayama[11] has made a study of the fluorescence spectra of various α,ω-diphenylalkanes, $C_6H_5(CH_2)_nC_6H_5$, and their derivatives in fluid solution at room temperature. Intramolecular excimer formation occurs only when $n = 3$. Hirayama pointed out that the three-carbon chain is the shortest that will allow a sandwich configuration and, further, that the C–H bond repulsions in the chain would be less important in the propane than in the butane. It is also noteworthy that the loss of entropy resulting from intramolecular excimer formation is expected to be substantially less than that for the intermolecular process. This is an important factor because the latter's contribution to the free energy is often large enough to prevent the existence for any appreciable time of excimers in dilute solutions at temperatures where thermally activated quenching and/or chemical reactions could occur.

We have studied intramolecular excimer formation in the dinaphthylalkanes as we thought that we could obtain more information about excimer geometry from this system than could be gotten from the diphenylalkanes. One can have symmetrically substituted dinaphthylalkanes (α,α or β,β) or an unsymmetrical (α,β) compound. The alkyl chain imposes a steric constraint upon the system and by the use of molecular models we can make some qualitative statements about the relative orientations of the naphthalene nuclei that would be possible in the excimer. We used Courtauld space-filling models which have naphthalene nuclei constructed of a single block. The thickness of each block was decreased by removing an amount equivalent to 0.5 Å; this permits the models to attain a 3.0-Å interplanar spacing in a sandwich configuration which should approximate that of the excimer.

We studied the fluorescence behavior of the following compounds: 1,2-di-α-naphthylethane ($\alpha\alpha$DNE); 1,3-di-α-naphthylpropane ($\alpha\alpha$DNP); 1,3-di-β-naphthylpropane ($\beta\beta$DNP); 1-α-naphthyl-3-β-naphthylpropane ($\alpha\beta$DNP); and 1,4-di-α-naphthylbutane ($\alpha\alpha$DNB). The models indicate that in $\alpha\alpha$DNE the two-carbon chain forces the nuclei to have a dihedral angle of *ca.* 45° at their closest approach. In actual fact this could be less but it is unlikely that the geometry could change toward a parallel plane arrangement by very much. In both symmetrical propanes the perfect overlap sandwich configuration with molecular axes parallel is easily achieved. In both the $\alpha\alpha$- and $\beta\beta$DNP excimers it is possible to have some lateral displacement of the naphthalene nuclei from the perfect sandwich configuration. In $\alpha\alpha$DNP the displacement (<0.5 Å) would be along the short axis; in $\beta\beta$DNP it would be along the long axis; again less than a 0.5-Å shift is possible. These displacements are much less than those suggested for the benzene and pyrene excimers.[6] It is also possible to rotate the naphthalene nuclei in both excimers with respect to each other so that the molecular axes are not parallel, generating a series of configurations which would shorten the lifetime of the excimer state as suggested by Lim.[3]

In $\alpha\beta$DNP a sandwich configuration is also attainable but the axes of the two naphthalenes cannot be parallel and still allow more than *ca.* 25% overlap. Fairly good overlap (*ca.* 75%) is possible when the axes are at 45° and various intermediary combinations of overlap and angle seem to be equally accessible. Finally, in $\alpha\alpha$DNB the chain must be deformed to allow the 3-Å symmetrical excimer configuration to be achieved. This configuration also introduces two hydrogen–hydrogen repulsions between the *peri* hydrogen of each ring and the CH_2 group adjacent to that ring. The same H–H interaction is present in $\alpha\alpha$DNP.

Syntheses of the Dinaphthylalkanes. The syntheses of the three previously unknown propanes were accomplished *via* the same route.



Two of the chalcones are known compounds and the third (the $\beta\beta$ isomer) was prepared readily. The reductions of the chalcones were troublesome. It was not possible to hydrogenate two of the chalcones to the alkanes directly. These reactions were not investigated in detail since we were interested in obtaining only small quantities of material and improvements are undoubtedly possible. The dinaphthylpropanes as well as the other compounds were purified by repeated chromatography on silica gel until solutions of these compounds (10^{-2}–10^{-3} *M*) showed no extraneous fluorescence.

Experimental Section

The chalcones were prepared by stirring overnight under nitrogen an alkaline (0.09 *M* NaOH) ethanol solution of naphthaldehyde (0.16 *M*) and acetonaphthone (0.16 *M*). The $\beta\beta$ and $\alpha\beta$ chalcones precipitated from the reaction mixture and were filtered and recrystallized. The $\alpha\alpha$ chalcone precipitated as an oil and was isolated by evaporating the ethanol and subsequent partitioning between ether and water. The chalcone solidified on standing but it could not be recrystallized and it was used without further purification: 1-α-naphthoyl-2-α-naphthylethylene,[12] mp 68–72° (lit. mp 75–81°); 1-β-naphthoyl-2-α-naphthylethylene,[13] mp 162–163° (lit. mp 158–160°); 1-β-naphthoyl-2-β-naphthylethylene, 77% crude yield, mp 201–202° (after recrystallization from benzene–chloroform), ir 1660, 1590 cm^{-1}.

Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23. Found: C, 89.33; H, 5.32.

1,3-Bis(α-naphthyl)propane ($\alpha\alpha$DNP). A solution of the $\alpha\alpha$ chalcone in ethanol (0.065 *M*) was hydrogenated over 5% Pd/C in a Parr shaker (*ca.* 2 atm of H_2). The saturated ketone, 1-α-naphthoyl-2-α-naphthylethane, was obtained (82%) as colorless crystals:

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(10) M. T. Vala, Jr., J. Haebig, and S. A. Rice, *J. Chem. Phys.*, 43, 886 (1965).

(11) F. Hirayama, *ibid.*, 42, 3163 (1965).

(12) L. Wolf and C. Tröltzsch, *J. Prakt. Chem.*, **17**, 69 (1962).

(13) R. H. Wiley, *et al.*, *J. Org. Chem.*, **23**, 732 (1958).

