Nmr spectrum ($CDCl_3$) (ppm): 1.51–2.09 (10 H), 2.27 (3 H), and 6.72, 6.87, 6.98, 7.13 (4 H).

Methoxy Lactone 13. To a solution of 204 mg (0.87 mmol) of the acid **12** and 400 mg (4 mmol) of potassium bicarbonate in 3 ml of water was added at 0° with rapid stirring bromine (0.87 mmol) in aqueous potassium bromide solution. After 3 min Celite 545 was added, and the insoluble bromo lactone was collected by filtration, washed with water, and dissolved in methanol at −20°. The solution was filtered by suction immediately into a solution of 510 mg (3 mmol) of silver nitrate in 25 ml of methanol at −50°. The mixture was allowed to warm slowly to room temperature, and 1 g of sodium acetate (solid) was added. The solid material was filtered, and the methanol was removed at 30° *in vacuo*. The residue was taken up in water, extracted with ether, and the ethereal solution was extracted with sodium bicarbonate solution, dried with magnesium sulfate, and evaporated to give 197 mg of a partly crystalline product. An analytical sample was prepared by thick layer chromatography on silica gel with chloroform as eluent to give 107 mg (46.6%), mp 110–112°.

Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.19; H, 7.65.

The infrared spectrum showed carbonyl absorption ($CHCl_3$) at 5.58 μ. The nmr spectrum ($CDCl_3$) showed peaks at (ppm): 1.33, 1.37 (3 H), 1.75 with a shoulder at 1.57 (10 H), 3.11, 3.15 (3 H), and 5.95 (4 H).

α-Tetrahydro-β-naphthyloxyisobutyric Acid (16). To a solution of 445 mg (3 mmol) of tetrahydro-β-naphthol (**14**)[23] and 1.281 g (6 mmol) of chloretone dihydrate in 4 ml of acetone was added with stirring 960 mg (24 mmol) of sodium hydroxide powder in small portions in intervals of *ca.* 30 min over a period of 4 hr. Before each addition the mixture was cooled to about 5° and was then allowed to warm to room temperature. Each time the slurry became solid, 2 ml of acetone was added (total amount of acetone 26 ml). After stirring at 25° for 21 hr (final pH 8–9), the solvent was removed *in vacuo*, and the residue was taken up in water, acidified with hydrochloric acid, and extracted with ether. Extraction of the ethereal solution with sodium bicarbonate, acidification with hydrochloric acid, and extraction of the aqueous phase with ether gave the acid **16** as an oil (650 mg) which crystallized on standing. Recrystallization from benzene–*n*-pentane gave 580 mg (82.4%), mp 98–101°. The analytical sample melted at 100–101°.

(23) H. Brown, H. W. Durand, and C. S. Marvel, *J. Amer. Chem. Soc.*, **58**, 1594 (1936).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.72; H, 7.92.

The nmr spectrum ($CDCl_3$) showed peaks at (ppm): 1.58 (6 H), 1.70, 1.75, 1.78, 1.86 (4 H), 1.68 (4 H), and 6.64, 6.67, 6.72, 6.87, 7.03 (3 H).

Methoxy Lactone 18. To a solution of 234 mg (1 mmol) of the acid **16** and 400 mg (4 mmol) of potassium bicarbonate in a mixture of 8 ml of water and 2 ml of dimethyl sulfoxide was added at −22° with rapid stirring 2 ml (1 mmol) of aqueous sodium bromide–bromine solution. As soon as the reaction was finished (2–3 min), Celite 545 was added, the mixture was diluted to 25 ml with ice-cold water and was filtered through a Büchner funnel. The insoluble bromo lactone **17**–Celite mixture was treated with methanol (−20°) and was filtered by suction immediately into a solution of 510 mg (3 mmol) of silver nitrate in 25 ml of methanol (−50°) with stirring. The mixture was allowed to warm to room temperature over 0.5 hr. Solid potassium acetate (1 g) was then added, and the solid material was filtered off after 3 min. The solvent was removed *in vacuo*, the residue was taken up in water and extracted with ether. The ethereal solution was extracted with sodium bicarbonate solution to remove acidic components, dried with magnesium sulfate, and evaporated to give 140 mg (53%) of methoxy lactone **18** as an oil. The nmr spectrum of **18** in $CDCl_3$ showed peaks at (ppm): 1.25–2.12 (8 H), 1.54 (6 H), 3.01 (3 H), and 5.67, 5.89, 5.92 (3 H).

