Chemistry of Radical Anions of Heterocyclic Aromatics. I. Electron Spin Resonance and Electronic Spectra

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Abstract: Radical anions of pyridine, quinoline, isoquinoline, acridine, and 9,10-diazaphenanthrene (benzcinoline) were prepared at room temperature by reducing the parent compounds with metallic sodium, or with sodium biphenylenide, in hexamethylphosphoramide (HMPA). In tetrahydrofuran (THF) these radical ions rapidly dimerize, virtually quantitatively, yielding the corresponding dianions. However, in HMPA the equilibrium favors the dissociated form (the monomeric radical ions), and the dimerization is not observed (pyridine radical ion being an exception). The radical ions form ion pairs in THF but are present as free ions in HMPA. This accounts for the pronounced shift in the dimerization equilibrium; ion pairs form stable salts of the dimeric dianions, while the free dianions dissociate into unpaired monomeric radical ions. The esr and optical spectra of the aza radical ions are reported and the assignment of the splitting constant is discussed.

Conventional reduction with alkali metals of ethereal solutions of many heteroaromatics does not yield their respective radical anions. Although these species are formed as the first intermediates of an electron-transfer process, their rapid dimerization, often followed by the aromatization of the dimeric dianions, removes them from the system. The radical anions paired with cations (*i.e.*, ion pairs) dimerize faster than the unpaired anions. Therefore, the dimerization is substantially slower in hexamethylphosphoramide (HMPA), where the pairing of ions is negligible, than in tetrahydrofuran (THF) or dimethoxyethane (DME). Indeed, the preparation of stable solutions of radical anions of quinoline, by reducing the parent compound with sodium in HMPA, was reported in our preliminary communication.[1] Solutions of other heteroaromatic radical anions also may be prepared in this solvent, and the results attained with pyridine, quinoline, isoquinoline, acridine, and 9,10-diazaphenanthrene are presented now. The esr and electronic spectra of these radical ions have been investigated, and their electron affinities have been determined by potentiometric and by equilibrium methods. These will be reported in part II of the series.

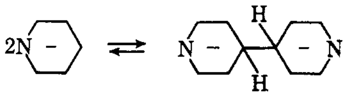
Experimental Section

Commercial HMPA was degassed on a high-vacuum line and then triple distilled under vacuum from the solution of the pertinent radical anion. The distillate was then kept on a high-vacuum line for 24 hr in order to remove the residual amines. All reductions were performed either by metallic sodium or by sodium biphenyl.

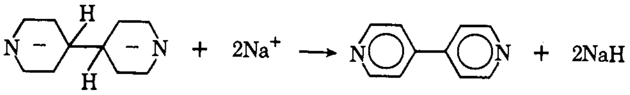
The esr spectra were determined at room temperature on a Varian 1502 spectrometer using a flat quartz cell and an "all-purpose" cavity. The electronic spectra were recorded on a Cary 14 spectrophotometer.

Results and Discussion

The radical ions of pyridine rapidly dimerize even in HMPA; the yellow color disappears in a few seconds. Nevertheless, the equilibrium



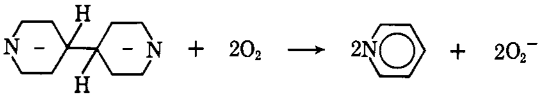
provides a sufficiently high concentration of radical ions $(\sim 10^{-5}\ M)$ to permit observation of the esr spectrum. The aromatization of the dimeric dianions is slow in the absence of metallic sodium, but it is catalyzed by its presence. Its outcome is represented by the over-all reaction



yielding bipyridyl which is subsequently converted into its radical ion.[2,3]

Formation of the pyridine radical ion in THF was reported by Hush and his associates.[4] However, neither we nor other workers[2,3] could observe the esr spectrum of the pyridine radical ion in this solvent. Apparently, the optical spectrum recorded by Hush, *et al.*,[4] and attributed to the radical ion is that of the dimeric dianion. On admission of oxygen, pyridine was regenerated. This result Hush explained by postulating the reaction

and subsequently considered it as evidence for the presence of the pyridine radical ion in the original solution, However, we found[5] that various dimeric dianions, *e.g.*, those formed from 1,1-diphenylethylene or α-methylstyrene, decompose into the parent molecules when a suitable electron acceptor is available. We propose, therefore, that the process observed by Hush, *et al.*,[4] results from the over-all reaction



The esr spectrum of the pyridine radical ion is shown in Figure 1. The assignment of the splitting constants is straightforward for the nitrogen and for

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[1] A. Cserhegyi, J. Chaudhuri, E. Franta, J. Jagur-Grodzinski, and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 7129 (1967).