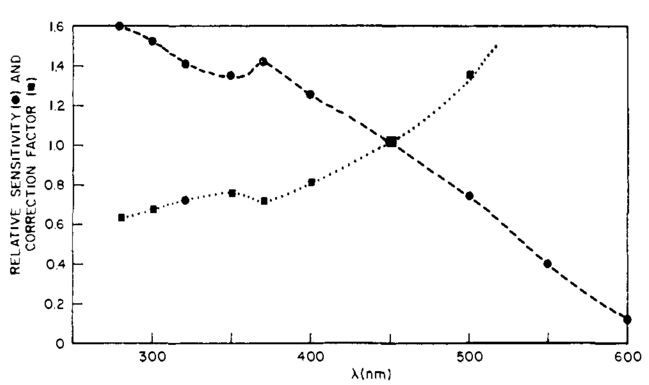

Figure 1. Relative sensitivity *vs.* wavelength and associated correction factors for the spectrometer.

mp 76–77° (after recrystallization from benzene–ethanol); ir 1680, 1600 cm^{-1}.

Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.99; H, 5.90.

The ketone (2 g) was reduced in refluxing (2 hr) diethylene glycol (20 ml) containing hydrazine (1 ml, 95%) and sodium hydroxide (0.9 g). The mixture was diluted with water and extracted with benzene. The yellow oil thus obtained was filtered through silica gel with benzene and gave colorless, crystalline ααDNP (1.6 g). It was recrystallized from benzene–hexane: mp 68.5–69°; λ_{max} (ϵ) 314 (1180), 295 (13,500), 284 (18,300), 273 (14,400) nm; nmr τ (peak, relative area) 7.8 (m, 1), 6.9 (unsymmetrical t, 2), 2.5 (m, 7.9).

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.40; H, 6.83.

1,3-Bis(β-naphthyl)propane (*ββ*DNP). Zinc dust (25 g) was added in small batches to a solution of the ββ chalcone (5 g) in refluxing acetic acid (150 ml). The solution was refluxed for an additional 2 hr, and then it was poured into water and extracted with methylene chloride. This solution was dried and evaporated. The residue was crystallized from carbon tetrachloride to give colorless crystals (1.2 g, 24%) of 1-β-naphthoyl-2-β-naphthylethane, mp 137.5–139°. The analytical sample was recrystallized three times from carbon tetrachloride and sublimed: ir ($CHCl_3$) 1680 cm^{-1}; nmr τ 1.6 (s, 1), 2.4 (m, 13), 6.7 (m, 4). It was not possible to obtain a satisfactory elemental analysis.

Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 87.60; H, 5.80.

The ketone was reduced to ββDNP by the same method used for the αα isomer (97%). A small amount of material with visible fluorescence was removed by chromatography on silica gel with benzene–petroleum ether (40–60°) (1:9) as eluent. The colorless crystals (hexane) had mp 101–101.5°; uv λ_{max} (ϵ) 319 (910), 312 (605), 305 (1025), 287 (7170), 277 (10,850), 267 (10,400), 260 (8860); nmr τ 7.9 (m, 1), 7.3 (unsymmetrical t, 2), 7.4 (m, 7).

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.24; H, 6.88.

1-α-Naphthyl-3-β-naphthylpropane (*αβ*DNP). This isomer was prepared by hydrogenating the chalcone (4.0 g) in warm (*ca.* 50°) acetic acid (180 ml) over 5% Pd/C in a Parr shaker. The mixture was filtered and the filtrate was diluted with water and extracted with methylene chloride. After washing with aqueous sodium carbonate, drying, and evaporating the solvent, an oil was obtained which had three components on a tlc plate. This oil was washed through silica gel with benzene–petroleum ether (1:1) to give a colorless oil: ir ($CHCl_3$) 1600, 1635 cm^{-1}. The oil could not be crystallized and was converted to a trinitrobenzene complex in ethanol. The complex was recrystallized three times (32%) from ethanol, mp 155–156°. It was decomposed by washing a benzene solution through a column of basic alumina. The crystalline solid obtained from the eluate was recrystallized from hexane: mp 57–59°; nmr τ 7.8 (m, 1), 7.1 (unsymmetrical q, 2), 2.5 (m, 7.9); uv 319 (580), 314 (690), 283 (13,000), 274 (12,500).

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.25; H, 7.04.

1,2-Di-α-naphthylethane. Commercial 1-chloromethylnaphthalene was reduced to the ethane (26%, mp 163.5–164.5°, lit. 160–161°) with Mg.[14] The product was recrystallized from methylene chloride–ethanol.

1,4-Di-α-naphthylbutane. 1-Bromo-2-α-naphthylethane was converted into the Grignard reagent in the usual manner. Oxidative dimerization was accomplished with silver chloride.[15] The butane (mp 100–100.5°, lit. 101°, 52%) was chromatographed on neutral alumina with benzene–petroleum ether (1:5) eluent. This removed a small amount of fluorescent impurity present in the crude material. Ethanol was used for crystallization.