Methoxy Dienone 15. Methoxy lactone **18** (620 mg) was stirred for 5.5 hr at 0° under nitrogen in a solution of 223 mg (1.5 equiv based on 90% purity) of potassium hydroxide in 14 ml of dimethyl sulfoxide and 5 ml of water. The mixture was then extracted with ether, and the organic phase was washed with water, dried with magnesium sulfate, and evaporated to give 357 mg of a yellow oil. The compound was purified by preparative layer chromatography on silca gel with chloroform to yield 256 mg of a colorless oil (61.2% or 32.4% based on the acid **16**). The analytical sample was distilled at a bath temperature of 85–90° (0.05 mm). It solidified to colorless crystals, mp 42° (lit.[20] mp 42–43°).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.19; H, 7.89.

The nmr spectrum of **15** in $CDCl_3$ showed peaks at (ppm): 1.22–2.40 (8 H), 2.97 (3 H), and 6.10, 6.17, 6.52, 6.69 (3 H).

Acknowledgment. This work was supported by the National Science Foundation.

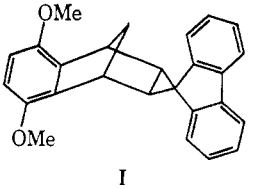
Intramolecular Excitation Transfer in 1,4-Dimethoxy-5,8-Methano-6,7-*exo*-[fluorene-9′-spiro-1″-cyclopropane]naphthalene

Angelo A. Lamola

Contribution from the Bell Telephone Laboratories, Inc., Murray Hill, New Jersey 07974. *Received March 3, 1969*

Abstract: The recent reports[1,2] that no excitation transfer takes place between the chromophores in the title compound (I) are unexpected from theory and past experience, and, indeed upon investigation we found entirely different results. Because of the nature of the absorption spectrum of I, it is dangerous to consider excitation transfer within that molecule, at least in the very weak coupling limit. However, assuming that such considerations are legitimate our measurements of the emissions from I and proper models are consistent with a scheme which requires very efficient singlet excitation transfer from the *p*-methoxybenzene group to the fluorene moiety in I.

Filipescu reported[1] that there is neither singlet excitation transfer nor triplet transfer between the chromophores in the title compound I and that the spectral characteristics of the fluorene and *p*-dimethoxybenzene chromophores in I are very similar to what they are for the individual chromophores in appropriate



I

(1) N. Filipescu in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 697.

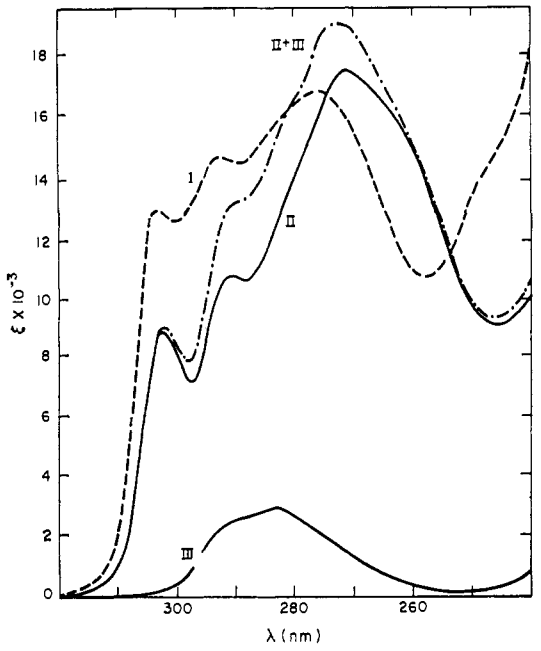


Figure 1. Absorption spectra of I (ε(277 nm) 16,600), II (ε(271 nm) 17,400), and III (ε(285 nm) 2820). The sum of the spectra of II and III is also shown.