[2] R. L. Ward, *ibid.*, **83**, 3623 (1961).

[3] A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

[4] J. W. Dodd, F. J. Hopton, and N. S. Hush, *Proc. Chem. Soc.*, 61 (1962).

[5] J. Jagur-Grodzinski and M. Szwarc, *Proc. Roy. Soc.* (London), **A288**, 224 (1965); *Trans. Faraday Soc.*, **59**, 2305 (1963).

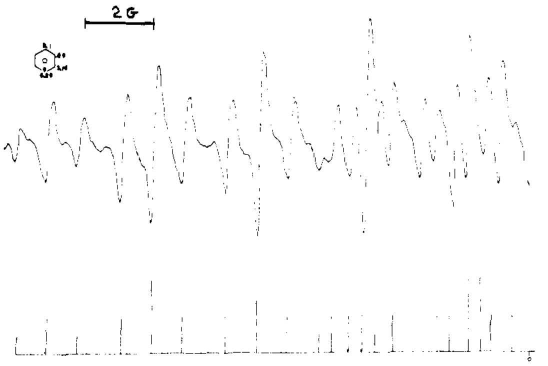

Figure 1. (a) Radical anion of pyridine in HMPA at 20°. Low-field half of first derivative esr spectrum, scan time 10 min, range 25 G. (b) Theoretical stick model using the splitting constants given in the text.

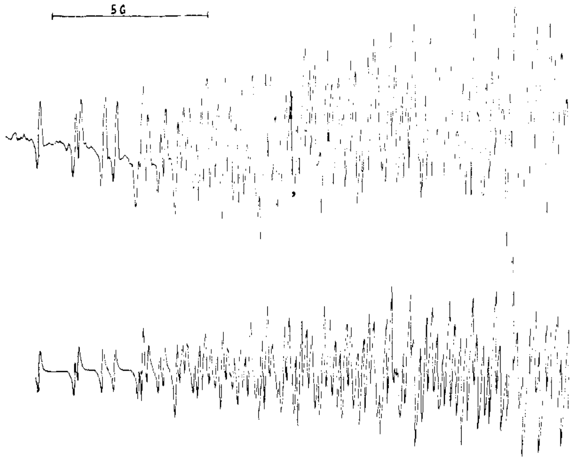

Figure 2. (a) Radical anion of quinoline in HMPA at 20°. Low-field half of first derivative esr spectrum, scan time 10 min, range 25 G. (b) Simulated spectrum obtained by using coupling constants given in the text; line width of 0.07 G and a Lorentzian line shape.

the C(4) proton. The other two constants were assigned to C(2) and C(3) protons, respectively, on the basis of Hückel or McLachlan calculations which predict higher electron density at C(2) than C(3). Our results are given in Table I together with those reported recently by Talcott and Myers.[6] These workers reduced pyridine electrochemically in liquid ammonia at −75°. The small differences between their values and ours for the splitting constants are probably genuine and are caused by solvent and temperature effects which are different for the two investigated systems.

The reduction of quinoline, Q, in tetrahydrofuran leads to the formation of the dimeric dianion, $^{-}QQ^{-}$ (a derivative of dihydroquinoline). The equilibrium greatly favors dimerization; judging from the esr signal the proportion of the radicals is lower than 1% in a 10^{-3}*M* solution. On replacement of tetrahydrofuran by HMPA the dimer dissociates into monomeric radical ions, $Q\cdot^{-}$. Hence, reduction of quinoline in HMPA leads to its quantitative conversion into $Q\cdot^{-}$.