Variable Temperature Fluorimeter. The light source is a Bausch and Lomb stabilized xenon arc lamp (150 W) and high-intensity monochromator (200–400-nm grating blazed at 250 nm, F3.5) equipped with a chromatic condenser lens. Fluorescence measurements were made with 90° excitation involving one reflection of the exciting light by a front surface mirror. A small fraction of the exciting light was reflected from a quartz plate onto a masked photomultiplier photometer which revealed any changes in intensity, usually due to arc wander. Slit widths were maintained so as to have a band pass of 3–3.5 nm. The sample fluorescence was focused by a quartz lens into the entrance slit of a Jarrell-Ash 0.25-m grating monochromator. The 300-nm blaze grating of this monochromator was used; the detector was an EMI 6256S photomultiplier powered by a Fluke 412 stabilized power supply operated at 1200 V. The spectral response, determined with a standard quartz–iodine lamp, is given in Figure 1. The curve is fairly flat in the region of interest and the fluorescence spectra are not corrected. A Keithley electrometer was used to amplify the photocurrent (1–100 nA). The samples were contained in 8-mm Supersil tubes equipped with graded seals which were degassed by four freeze–thaw cycles at 1 μ of pressure. The dewar is a flow-through type in which the nitrogen gas used for temperature control is passed through a copper coil immersed in liquid nitrogen and then over a heater wound of nichrome wire on an asbestos covered glass tube. The heater is controlled by a Honeywell Versatronic controller operating from a thermocouple in the sample compartment; independent temperature measurement is carried out by means of a second such thermocouple and a potentiometer. Temperature regulation is easily better than ±1°; no attempt was made to improve this range which is considered to be quite satisfactory for our needs. Spectra were run at 10° intervals, starting at −120°. Ample time was allowed for the stabilization of the sample temperature after it was raised. Variable temperature runs were begun at low temperatures and were frequently returned to these temperatures at the end of a run to check system reproducibility which was usually good to a few per cent. The major difficulty in maintaining reproducibility is wander of the xenon arc. This can be made less troublesome to some extent by defocusing the image of the arc upon the entrance slit of the monochromator, but the monitor photometer is still necessary to warn of changes in intensity. Ratio recording seems to be desirable.

The absorption spectra of the various dinaphthylalkanes are very similar to those of the parent α- or β-methylnaphthalene, both at 77 and at 300 °K, and there are no significant differences. All of the fluorescence spectra were measured with 310-nm exciting light with the dinaphthylalkanes at 1×10^{-3} *M*, α- and β-methylnaphthalene at 2×10^{-3} *M* in 9:1 methylcyclohexane–isopentane. Thus the optical densities of the standard solutions are the same as those of the dinaphthyl derivatives and comparisons can be made directly without worrying about changes in absorption depth and concomitant apparent changes in fluorescence intensity. The mixed solvent was chosen because pure methylcyclohexane frequently caused the quartz tubes to crack upon freezing in liquid nitrogen; the addition of isopentane decreased the likelihood of cracking of the organic glass. The solvents were Matheson Spectrograde and were passed through a silica gel column before use.

Results and Discussion

Low Temperature Fluorescence Behavior (−100–0°). The fluorescence spectra of the various dinaphthylalkanes at low temperatures are given in Figures 4–6, 8, and 9. At or below 173 °K (−100°) each spectrum is identical with that of the respective monomer, α- or β-methylnaphthalene. The shapes and intensities are essentially the same. The fluorescence

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(14) A. M. Khaletskii, *Zh. Obsch. Khim.*, **26**, 762 (1956); *Chem. Abstr.*, **50**, 14670 (1956).

(15) J. H. Gardner and P. Bergstrom, *J. Amer. Chem. Soc.*, **51**, 3375 (1929).

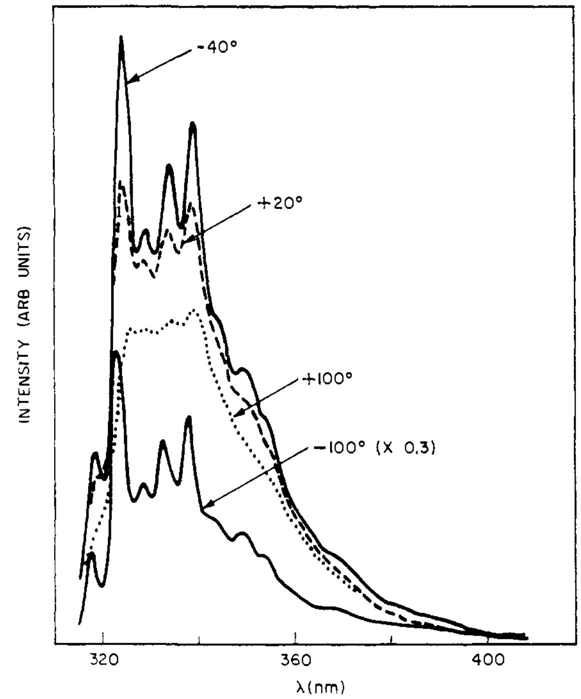

Figure 2. Fluorescence spectrum of 2×10^{-3} M α-methylnaphthalene (αMN) at various temperatures.

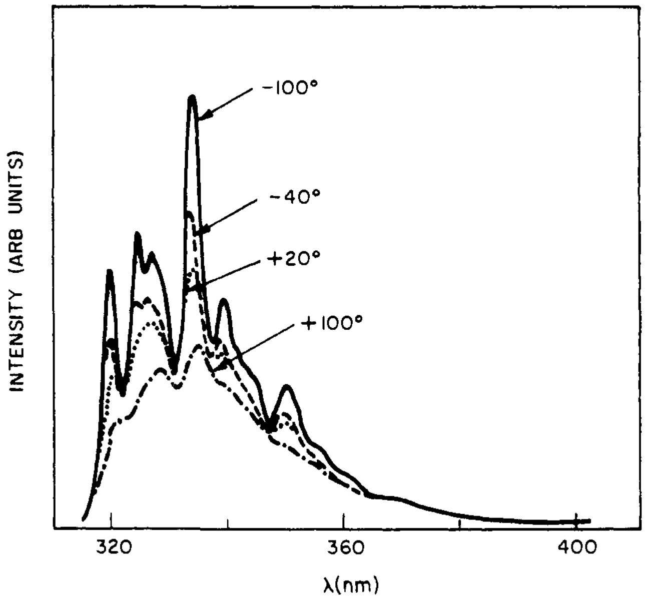

Figure 3. Fluorescence spectrum of 2×10^{-3} M β-methylnaphthalene (βMN) at various temperatures.

of αβDNP has an intensity distribution characteristic of β-methylnaphthalene, which has a lower lying excited state than does α-methylnaphthalene. The spectra of αMN and βMN over a range of temperatures are given in Figures 2 and 3. The latter model compounds show a gradual decrease in fluorescence intensity accompanied by a loss in vibrational structure as the temperature is increased above room temperature. There is no marked exponential decrease; this is characteristic of monomer aromatic hydrocarbon fluorescence.