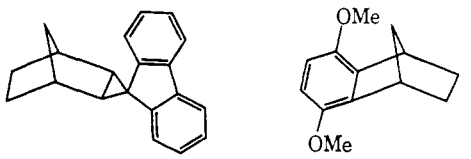
model compounds. These results were rationalized[1,2] with the proposal that the transition dipoles of the electronic transitions of interest in the two chromophores are mutually perpendicular in I thus disallowing the dipole–dipole interaction mechanism for excitation transfer.

We found Filipescu's report to be rather surprising in that (1) an orientation factor near zero seemed improbable (see below) and (2) other mechanisms (*e.g.*, exchange) besides the dipole–dipole interaction mechanism should be operable in I. The appearance of the paper by DeMember and Filipescu[2] describing their experimental data in detail did not allay our skepticism concerning this work, and so we prepared the necessary compounds and have reinvestigated the question.

Our results, which are described below, can be interpreted using a model which involves completely efficient transfer of singlet excitation from the dimethoxybenzene moiety to the fluorene chromophore in I.

Results

Compound I and model compound II were prepared essentially according to the directions of DeMember and Filipescu.[2,3] Model compound III was prepared



II III

by hydrogenating the corresponding benzonorbornadiene.

The absorption spectra (in ethanol) of I, II, and III,[4] are shown in Figure 1. Contrary to the report of

(2) J. R. DeMember and N. Filipescu, *J. Am. Chem. Soc.*, **90**, 6425 (1968).

(3) N. Filipescu and J. R. DeMember, *Tetrahedron*, **24**, 5181 (1968).

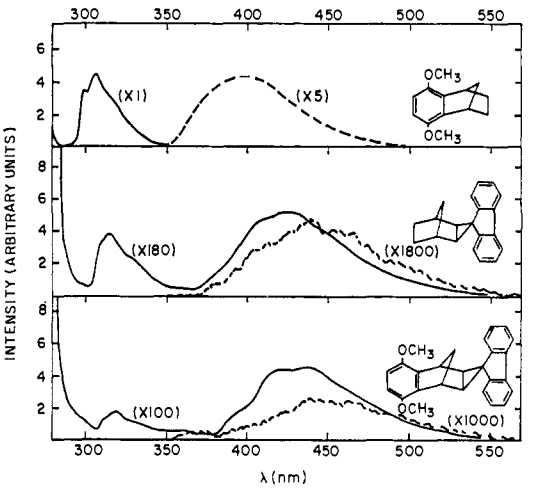


Figure 2. Emission spectra of (a, top) III, (b, middle) II, and (c, bottom) I recorded from dilute (3×10^{-3} *M*) samples in ethanol at 80°K and excited at 281 nm. The dashed curves were recorded in the phosphorescence mode and the solid curves in the fluorescence mode. The latter also show scattered exciting light.

DeMember and Filipescu[2] the spectrum of I is significantly different than the sum of the spectra of II and III (Figure 1). The intensity differences are not as important as the distinct spectral shifts observed in the wavelength region below 300 nm which indicate that the interactions between the chromophores in I are not negligible (see below).

The fluorescence and phosphorescence spectra of III in ethanol at 80°K, excited at 281 nm, are shown in Figure 2a. All the emission spectra shown in this report have been normalized (but not corrected for the wavelength dependence of the response of the instrument) such that the indicated relative intensities are meaningful. The quantum yield of the fluorescence, which has an onset at 294 nm and a maximum at 308 nm, was found to be 0.5. The unstructured phosphorescene (τ_p = 0.78 sec) is about five times weaker and exhibits an onset at 350 nm and a maximum at 400 nm. These spectra were found to be independent of concentration in the range 10^{-4}–10^{-2} *M*.