Two equilibria should be distinguished, *viz.*

$$2Q\cdot^{-}, Na^{+} \rightleftarrows Na^{+}, {}^{-}QQ^{-}, Na^{+}$$

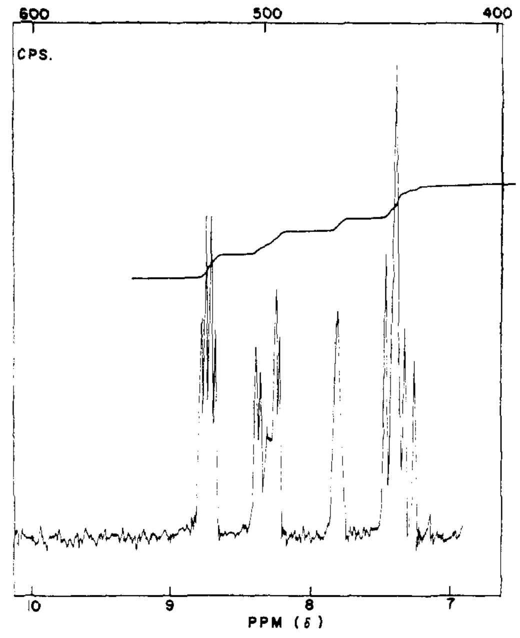

Figure 3. Proton resonance spectrum at 60 Mc/sec of quinoline deuterated in the benzene ring with deuterium partially replaced by hydrogen on C(8); 3 *M* solution in HMPA, temperature 40°.

and

$$2Q\cdot^{-} \rightleftarrows {}^{-}QQ^{-}$$

The former favors dimerization, while the latter is shifted far to the left. The repulsion between the negative charges of $^{-}QQ^{-}$, which is reduced, or perhaps even avoided, in the salt makes the dianion less stable than its salt.

The esr spectrum of $Q\cdot^{-}$ is shown in Figure 2 and the respective splitting constants are listed in Table I. Their assignment is based on the evidence provided by the nmr studies and by the investigation of the radical ions derived from quinoline deuterated in the benzene ring.

The nmr spectrum of quinoline was reported.[7,8] In pure liquid and in carbon tetrachloride solution the proton shifted most downfield was identified as H(2). Its signal appears as a quartet at about 530 cps (at 60 Mc). The H(8) proton was shown to absorb at lower field than the H(4) while the H(3) proton absorbs at the highest field. These results were confirmed by our own studies, in the course of which the spectra of the deuterated and methylated quinolines were compared with that of the parent compound. However, when nmr spectra of pure quinolines are compared with that of their HMPA solutions, one finds that the solvent shifts the absorption of H(8) by 22 cps upfield, while the absorption of H(4) moves downfield by 29 cps (see Figure 3). Consequently, the relative positions of these two lines are reversed.

Having established the identity of the various lines in the nmr spectrum of quinoline in HMPA solution, we investigated their exchange broadening caused by the presence of $Q\cdot^{-}$. The largest broadening was

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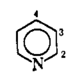
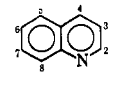
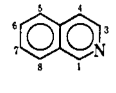
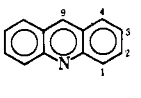
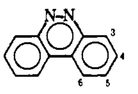
(6) S. R. Talcott and R. J. Myers, *Mol. Phys.*, **12**, 549 (1967).

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Publishing Co., Inc., New York, N. Y., 1959, p 268.

(8) E. Vander Donckt, R. H. Martin, and F. Geerts-Evrad, *Tetrahedron*, **20**, 1495 (1964).