The spectra of ααDNE (Figure 4) do not show any marked variation from that of αMN except for an increase in thermal quenching. There is no indication for interaction between the naphthalene nuclei in the ground state, and that, if any, in the excited state must be weak.

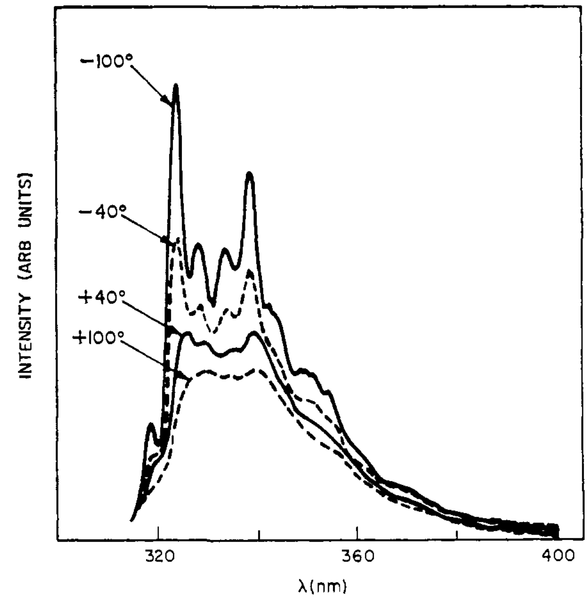

Figure 4. Fluorescence spectrum of 1×10^{-3} M 1,2-bis(α-naphthyl)ethane (ααDNE) at various temperatures.

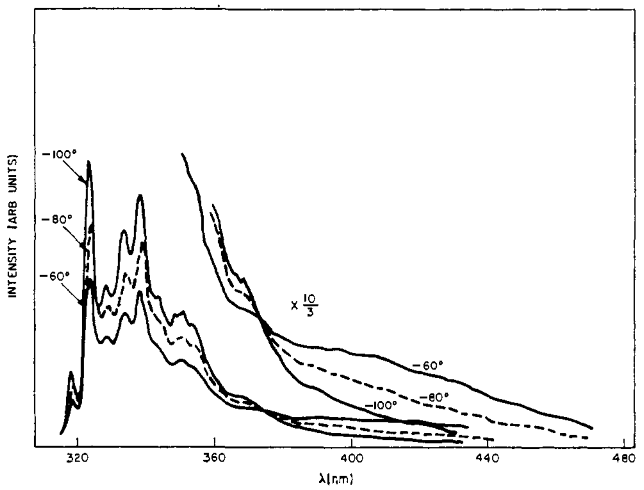

Figure 5. Fluorescence spectrum of 1×10^{-3} M 1,3-bis(α-naphthyl) propane (ααDNP) at various temperatures.

The spectra of both ααDNP (Figure 5) and ββBNP (Figure 6) show a marked variation with temperature above −100° where each has the same fluorescence as the respective monomer. As the temperature is raised there is a steady decrease in monomer fluorescence accompanied by the development of a broad, red-shifted band. The shape of the latter as well as the wavelength for maximum emission is characteristic of the various naphthalene excimers studied previously. Thus it appears that intramolecular excimer formation is an activated process and that the rate of excimer formation begins to compete with monomer fluorescence at temperatures above −100°.

This situation can be treated with a straightforward kinetic analysis analogous to that developed by Stevens and Ban in their study of intermolecular excimers

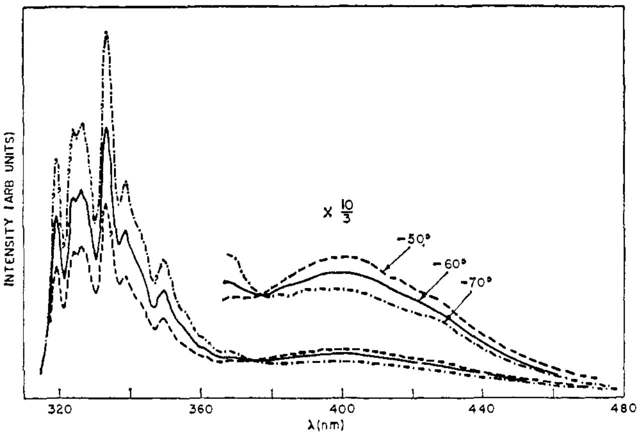

Figure 6. Fluorescence spectrum of 1×10^{-3} *M* 1,3-bis(β-naphthyl)propane ($\beta\beta$DNP) at various temperatures.

formed by substituted naphthalenes.[16] We consider the following processes

$$^1M^* \longrightarrow M + h\nu_M \qquad k_{fM}$$

$$^1M^* + M \underset{d}{\overset{a}{\rightleftharpoons}} {}^1D^* \quad \text{(unimolecular) } k_a,\ k_d$$

$$^1D^* \longrightarrow M + M + h\nu_D \qquad k_{fD}$$

$$^1D^* \longrightarrow M + M + \text{heat} \qquad k_Q$$

Then, using the steady-state approximation

$$\frac{d[^1D^*]}{dt} = 0 = k_a[^1M^*] - (k_d + k_{fD} + k_Q)[^1D^*]$$

Rearrangement gives

$$\frac{[^1D^*]}{[^1M^*]} = \frac{k_a}{k_d + k_Q + k_{fD}}$$

We define F_D to be the fluorescence intensity of the dimer at a given wavelength where only the dimer fluoresces and note that $F_D = C_D k_{fD}[^1D^*]$. The constant contains an instrumental sensitivity term and a factor which converts the intensity at a given wavelength into total integrated fluorescence efficiency; neither of these factors is necessary for our purpose. Then, after defining the analogous F_M, we write