The luminescence spectra from a sample of II in ethanol solution at 80°K excited at 281 nm are shown in Figure 2b. The spectrum of the weak emission ($\phi \approx 0.005$) recorded with the spectrometer[5] in the fluorescence mode shows two bands with maxima at 315 and 425 nm. In contrast fluorene gives only a single strong ($\phi \approx 0.6$) fluorescene band with a maximum at 308 nm (Figure 3). Thus, incorporation of the fluorene chromophore into the spiro compound II leads to severe quenching in the excited singlet state. The second band at 425 nm in the spectrum of II is anomalous. It is very unlikely that this emission is due to an impurity since a very similar emission is obtained from samples of I. Association effects can be ruled out because the spectrum is independent of the concentration of II in the range 10^{-2}–10^{-4} *M*. This 425 nm[6] emission is cer-

(4) DeMember and Filipescu[2] used *p*-dimethoxybenzene as the model. However, the small differences between the spectral characteristics of *p*-dimethoxybenzene and III do not explain the differences between the results and interpretations given by those authors[2] and those reported here.

(5) J. Eisinger, *Photochem. Photobiol.*, **9**, 247 (1969).

(6) The spectra given by DeMember and Filipescu[2] are shifted 10 nm to the red relative to the spectra reported here. The wavelength indi-

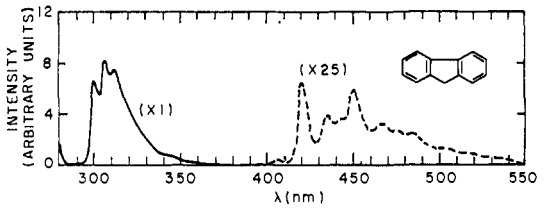


Figure 3. The fluorescence (solid curve) and phosphorescence (dashed curve) spectra of fluorene in ethanol at 80°K.

tainly not a phosphorescence[2] because (1) it does not appear in the spectrum recorded in the phosphorescence mode and (2) the intensity of the band recorded in the fluorescence mode would demand that it arise from a state which possesses a radiative lifetime shorter than 1 msec.

The emission from II recorded in the phosphorescence mode is extremely weak; the spectrum (Figure 2b) shows a maximum near 440 nm. Most of this emission is probably spurious (impurity, scattered light, etc.) since only a minor component exhibits a decay time (~3 sec) which might be assigned to the fluorene (τ_p = 6.6 sec) derivative.

The emission spectra from a sample of I (3×10^{-3} *M*) in ethanol at 80°K excited at 281 nm are shown in Figure 2c. The intensities and spectra are very similar to those observed for II. Apparently the only difference is that the long-wavelength fluorescence band of I is a bit more structured than that of II.

The fluorescence spectra in the wavelength range 300–360 nm recorded from equimolar mixtures of II and III in ethanol at 80°K and excited at 281 nm are shown for two concentrations 5×10^{-3} and 5×10^{-4} *M* in parts b and c, respectively, of Figure 4. The spectrum from a sample of III in the absence of II is shown in Figure 4a. All three samples were optically thick at 281 nm and from the absorption spectra it can be calculated that in the mixtures of II and III about 10% of the exciting light was absorbed by III. Considering this fact in conjunction with the absorption spectrum of II and the much weaker emission observed from II, one can readily assign these spectra from the equimolar mixtures as fluorescence from III distorted because of absorption (trivial transfer) by II.