Table I. Splitting Constants in Esr Spectrum of Heteroaromatic Radical Anions in HMPA

Parent molecule	Position	Experimental splitting constant, G	Hückel splitting[f] $\alpha_N = \alpha_C + 0.5\beta$	Observed relative broadening in nmr	Ratio of electron densities (exptl)
	N	6.28 ± 0.03 (6.28)[a]	5.22 (6.56)[c]		
	C(2)	3.14 ± 0.03 (3.55)[a]	6.90 (3.95)[c]		
	C(3)	0.88 ± 0.03 (0.82)[a]	1.28 (0.18)[c]		
	C(4)	9.10 ± 0.05 (9.70)[a]	7.45 (10.5)[c]		
	Total width	29.7 (31.0)[a]			
	N	3.95 ± 0.10	4.48		
	C(2)	3.29 ± 0.02	3.20	2.8	2.6
	C(3)	1.26 ± 0.02	1.45	(1)	(1)
	C(4)	7.80 ± 0.02	5.80	4.5	6.2
	C(5)	3.90 ± 0.10	3.90		
	C(6)	1.14 ± 0.02	1.27		
	C(7)	2.02 ± 0.02	1.93		
	C(8)	3.46 ± 0.02	3.44		
	Total width	30.6 ± 0.35	29.95		
	C(1)	5.38 ± 0.02	6.15	11–12	14.5
	N	1.92 ± 0.02	3.82		
	C(3)	0.37 ± 0.02	0.59	(1)	(1)
	C(4)	4.01 ± 0.02	4.20		
	C(5)	3.95 ± 0.02	3.90		
	C(6)	3.26 ± 0.02	2.40		
	C(7)	.04 ± 0.04	1.20		
	C(8)	6.26 ± 0.02	7.35		
	Total width	27.07 ± 20	33.6		
	N	3.72 ± 0.04 (3.48)[b]	3.02		
	C(1)	1.82 ± 0.04 (1.60)[b]	1.25	(1)	(1)
	C(2)	2.02 ± 0.04 (2.19)[b]	1.93		
	C(3)	0.91 ± 0.04 (0.81)[b]	0.57		
	C(4)	2.78 ± 0.04 (2.73)[b]	2.50		
	C(9)	7.60 ± 0.04 (7.74)[b]	7.70	4.3	4.2
	Total width	30.10 ± 0.10 (29.4)[b]	26.24		
	N	4.94 ± 0.05 (5.27)[d]	5.3[e]		
	C(3)	3.66 ± 0.04 (3.58)[d]	2.16[e]		
	C(4)	0.17 ± 0.02 (0.28)[d]	0.18[e]		
	C(5)	2.91 ± 0.03 (2.83)[d]	1.83[e]		
	C(6)	0.81 ± 0.02 (0.77)[d]	0.63[e]		
	Total width	34.8			

[a] S. R. Talcott and R. J. Myers, *Mol. Phys.*, **12**, 549 (1967). [b] G. H. Hoeve and W. A. Yeranos, *ibid.*, **12**, 597 (1967). [c] Calculated by McLachlan approximation. [d] D. H. Geske and G. R. Padmanabhan, *J. Am. Chem. Soc.*, **87**, 1651 (1965). [e] Calculated by Hückel appproximation with $\alpha_N = \alpha_C + 0.75\beta$. [f] Calculation of splitting constants from Hückel approximations were performed on the basis $Q_C = 26$, $Q_{NN} = 20, Q_{CC} = 7$.

found for the H(4) line and, therefore, the splitting constant 7.80 was attributed to C(4). The broadening of the nmr spectrum also indicates that the C(2) splitting constant is 3.29 or 3.46; the former value is favored. The presence of the 1.26 splitting in the esr spectrum of Q·⁻ deuterated in the benzene ring, coupled with the broadening of the relevant nmr line, indicates that this splitting constant should be assigned to C(3). Finally, the comparison of the esr spectra of the ordinary and the deuterated quinolines (differences in the hyperfine structure and in the total widths) leads to the conclusion that the remaining four splitting constants derived from the analysis of the esr spectrum, namely, 3.90, 3.46, 1.14, and 2.02, belong to protons on C(5), C(8), C(6), and C(7). Their final assignment to the respective protons is somewhat arbitrary and based on the agreement with Huckel calculation.

The comparison of the experimental splitting constants with those calculated by the Hückel method shows a surprisingly good agreement; the electron density on nitrogen seems to be slightly lower than calculated and that on C(4) somewhat higher.

