

correct conformation.¹¹ Syntheses of longer oligonucleotides, whose sequences incorporate that of the above nonamer and which can form "hairpin" duplicates, are in progress. Intramolecular cyclization of the protected nonamer (18) is also under investigation.

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(11) B. F. C. Clark, S. K. Dube, and K. A. Marcker, *Nature (London)*, **219**, 484 (1968).

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2,3-Naphtho-2,5-bicyclo[2.2.0]hexadiene

Sir:

This communication deals with the chemistry of 2,3-naphtho-2,5-bicyclo[2.2.0]hexadiene (1). The fluorescence of 1 at room temperature is a superposition of emission from 1 and its photorearranged product, anthracene (Figure 1). This observation suggests that an appreciable amount of the anthracene formed in the photorearrangement is in the singlet excited state. The reaction thus provides the first example known to us of the rearrangement of one excited molecule to another, both being in their respective singlet excited states. Although there are known examples of photochemical formation of electronically excited products, most of these reactions involve fragmentation, ionization, or complex formation rather than rearrangement.¹ Turro, *et al.*, have reported the photorearrangement of naphthalene to triplet naphthalene at 77°K, which illustrates the rearrangement of one excited molecule to another in a different spin state.² Based on the analysis of the behaviors of various transients formed during the nanosecond laser photolysis of triphenylamine or tetramethyldianthrone,^{3,4} the rearrangement of one triplet state molecule to another has been suggested.

Compound 1 was synthesized by a scheme similar to that reported for benzobicyclo[2.2.0]hexadiene⁵ and exhibits the following properties: mp (uncor) 67°, 208°; *Anal.* (found) C, 93.92 and H, 6.04; ir (KBr) 3100, 2950, 880, and 760 cm⁻¹; ν_{\max} (cyclohexane) 231 (60,700), 266 (5860), 275 (6280), 287 (4180), 307 (700), 316 (335), and 321 nm (921); nmr (CD₃CN) δ 4.61 (m, 2), 6.67 (m, 2), 7.41 (sextet, 2), 7.64 (s, 2), and 7.83 ppm (sextet, 2). The sextets at 7.41 and 7.83 δ are those of an A₂X₂ system, and the analysis indicates that $J_{1,2} = 8.0$, $J_{1,3} = 2.0$, and $J_{2,3} = 6.5$ Hz.⁶ No peaks attributable to anthracene were detected in the ir and nmr spectra; however, peaks at 253 (8170) and 338 nm (68) in the uv spectrum indicate the presence of about 1.5% of anthracene.

(1) A. Zweig, *Pure Appl. Chem.*, **33**, 406 (1973).

(2) N. J. Turro, P. Lechtken, A. Lyons, R. R. Hautala, E. Carnahan, and T. J. Katz, *J. Amer. Chem. Soc.*, **95**, 2035 (1973).

(3) E. W. Förster and K. H. Grellman, *Chem. Phys. Lett.*, **14**, 536 (1972).

(4) E. W. Förster and E. Fischer, *J. Chem. Soc., Chem. Commun.*, 1315 (1972).

(5) R. N. McDonald, R. G. Frickey, and G. M. Muschik, *J. Org. Chem.*, **37**, 1304 (1972); R. N. McDonald and G. M. Muschik, *J. Amer. Chem. Soc.*, **90**, 5315 (1968).

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *Can. J. Chem.*, **97**, 2798 (1964).