Discussion

Compounds I and II prepared by us were, as far as we could tell, identical in physical properties with those prepared by DeMember and Filipescu.[2,3] Furthermore, we concur with the structures assigned for these compounds.[2,3]

The absorption spectrum of I is sufficiently different from the sum of the absorption spectra of II and III to make the question of intramolecular excitation transfer to I somewhat ambiguous.[7] In the absence of an analysis of the absorption spectrum of fluorene, no clear understanding of the interactions between the chromophores in I which lead to this deviation from additivity can be achieved. However, it should be pointed out that shifts in the spectrum of I compared to the sum of

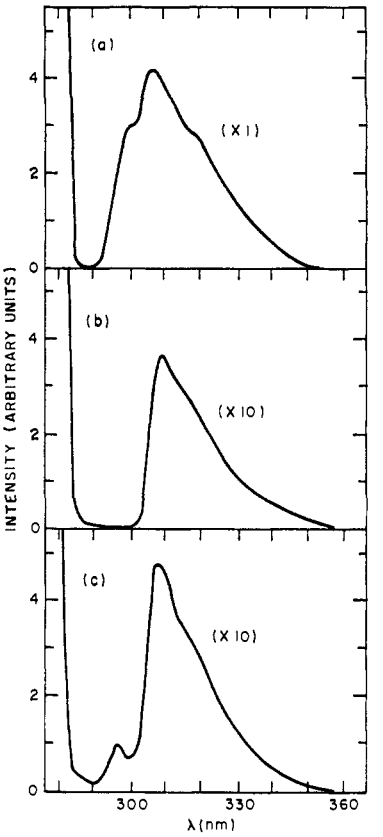


Figure 4. The fluorescence spectra recorded from (a) 10^{-2} *M* III, (b) an equimolar mixture of II and III each at 5×10^{-3} *M*, and (c) an equimolar mixture of II and III each at 5×10^{-4} *M* in ethanol at 80°K excited at 281 nm.

the spectra of II and III can be accommodated within the framework of coupling of excited states through the dipolar interaction between their transition moments. The lowest energy transition (285 nm) in *p*-dimethoxybenzene is polarized primarily in plane and perpendicular to the line connecting the two substituents.[8] Thus in I the lowest excited singlet state of the dimethoxybenzene moiety can mix, through the dipolar interactions between transition moments, with those close-lying π,π^* states of the fluorene chromophore whose transition dipoles have a short-axis component. Since it is likely that the low-lying transitions in fluorene would be at least 10% short-axis polarized, one can expect, from the small distance (~7 Å center-to-center) between the chromophores together with the reasonably large oscillator strengths, shifts on the order of those observed (~500 cm^{-1}).[9]

The low fluorescence yield of II in contrast to the strong fluorescence of fluorene was not pointed out in the paper by DeMember and Filipescu.[2] In addition these investigators erroneously assigned the anomalous band in the luminescence recorded from the samples of II as the phosphorescence spectrum of II. We cannot assign this emission at this time but we do feel that it is connected with the quenching of the fluorene-like fluorescence. That the spiro cyclopropane structure provides fast relaxation paths not available in fluorene itself gains strong support from the fact that the isomers

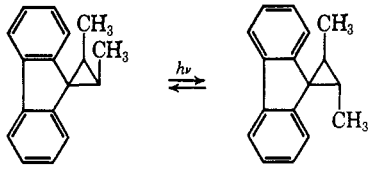
cator on our instrument has been carefully calibrated using the mercury lines.

(7) For a discussion see J. N. Murrel, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley & Sons, Inc., New York, N. Y., 1963.

(8) (a) A. C. Albrecht and W. T. Simpson, *J. Chem. Phys.*, 23, 1480 (1955). (b) This result was misquoted by DeMember and Filipescu.[2]

(9) G. L. Levinson, W. T. Simpson, and W. Curtis, *J. Am. Chem. Soc.*, 79, 3414 (1957).