Further evidence for the proposed assignment of the esr spectrum is obtained by computer simulation (see Figure 2). The agreement is most satisfactory; however, it should be mentioned that nearly as good

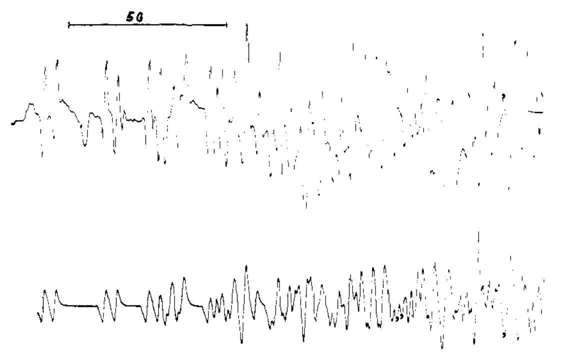


Figure 4. (a) Radical anion of isoquinoline in HMPA at 20°. Low-field half of first derivative esr spectrum, scan time 10 min, range 25 G. (b) Simulated spectrum obtained by using coupling constants given in the text, line width of 0.07 G, and a Lorentzian line shape.

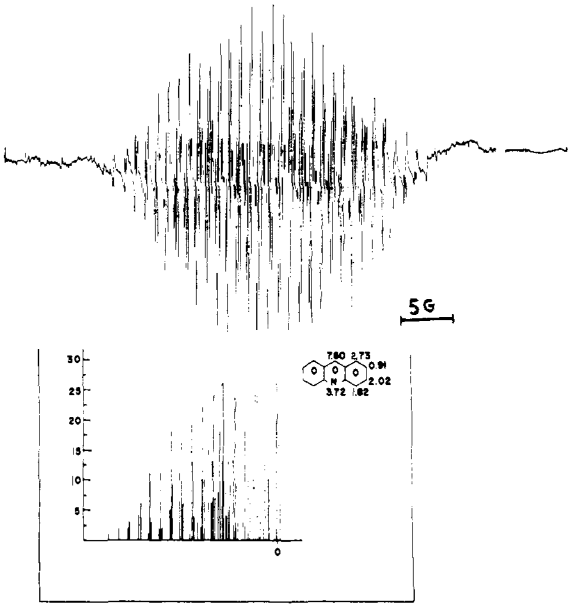


Figure 5. (a) Radical anion of acridine in HMPA at 20°. First derivative esr spectrum, scan time 10 min, range 50 G. (b) Theoretical stick model (for the lower half of the spectrum) using the splitting constants given in the text.

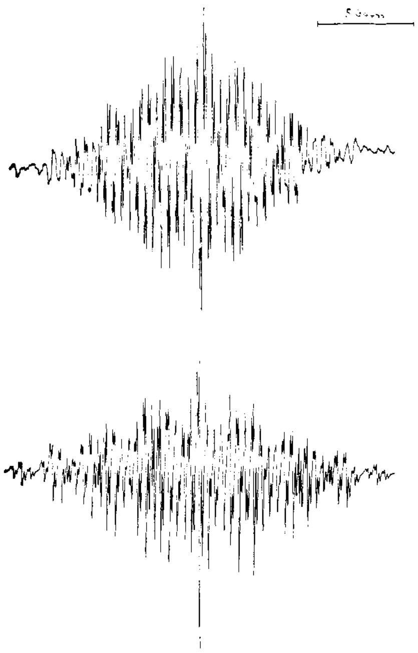


Figure 6. (a) Radical anion of 9,10-diazaphenanthrene (benzcinoline) in HMPA at 20°. First derivative esr spectrum, scan time 5 min, range 50 G. (b) Simulated spectrum obtained by using coupling constants given in the text, line width of 0.07 G, and a Lorentzian line shape.

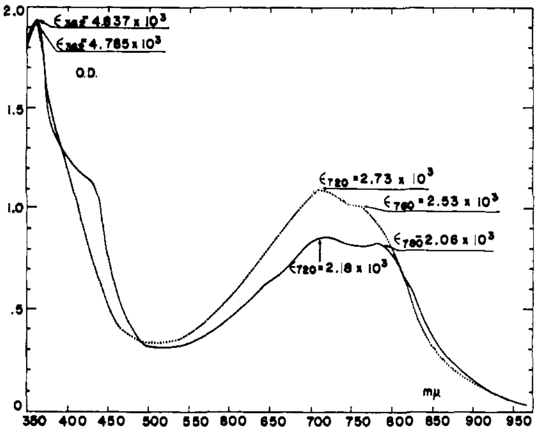


Figure 7. ······, Quinoline radical ion in HMPA at 25°, Na$^+$ counterion; ———, isoquinoline radical ion in HMPA at 25°, Na$^+$ counterion.