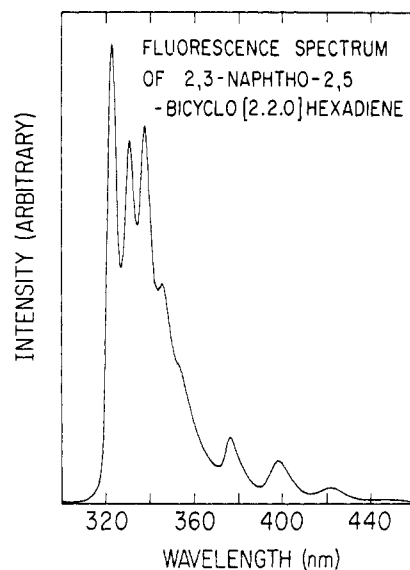
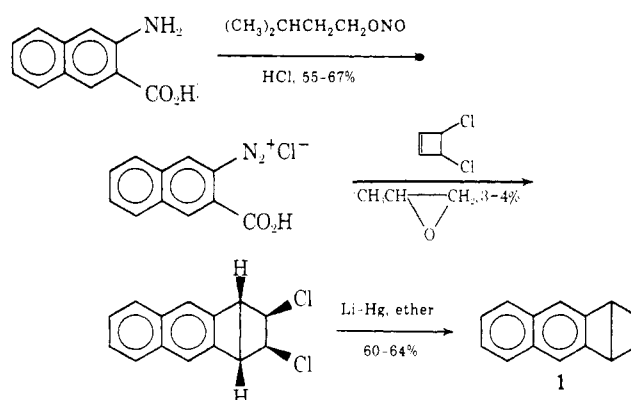


Figure 1.



Compound 1 decomposes thermally and photochemically ($\phi_{313\text{nm}} = 0.41 \pm 0.02$) to give anthracene quantitatively. From the rates of thermal decomposition in *n*-heptane between 36–60°, the activation energy was found to be 26.5 kcal. We were unable to detect chemiluminescence when 1 or a mixture of 1 and 9,10-dibromoanthracene was heated rapidly above 100°; *i.e.*, we were unable to detect the adiabatic formation of S₁ of anthracene by direct population, T–T annihilation, or energy transfer to dibromoanthracene.

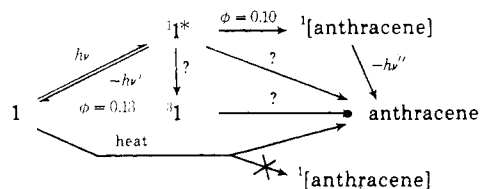
The fluorescence spectrum of 1 (Figure 1, $\lambda_{\text{excitation}}$ 270–275 nm), which differs from those typical of naphthalenes, shows two progressions, a naphthalene-like emission beginning around 320 nm and the characteristic anthracene emission beginning around 370 nm. The uncorrected excitation spectra monitored at either 330 or 400 nm correspond, qualitatively, to the absorption spectrum of 1. The emission spectrum from a nitrogen saturated solution does not vary appreciably with exciting light intensity at 270–275 nm nor with concentration ranging from 2.1×10^{-5} to 1.8×10^{-4} M (which contain about 3.6×10^{-7} to 3.1×10^{-6} M of anthracene, respectively). The lifetime of emission, measured by the time-controlled single photon counting technique at 330, 379, and 400 nm, was found to be 24.5 ± 0.3 nsec, compared to that of anthracene which is 4.9 nsec.⁷ The possibility of the anthracene emission

(7) I. Beriman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 123.

from **1** being from the singlet energy transfer from excited **1** to the anthracene present was further excluded by examining the fluorescence spectrum of a model compound, 2,3-dimethylnaphthalene, in the presence of anthracene under identical conditions. 2,3-Dimethylnaphthalene ($2.1 \times 10^{-5} M$) which has an appreciably longer fluorescence lifetime than **1** (78 nsec,⁸ 91.5 nsec⁹) exhibits no appreciable emission in the 390–440 nm region in the presence of an amount of anthracene equivalent to that present in **1** ($3.6 \times 10^{-7} M$). These observations demonstrate that the anthracene emission is derived from excited **1** and not from the small amount of anthracene present.