IVa and IVb are interconverted with high efficiency with ultraviolet light.[10]



IVa IVb

Furthermore, there are several reports that irradiation of phenyl-substituted cyclopropanes with ultraviolet light gives carbenes and olefins as primary products[11-13] involving the cleavage of the cyclopropane ring. Thus one possible source of the 425 nm emission is some photoproduct of II. Unfortunately, we did not determine the time dependence of this emission band nor did we determine its excitation spectrum. However, the question of energy transfer in the case at hand can be decided without understanding the 425 nm emission since the fluorene moiety is expected to be the energy acceptor. Such is not the case for compounds in which the spiro-linked fluorene is expected to be the donor.[1]

No Förster-type transfer of singlet excitation is expected from II to III since there is no overlap between the fluorescence spectrum of II (or fluorene) and the absorption spectrum of III. We have calculated the Förster critical distance R_0 for transfer from III to II to be 24 Å which corresponds to a critical concentration (random distribution) of 0.03 M.[14] Thus little radiationless transfer from III to II is expected in the two samples examined which contained equal concentrations of the two compounds at 5×10^{-3} and 5×10^{-4} *M*. For excitation at 281 nm about 10% of the light is absorbed by the III in the mixture. Thus because the fluorescence from II is so weak, the fluorescence spectrum recorded from the mixtures should be very similar to that from III alone with one-tenth the intensity. This is what is observed (Figure 4) except that the spectrum from the mixtures is distorted due to absorption (trivial transfer) by the II present.

If the two chromophores in I were indeed noninteracting its fluorescence spectrum would be identical with that from the equimolar mixture of II and III. However, the fluorescent emission from I (Figure 2) is nearly identical with that from II even when excited at wavelengths where the *p*-dimethoxybenzene moiety "absorbs." Thus, to the extent that it is legitimate to consider excitation transfer in I, one would conclude from this result that there is very efficient singlet excitation transfer from the *p*-dimethoxybenzene group to the fluorene moiety in I. Furthermore, triplet excitation transfer is precluded because of this fast singlet transfer.

Finally, we would like to point out the complications associated with the use of compounds such as I[1,2,15] in experimental tests of the predicted dependence of long-range Förster-type excitation transfer on the mutual orientation of donor and acceptor transitions dipoles. These complications fall into two categories; those associated with small donor–acceptor distances, and those associated with arriving at a donor–acceptor system which is indeed sufficiently sensitive to the orientation factor. The quantitative treatment of long-range excitation transfer due to Förster[14] is valid strictly for large donor–acceptor distances where the coulombic interaction between the donor and acceptor oscillators predominates and where the point dipole approximation is valid.[16] At donor–acceptor distances of less than 10 Å, neither of these conditions can be assumed to hold.

Some of the other difficulties are exemplified by I. Assume that it is legitimate to consider singlet excitation transfer in from the *p*-dimethoxybenzene group to the fluorene moiety I and, furthermore, that the Förster formulation is valid for this case. One then calculates R_0 from the spectral data to be $26(K^2)^{1/6}$ Å where K is the dipolar orientation factor.[18] For >90% transfer at 7 Å R_0 need be only about 10 Å, that is, $K^2 = 0.003$. Thus, the observation of very efficient transfer only means the $K^2 \geq 0.003$ which is very little information indeed since $0 \leq K^2 \leq 4$. Even if one could vary either the distance between the chromophores or the oscillator strengths of the transitions to make the transfer efficiency more sensitive to the orientation factor, a meaningful experiment would be difficult to design. This is because the transfer efficiency goes as the sixth-root of K^2 so that the sensitivity if not large unless the orientation factor is very small. We contend that it would be very difficult to arrive at a compound containing well-behaved donor and acceptor moieties rigidly held so that the orientation factor is sufficiently small because the transitions are almost always of mixed polarization, that is, almost never polarized completely along one or another of the molecular axes.[19]

In summary the results reported by DeMember and Filipescu[1,2] concerning excitation transfer in I are unexpected for a number of reasons and, indeed, upon reinvestigation we found entirely different results. Because of the nature of the absorption spectrum of I it is dangerous to consider excitation transfer within that molecule, at least in the very weak coupling limit.[14] However, assuming that such considerations are legitimate, our data are consistent with very efficient singlet excitation transfer from the *p*-dimethoxybenzene group to the fluorene moiety in I.