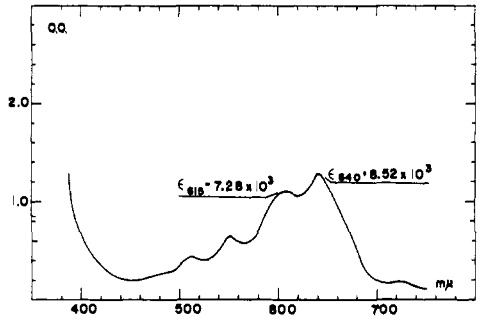


Figure 8. Acridine radical ion in HMPA at 25°, Na$^+$ counterion.

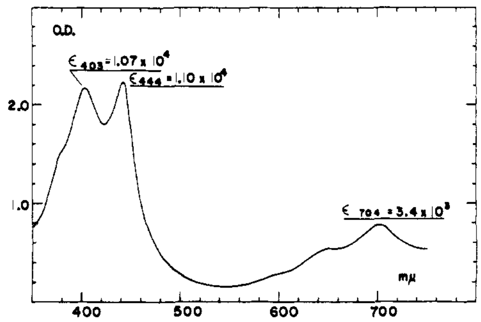


Figure 9. 9,10-Diazaphenanthrene (benzcinoline) in HMPA at 25°, Na$^+$ counterion.

agreement is obtained if splitting 5.70 is attributed to nitrogen and 4.00 to C(4).

The unequivocal assignment of the splitting constants of the esr spectrum of isoquinoline is feasible for C(1) and C(3) because the respective nmr lines are perceptible and their broadening by exchange with the radical ion has been determined (see again Table I). Thus the splitting constants of C(1) and C(3) were found to be 5.54 and 0.39, respectively. The assignment of the remaining constants is again somewhat arbitrary and based on the comparison of experimental data with the Hückel calculation. The computer simulation reproduced the observed spectrum as shown in Figure 4.

The esr spectra of acridine and benzcinoline[9] radical ions were reported.[10] Our constants are similar to those given by the other workers, the differences being attributed to effects caused by different solvents. The assignment for the C(1) and C(9) in the esr spectrum of the acridine radical ion is again confirmed by the exchange broadening of the nmr lines. The results

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[9] The radical ions of acridine dimerize in THF. The behavior of benzcinoline radical ions in THF was not investigated.

[10] (a) H. G. Hoeve and W. E. Yeranos, *Mol. Phys.*, 12, 597 (1967); (b) D. H. Geske and G. R. Padmanabhan, *J. Am. Chem. Soc.*, 87, 1651 (1965). Only the splitting constant due to N was reported in two papers published later, namely, (c) E. F. Strom, G. E. Russell, and R. Konake, *J. Chem. Phys.*, 42, 2033 (1965); (d) D. J. Black and C. A. McDowell, *Mol. Phys.*, 12, 242 (1967).

are listed in Table I and the spectra are shown in Figures 5 and 6.

The optical spectra of all these radical anions but that of pyridine are shown on Figures 7, 8, and 9. The λ_{max} and the respective extinction coefficients are marked on the drawings. There is a striking similarity in the absorption spectra of naphthalene and quinoline and isoquinoline radical ions as well as that of the anthracene and acridine radical ions. However, in both systems the absorption maxima of the aza compounds are shifted to the shorter wavelength when compared with the relevant hydrocarbons; the respective energy gaps are increased by about 4–5 kcal/mol.

Acknowledgment. We thank Dr. Cserhegyi for preparing the deuterated quinoline, and we gratefully acknowledge the financial support of this investigation the National Science Foundation, the United States Air Force, Contract AF33(615)3788, and the Petroleum Research Fund administered by the American Chemical Society.