$$\frac{F_D}{F_M} = \frac{C_D}{C_M}\frac{k_a}{k_d + k_Q + k_{fD}}$$

As long as the monomer–excimer spectra have an isoemissive point the various constants will not have changed with temperature.[17] We measured the temperature dependence of monomer fluorescence of 10^{-3} *M* α- and β-methylnaphthalenes over the temperature range to be discussed and found only a slow decrease of intensity with increasing temperature. Further, as long as we find an isoemissive point in the spectra, we infer that quenching processes are not competing with fluorescence; $k_Q \ll k_{fD}$. As the temperature is increased in the range -100 to *ca.* $-30°$ the increasing amount of dimer fluorescence implies that we have not approached the region where dissociation competes with dimer fluorescence; $k_d \ll k_{fD}$. Under these two conditions the equation simplifies to

$$\frac{F_D}{F_M} = C\frac{k_a}{k_{fD}}$$

and $\partial \ln (F_D/F_M)/\partial(1/T) = -E_a/R$ for excimer formation.

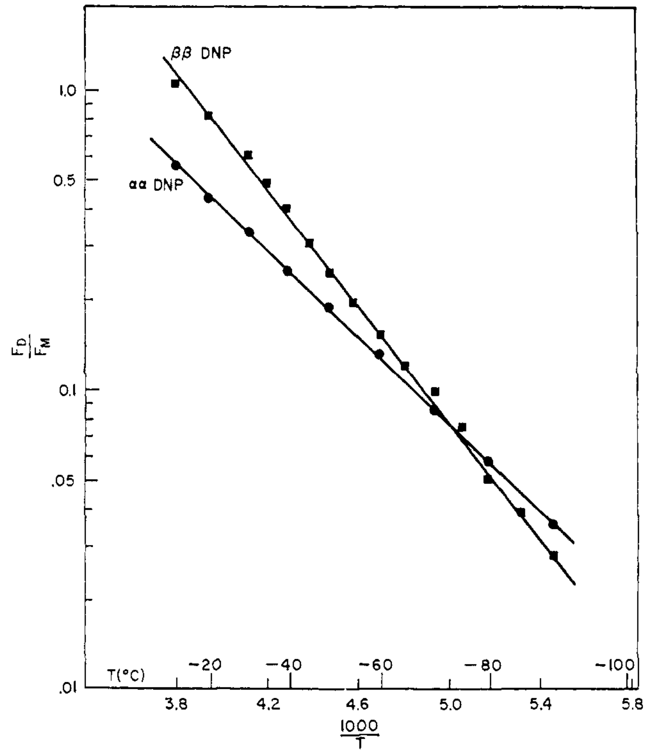

Figure 7. Kinetic plot for the determination of the activation energy for intramolecular excimer formation in $\alpha\alpha$DNP (●) and $\beta\beta$DNP (■).

The data, plotted in this form, are shown in Figure 7. The wavelengths used for the measurements were $\alpha\alpha$DNP, 324 and 425 nm; $\beta\beta$DNP, 319 and 420 nm. The activation energy required for intramolecular excimer formation in $\alpha\alpha$DNP is 3.3 kcal mol^{-1} and that for $\beta\beta$DNP is 4.0 kcal mol^{-1}. These energies are comparable to the rotation barrier in a methylene chain and there does not appear to be any other appreciable activation energy required for excimer formation. This was anticipated as Förster found excimer formation to be diffusion controlled.[18] It is not possible to assess the role of the solvent. Its viscosity would be expected to have an influence and we found that the activation energy for $\alpha\alpha$DNP in ethanol is 4.0 kcal mol^{-1}, presumably reflecting the higher viscosity of the hydroxylic medium. The absorption and fluorescence spectra are not appreciably different from those in the hydrocarbon solvent, indicating that there is no significant change in solvation of the monomer in either the ground or excited state.

The mixed propane, $\alpha\beta$DNP, exhibits little excimer formation. Its temperature-dependent fluorescence spectrum is shown in Figure 8. The excimer band is relatively much weaker than those exhibited by either of the two symmetrical compounds and appears as a red shift in the red side of the monomer fluorescence. The excimer fluorescence decreases as the tem-

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[16] B. Stevens and M. I. Ban, *Trans. Faraday Soc.*, 60, 1515 (1964).

[17] T. D. S. Hamilton and K. Razi Naqvi, *Chem. Phys. Lett.*, 2, 374 (1968).

[18] T. Förster, *Angew. Chem., Int. Ed. Engl.*, 8, 333 (1969).

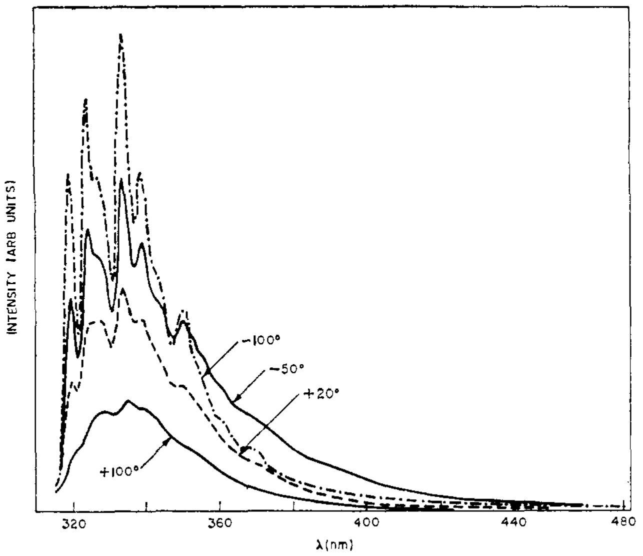

Figure 8. Fluorescence spectrum of 1 × 10^{-3} *M* 1-α-naphthyl-3-β-naphthylpropane (αβDNP) at various temperatures.

perature exceeds −50° and we interpret this as showing that the binding energy is much less than it is in the symmetrical compounds and that, as the temperature is raised, the entropy term outweighs the enthalpy of association so that dissociation to excited monomer is favored. It seems reasonable to assume that the loss of entropy caused by excimer formation should be about the same in all three compounds, and thus the binding energy must be decreased appreciably when the symmetrical sandwich configuration is not attainable. This finding suggests that the latter configuration, or one close to it, is lowest in energy and that the highly offset structure proposed by Birks[6] is not a good one.