Experimental Section

Preparation of I and II. Compounds I and II were prepared following Filipescu and DeMember[2,3] except that the intermediate pyrazolines were prepared in ether from which they precipitate as crystalline materials upon cooling of the reaction mixtures.

(10) W. von E. Doering and M. Jones, Jr., *Tetrahedron Letters*, 791 (1963).
(11) D. B. Richardson, L. R. Durrett, J. M. Martin, Jr., W. E. Putnam, S. C. Slaymaker, and I. Dvoretzky, *J. Am. Chem. Soc.*, **87**, 2763 (1965).
(12) M. Jones, Jr., W. H. Sachs, A. Kulczycki, Jr., and F. J. Waller, *ibid.*, **88**, 3167 (1966).
(13) H. Kristinsson, K. N. Mehrotra, G. W. Griffin, R. C. Petterson, and C. S. Irving, *Chem. Ind.* (London), 1562 (1966).
(14) Th. Förster in "Modern Quantum Chemistry," Vol. III, O. Sinanoglu, Ed., Academic Press, New York, N. Y., 1965, p 93.
(15) R. A. Keller, *J. Am. Chem. Soc.*, **90**, 1940 (1968).
(16) For conditions under which the Förster formulation is valid its quantitative predictions of transfer rates are extremely good.[17]
(17) For example see R. G. Bennett, *J. Chem. Phys.*, **41**, 3037 (1964).
(18) The orientation factor

$$K = \frac{\vec{M}_D \cdot \vec{M}_A}{|\vec{M}_D||\vec{M}_A|} - 3\frac{\vec{M}_D \cdot \vec{n}}{|\vec{M}_D|}\frac{\vec{M}_A \cdot \vec{n}}{|\vec{M}_A|}$$

where M_D and $\vec{M}_A$ are the transition dipole moments of the donor and acceptor, respectively, and $\vec{n}$ is the normal between the two dipoles.
(19) See F. Dörr, *Angew. Chem. Intern. Ed. Engl.*, **5**, 478 (1966), and references therein.

Preparation of 3′,6′-Dimethoxybenzonorbornylene (III). 3′,6′-Dimethoxybenzonorbornadiene[20] was hydrogenated using 5% Pd–C (Parr apparatus, 40 psi H_2, 2 hr). After removing the catalyst and the ethanol, the crude 3′,6′-dimethoxybenzonorbornylene was purified by sublimation under reduced pressure; mp 38–40°; nmr (CCl_4): δ 1.48 (4 H, $H_{5,6}$) AB multiplet, 1.52 (2 H, H_7) AB multiplet, 3.51 (2 H, $H_{1,4}$) singlet, 3.68 (6 H, $-OCH_3$) singlet, 6.46 (2 H, $H_{4',5'}$) singlet.

Spectroscopic Data. Absorption spectra were recorded with a Bausch and Lomb Spectronic 505 and with a Carey Model 14 spectrophotometer. Emission spectra were recorded at 80°K using a recording instrument which has been described in detail elsewhere.[5] The slit width on the emission monochromator was 2 nm giving 32-Å resolution. Samples were contained in sealed 1.5 mm o.d. quartz tubes. The standard for quantum yield determinations was a sample of *p*-terphenyl in hexane for which a fluorescence yield of 0.9 (room temperature) was assumed.[5]

(20) J. Meinwald and G. A. Wiley, *J. Am. Chem. Soc.*, **80**, 3667 (1958).

Acknowledgments. We thank Mrs. B. Feuer for her capable technical assistance and Dr. J. Eisinger for the use of his emission spectrophotometer and for helpful discussions.