Intramolecular Energy Transfer between Nonconjugated Chromophores. Effect of Rigid Perpendicular Orientation

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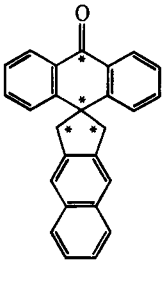
Contribution from the Department of Chemistry, The George Washington University, Washington, D. C. 20006. *Received April 29, 1968*

Abstract: Fluorene and *p*-dimethoxybenzene have been incorporated in the same molecule by attaching them rigidly to an inflexible frame. The lowest excited singlet and triplet states of the two chromophores are of proper energy to allow efficient energy transfer. Although in a random orientation in solution efficient energy transfer takes place between the separated chromophores, when they are held in a rigid perpendicular position even at close distance, no interaction was detected. The results verify the orientation requirements for electric dipole energy transfer.

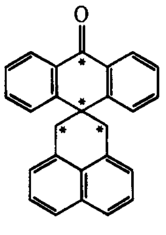
During the last five years several efforts have been made to verify experimentally the theory developed originally by Förster[2] for the transfer of electronic excitation energy between two nonconjugated chromophores on model compounds in which the two chromophores are connected to the same molecular frame.[3] The two important features in such compounds are the separation distance and the mutual orientation of the donor and acceptor chromophores.

An increase in the number of interposing methylene groups did not lead to known separations because of free rotation in the $-CH_2-$ links.[3a,b] Although the average distance was known more accurately in compounds in which the chromophores were connected to a saturated steroidal frame or to a polyamide helix, their mutual orientation was essentially random due to rotation about the connecting σ bonds.[3c,g]

Apparently, the author in only one recently reported work has prepared model compounds having a distinct donor–acceptor relative orientation. Thus, Keller[3e] presented evidence of triplet–triplet energy transfer between presumably perpendicular anthrone and naphthalene chromophores in compounds I and II.

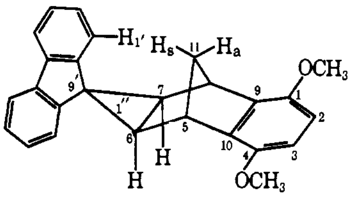


I



II

Presently we report the results of an energy transfer study on 1,4-dimethoxy-5,8-methano-6,7-*exo*-[fluorene-9′-spiro-1′′-cyclopropane]naphthalene (III).



III

Unlike I and II, the rigid frame between the *p*-dimethoxybenzene (DB) and fluorene (F) chromophores has no flexible connections and the two π systems are in a perfectly perpendicular orientation. It is known that singlet–singlet resonance interaction is effective at distances up to 200 Å[2] whereas triplet energy migration requires either collision or close molecular approach.[4]

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[1] In partial fulfillment of the Ph.D. requirement for J. R. D.

[2] (a) T. Förster, *Z. Elektrochem.*, **64**, 157 (1960); (b) *Discussions Faraday Soc.*, **27**, 1 (1959); (c) *Naturwissenschaften*, **33**, 1661 (1946); (d) *Ann. Phys.*, **2**, 55 (1948); (e) "Fluorezenz Organische Verbindungen," Vandenhoech and Ruprech, Gottingen, 1951, p 83–86.

[3] (a) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2670 (1963); (b) *ibid.*, **87**, 2322 (1965); (c) S. A. Latt, H. T. Cheung, and E. R. Blout, *ibid.*, **87**, 995 (1965); (d) D. E. Breen and R. A. Keller, *ibid.*, **90**, 1935 (1968); (e) R. A. Keller, *ibid.*, **90**, 1940 (1968); (f) N. Filipescu, S. Bjorklund, N. McAvoy, and C. R. Hurt, *Can. J. Chem.*, **45**, 1714 (1968); (g) L. Stryer and R. P. Haugland, *Proc. Nat. Acad. Sci. U. S.*, **58**, 719 (1967).

[4] (a) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953); (b) V. L. Ermolaev, *Opt. Spectry.*, **6**, 417 (1959); (c) V. L. Ermolaev, *Soviet Phys. Usp.*, **6**, 333 (1963).