The fluorescence spectra of ααDNB (Figure 9) at low temperatures indicate that a weakly bound excimer is formed. It appears, as suggested by Hirayama, that the butane chain destabilizes the excimer because of hydrogen-hydrogen repulsions in the methylene chain which are important in the excimer configuration.

Thermal Quenching of the Excimer Fluorescence. The excimer fluorescence of both αα- and ββDNP exhibits thermal quenching as the temperature is increased toward room temperature. This shows up initially as a shift in the isoemissive point of the spectrum and becomes more noticeable as an overall decrease in intensity as the temperature is raised further. The quenching is apparent at temperatures greater than −30° for the αα isomer but the spectrum is complicated further by an increase in the fraction of monomer fluorescence. Representative spectra are shown in Figure 10. The binding energy of the excimer is not large enough to prevent a monomer-excimer equilibrium from existing at higher temperatures; the change in the equilibrium constant is again a consequence of the $T\Delta S$ term outweighing the ΔH of association. The lower binding energy of the αα excimer, relative to that of the ββ isomer, is attributed to the steric interaction of the hydrogen at C-8 of naphthalene with the neighboring CH_2 group of the propane chain.

The behavior of the ββ excimer is much simpler. At room temperature the fluorescence is almost entirely that of the excimer and the small fraction of monomer fluorescence does not change appreciably as the temperature is raised. However the excimer band shows a marked decrease in intensity with increasing temperature. The spectra are given in Figure 11. The activation energy for the thermal quenching can be estimated, using the same set of equations given above for the analysis of the low temperature behavior.

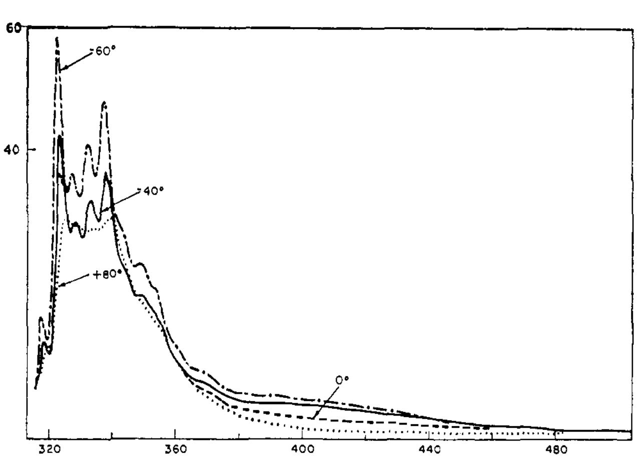

Figure 9. Fluorescence spectrum of 1 × 10^{-3} *M* 1,4-bis(α-naphthyl)butane (ααDNB) at various temperatures.

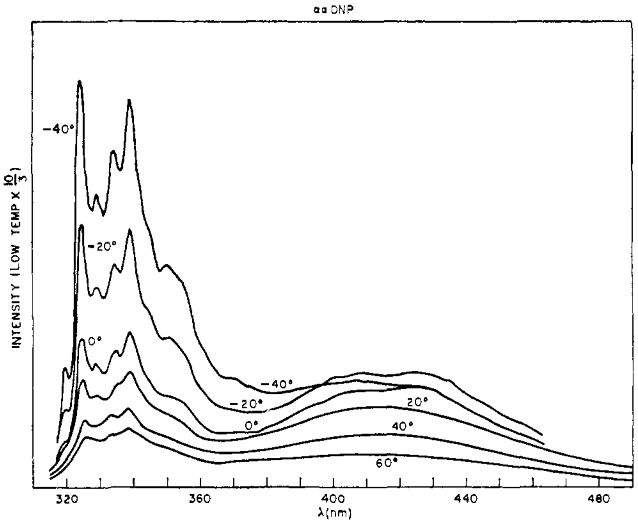

Figure 10. Fluorescence spectrum of ααDNP at higher temperatures showing reversion to monomer and thermal quenching.

The approximations involved are as follows. (1) Thermal quenching is important only at temperatures above that required for complete conversion of excited monomer to excimer. Then k_a is large compared to all other rates involved except intersystem crossing in the monomer and thus $k_a[M^*]$ is a constant, dependent on [M] and light intensity (*I*). (2) Reversion to monomer can be neglected because very little monomer fluorescence is seen ($k_d \ll k_Q$).

The steady-state equation then reduces to

$$0 = \text{constant}[M](I) - (k_{fD} + k_Q)[^1D^*]$$

We can evaluate the first term by considering the data and assuming that at the point where F_D, which is equal to $k_{fD}[^1D^*]$, is a maximum (F_D^0) k_Q is still small compared with k_{fD}. We again assume that k_{fD} is a constant,

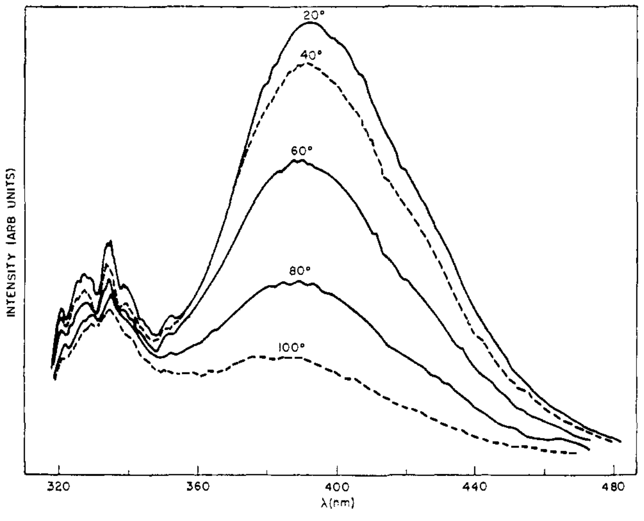

Figure 11. Fluorescence spectrum of $\beta\beta$DNP at higher temperatures showing thermally activated quenching.