Intramolecular Hydrogen Bonding in 2-Hydroxyalkylpyridines and 2-Hydroxyalkylpiperidines

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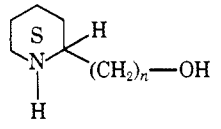
Contribution from Department of Chemistry, University of Delaware, Newark, Delaware 19711, and the U. S. Army Ballistic Research Laboratories, Aberdeen, Maryland 21005. *Received February 25, 1969*

Abstract: Strong intramolecular hydrogen bonds were found to be present in 3-hydroxypropylpyridine, 2-hydroxyethylpyridine, and the corresponding piperidines. The hydrogen bond in hydroxymethylpyridine is much stronger than anticipated. This is attributed to the fact that the hydrogen-donor group is on an sp^3 carbon and the acceptor group is on an sp^2 carbon, allowing the dihedral angle to be close to zero degrees and consequently producing a very short hydrogen bond. Hydroxymethylpiperidine has a normal $\Delta\nu$ but only a very small equilibrium constant for hydrogen bond formation. This hydrogen bond requires that the lone pair of electrons on nitrogen be equatorial. The small equilibrium constant can be rationalized by assuming that the lone pair of electrons on nitrogen prefers to be axial and the amino hydrogen to be equatorial.

Although there have been numerous studies[3] of hydrogen bonding in amino alcohols, compounds having the structures **1** and **2** have not been previously



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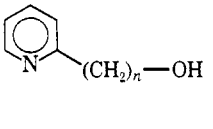

2

examined in this regard. We present here the results of a study of the infrared spectra of **1** and **2**, where n is 1, 2, and 3, and compare these with the available data on acyclic amino alcohols as listed in Table I.

Results and Discussion

The frequency shift of the O–H band, $\Delta\nu$, is an accepted measure of the strength of the hydrogen bond. Generally the strength of the hydrogen bond can be correlated with a polar factor and a steric factor. An estimate of the polar factor can be obtained from the $\Delta\nu$ of intermolecular hydrogen bonds in compounds without bulky groups which could give rise to steric hindrance. We see in Table I that the hydrogen bond CH_3OH–pyridine ($\Delta\nu$ = 275 cm^{-1}) is weaker than the hydrogen bond CH_3OH–diethylamine ($\Delta\nu$ = 430 cm^{-1}). Clearly pyridine is a weaker base and a poorer hydrogen acceptor than diethylamine. The diethylamino group forms a hydrogen bond which is 1.6 times stronger than the hydrogen bond having a pyridine moiety as the hydrogen acceptor.

Insofar as the polar effect is concerned, the $\Delta\nu$ of an intramolecular hydrogen bond should be the same as the $\Delta\nu$ of an intermolecular hydrogen bond involving the identical hydrogen donor and acceptor groups. However, intramolecular hydrogen-bonded systems show wide variations in $\Delta\nu$ which can be correlated with steric and geometric effects. In diols, 1,2 and 1,3 isomers exhibit weaker cyclic hydrogen bonding (smaller $\Delta\nu$) than the intermolecular hydrogen bonding between two alcohol molecules. On the other hand, 1,4 diols show an inverse characteristic; the intramolecular bond is stronger (larger $\Delta\nu$) than the intermolecular.[4] The data in Table I demonstrate that hydrogen bonding in cyclic and acyclic amino alcohols is closely parallel to what is observed for diols. Again, the 1,2 and 1,3 amino alcohols experience cyclic hydrogen bonding which is weaker than the intermolecular, but intramolecular hydrogen bonding in 1,4 amino alcohols is considerably stronger than that which occurs between two molecules possessing the same donor and acceptor functions. In attributing these differences in $\Delta\nu$ to geometric and steric effects we mean to consider both the length of the hydrogen bond and the O–H- - -N bond angle. It is unfortunate that these two parameters cannot be varied separately for we cannot tell which plays the larger role

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