independent of temperature. Then

$$0 = \text{constant}[\mathrm{M}](I) - F_{\mathrm{D}}{}^{0}$$

and the steady-state equation becomes

$$0 = F_{\mathrm{D}}{}^{0} - (k_{\mathrm{fD}} + k_{\mathrm{Q}})[{}^{1}\mathrm{D}^{*}]$$

Substituting $k_{\mathrm{fD}}[{}^{1}\mathrm{D}^{*}] = F_{\mathrm{D}}$ gives

$$F_{\mathrm{D}}{}^{0} - F_{\mathrm{D}} = k_{\mathrm{Q}}[{}^{1}\mathrm{D}^{*}]$$

and dividing by $F_{\mathrm{D}} = k_{\mathrm{fD}}[{}^{1}\mathrm{D}^{*}]$ yields

$$\frac{F_{\mathrm{D}}{}^{0}}{F_{\mathrm{D}}} - 1 = \frac{k_{\mathrm{Q}}}{k_{\mathrm{fD}}}$$

whence

$$\frac{\partial \ln\left(\dfrac{F_{\mathrm{D}}{}^{0}}{F_{\mathrm{D}}} - 1\right)}{\partial(1/T)} = \frac{\partial \ln k_{\mathrm{Q}}}{\partial(1/T)} = -E_{\mathrm{aQ}}/R$$

The data are plotted in this manner in Figure 12 and it seems that the errors involved in the assumptions are not too bad. We are not too interested in an exact value of the activation energy for thermal quenching because this quantity by itself does not tell us very much about the path of thermal quenching, but its magnitude does make crossover to a triplet excimer or triplet monomer unlikely.

The paths for fluorescence quenching which proceeds through an excimer state are

$$ {}^{1}\mathrm{D}^{*} \longrightarrow \mathrm{M} + \mathrm{M} + \text{heat} \qquad (1)$$

$$ {}^{1}\mathrm{D}^{*} \longrightarrow \text{photodimer (real or transient)} \qquad (2)$$

$$ {}^{1}\mathrm{D}^{*} \longrightarrow {}^{3}\mathrm{D}^{*} \longrightarrow {}^{3}\mathrm{M}^{*} + \mathrm{M} \qquad (3)$$

The activation energy for thermal quenching of the excimer derived from $\beta\beta$DNP is 12 kcal mol^{-1}. The rate constant for β-methylnaphthalene fluorescence is about 10^{7} sec^{-1}; that for the excimer is about the same.[9,19–21] In order for quenching to compete very effectively with excimer fluorescence, as it does at 100°, the quenching rate must be $>10^{8}$ sec^{-1}. We can then place a lower limit of *ca.* 10^{15} on the preexponential factor. This is larger than the A factor of 10^{13} usual for unimolecular processes and suggests that intersystem crossing (path 3) is not involved because the A factor would then have a spin prohibition of 10^{-3}–10^{-6} and would be expected to be 10^{7}–10^{10}. We did not find any evidence of photodimerization in $\beta\beta$DNP and can only say that the excimer quenching probably involves either path 1 or path 2 with a transient photodimer.

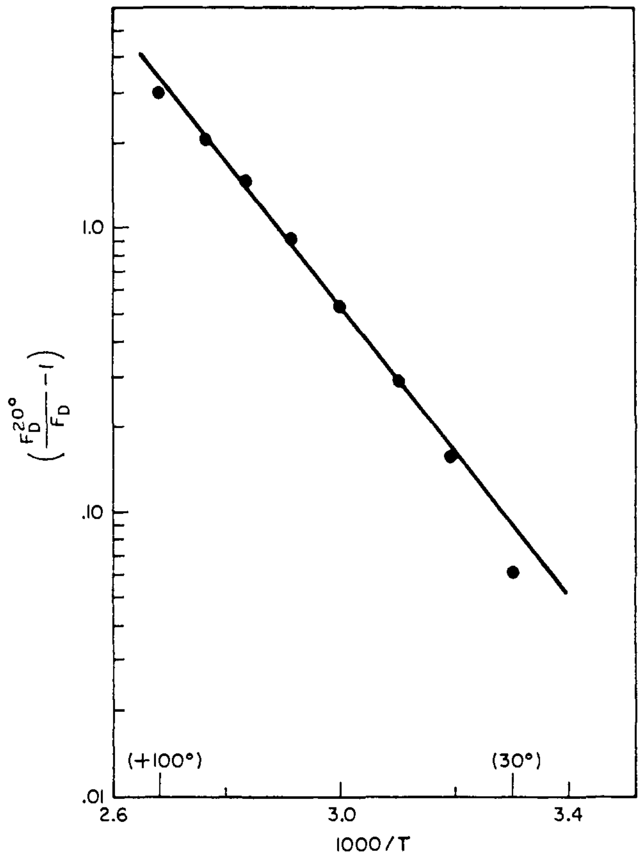

Figure 12. Kinetic plot for the determination of the activation energy for the thermally activated quenching of $\beta\beta$DNP excimer fluorescence. The 30° point, which is furthest from the line, has the largest probable error because of the nature of the function being plotted.

The activation energy of 12 kcal mol^{-1} for the thermal quenching of the $\beta\beta$DNP excimer is much higher than the value of 4 kcal mol^{-1} reported by Selinger[19] for concentrated solutions of α- and β-methylnaphthalene. These two results should probably not be compared because quenching in concentrated solutions may not be a unimolecular process of the excimer. The approximations used in our kinetic analysis introduce some error, but the data to give a reasonably linear plot and the activation energy obtained indicate that the quenching process does not involve a change in multiplicity. Transient photodimer formation in $\beta\beta$-DNP is a good possibility for the quenching process in view of our findings for $\alpha\alpha$DNP.

The thermal quenching of the fluorescence of $\alpha\alpha$DNP begins at a much lower temperature ($>-30°$) than

(19) B. Selinger, *Aust. J. Chem.*, **19**, 825 (1966).

(20) N. Mataga, M. Tomura, and H. Nishimura, *Mol. Phys.*, **9**, 367 (1965).

(21) We also estimated the lifetimes by using Berlman's technique (I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, Inc., New York, N. Y., 1965, p 35) of oxygen quenching for solutions of $\alpha\alpha$DNP and $\beta\beta$DNP at room temperature. The excimer lifetimes were about twice those of the respective monomers but the fluorescence quantum yields of the excimers are also substantially larger.

does that for the presumably similar ββDNP excimer. This observation led us to the discovery that ααDNP undergoes intramolecular photodimerization. We have isolated the crystalline photodimer and shown that it is an anthracene-like dimer. These findings are reported separately.[22] We found no evidence for photodimerization in ααDNE, ββDNP, or ααDNB when millimolar solutions in methylcyclohexane were photolyzed with "300-nm light"[23] through a Pyrex filter; the ultraviolet absorption spectra of these solutions (deoxygenated) did not change.

There is much less thermally activated quenching in the unsymmetrical αβDNP (Figure 8) where the excimer is much less stable than those formed by αα- and ββDNP. Similarly the fluorescence spectra of ααDNE and ααDNB show somewhat more thermally activated self-quenching than is found in the monomer αMN, but the quenching is still much less than is found for the two symmetrical propanes and we conclude that a stable, long-lived excimer is required for self-quenching to occur. This has also been suggested by Stevens and Dubois[24] who found that the self-quenching of naphthalene in dilute solution decreased with increasing temperature.

Conclusions

The observations of intramolecular excimer formation reported here are interpreted as showing that the preferred configuration of the naphthalene excimer is a symmetrical sandwich structure. The activation energy required to achieve this geometry in both αα-DNP and ββDNP is a consequence of rotation barriers in the methylene chain joining the naphthalene nuclei. Hirayama's conclusions regarding the geometrical requirements for intramolecular excimer formation in diarylpropanes are essentially verified in these systems.[25]

The thermally activated quenching of the excimer fluorescence of ββDNP does not involve intersystem crossing. Transient photodimer formation is a very good possibility. The dinaphthylpropanes which do not exhibit stable intramolecular excimer formation do not show the pronounced thermally activated quenching that is found in those compounds which do form excimers. Stable excimers appear to be required as intermediates for the self-quenching of aromatic hydrocarbon fluorescence.

(22) E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, **92**, 703 (1970).

(23) A Rayonet photochemical reactor containing mercury lamps, each coated with a phosphor having peak emission at 300 nm, was used.

(24) B. Stevens and J. T. Dubois, *Trans. Faraday Soc.*, **62**, 1525 (1966).

(25) NOTE ADDED IN PROOF. We unfortunately neglected to mention, in both the introductory section of this paper and in earlier work,[22] the studies of Leonard, Eisinger, *et al.*,[26,27] on intramolecular interactions in ground and excited states of various dinucleotides and similar compounds. They found intramolecular interactions in these systems to be optimal when the chromophores were linked by a trimethylene chain.

(26) N. J. Leonard, *et al., J. Amer. Chem. Soc.*, **91**, 5855 (1969).

(27) N. J. Leonard, H. Iwamura, and J. Eisinger, *Proc. Nat. Acad. Sci. U. S.*, **64**, 352 (1969).

Polarization of Electronic Transitions in Cytosine

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Abstract: In this paper polarized fluorescence experiments on 5-methylcytosine and specular reflectance measurements on cytosine monohydrate and 1-methylcytosine are reported. The results are brought together with the aim of establishing the directions of the transition moments for the first two singlet–singlet transitions, nominally the 265- and 230-mμ bands. It has been found possible to establish the directions with some fair degree of meaningfulness so that applications to the electronic theory of biopolymers may be envisaged and so that a critique of current π-electron theoretical results for cytosine can be attempted. Indeed such a critique is sketched in here in the latter part of the paper. Some results on thymine are included in passing in an Appendix which is mainly devoted to the problem of working up reflectance data inductively.

In the first section of the paper, experimental methods are briefly outlined. Results are then taken up in subsequent sections according to the experimental techniques employed.

I. Experimental Section

A. Materials. Cytosine was obtained from Nutritional Biochemicals Corp. 5-Methylcytosine (A Grade) was obtained from Calbiochem. 1-Methylcytosine was obtained from Cyclo Chemical Corp. For our purposes the compounds were found not to require further purification.

Isopropyl alcohol was Matheson Coleman and Bell Spectrograde quality and the isopentane was Phillips technical grade, purified by shaking with concentrated H_2SO_4, washing with water, and distilling with sodium hydride.

Cytosine monohydrate crystals were obtained by evaporating about 200 ml of saturated aqueous solution at *ca.* 20°. The crystals were kept immersed in mother liquor until just prior to taking their spectra since they slowly lose water upon standing in air. The crystals were distinctive plates lying on the (100) face.[1]

1-Methylcytosine crystals were obtained by slowly cooling a hot, saturated aqueous solution in a closed weighing dish.

B. Apparatus. 1. Polarized Fluorescence. The essential features of the method used have been described elsewhere.[2]

2. Reflection Spectra. Polarized normal incidence reflection spectra were taken with a spectrometer built by Clark and Gerhold which was a development of an earlier model.[3]

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(1) H. A. Rose, *Anal. Chem.*, **27**, 158 (1955).

(2) P. R. Callis, E. J. Rosa, and W. T. Simpson, *J. Amer. Chem. Soc.*, **86**, 2292 (1964).

(3) B. G. Anex and W. T. Simpson, *Rev. Mod. Phys.*, **32**, 466 (1960); L. Clark, Ph.D. Thesis, University of Washington, 1960.