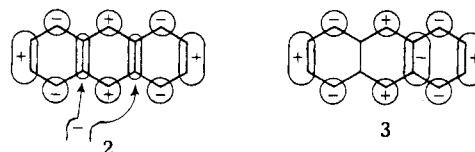
Using 2,3-dimethylnaphthalene fluorescence as a secondary standard, $\phi = 0.38$,⁸ the total fluorescence quantum yield of **1** was estimated to be 0.15 ± 0.02 , which is the sum of the naphthalene-like emission ($\phi = 0.13 \pm 0.02$) and the anthracene emission ($\phi = 0.024 \pm 0.004$). Since anthracene has a fluorescence quantum efficiency of 0.24 in benzene,¹⁰ our results suggest that the quantum yield of singlet excited anthracene formed in the photorearrangement of **1** is about 0.1.¹¹

Although **1** fluoresces with lower efficiency than do ordinary naphthalenes, its radiative lifetime (τ_f/ϕ_f) does not differ greatly from those of other naphthalenes.⁸ A principal mode of decay of photoexcited naphthalenes is intersystem crossing, and it is reasonable to expect that **1** will also undergo intersystem crossing but with lower efficiency. The lowest triplets (T_1) of naphthalenes are, of course, much longer lived than are the corresponding singlet states, so we expect that T_1 of **1** can also rearrange to give T_1 of anthracene. Unfortunately, neither the phosphorescence of naphthalenes nor that of anthracene is detectable in solution at room temperature, so that quantitative aspects of the observed rearrangement in the triplet manifold cannot presently be fully demonstrated. An appreciable fraction of the nonemitting anthracene formed in this rearrangement ($\phi = 0.31$) may arise *via* the triplet–triplet route mentioned, and it is probable that a much larger fraction of the anthracene formed from excited **1** is in some excited state.



Although the amount of energy available in the adiabatic conversion of **1** to anthracene may be estimated at 75–80 kcal, which is sufficient to populate the triplet state or the singlet excited state of anthracene, we have no experimental evidence that either of these two states were appreciably populated during the thermal decomposition of **1**. It has been reported that dewar benzenes decompose thermally to yield benzenes in their triplet states.¹² In spite of the fact that the conversion of **1** to

triplet anthracene is energetically a much more favorable process, it apparently does not occur. Since the lowest antibonding orbital of anthracene (ψ_8 , **2**) is symmetrical with respect to the xz and yz planes bisecting the molecule,¹³ while the molecular orbitals in **1**, a 2,3-disubstituted naphthalene can only be symmetrical with respect to the xz plane, the adiabatic conversion of **1** to excited anthracene is not favorable because of the lack of orbital symmetry.^{13,14} The lowest antibonding orbital of **1** also lacks symmetry with respect to the yz plane. However, it is interesting to note the similarity between ψ_8 of anthracene (**2**) and the molecular orbital of **1** constructed from ψ_6 of naphthalene¹⁵ and π_1 and σ_1 of cyclobutene followed by a disrotatory ring opening (**3**). This formal similarity suggests that conversion among the excited states is allowed. The significance of such orbital correlation in the interconversion among excited molecules and related processes is being examined.



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(13) E. Heilbronner and P. A. Straub, "Hückel Molecular Orbitals," Springer-Verlag, New York, N. Y., 1966, p Z14.

(14) Dewar benzenes possess symmetries in both xz and yz planes, and the orbital correlation between dewar benzene and the B_{1u} states (S_1 or T_1) of benzene has been pointed out by D. Bryce-Smith and H. C. Loungert-Higgins, *Chem. Commun.*, 593 (1966).

(15) Reference 13, p Z10.

(16) National Science Foundation Undergraduate Research Participant, 1972.

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Cross-Conjugated Pentadienyliron Tricarbonyl Cations. Dominance of Frontier Orbital Interaction in Metal–Carbon Bonding

Sir:

The Dewar–Chatt–Duncanson theory¹ of bonding in transition metal π -complexes has been of immense utility in understanding the structure, spectral properties, and chemical reactivity of these compounds.² Bonding is treated as charge transfer interactions of

(1) (a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, C71 (1951); (b) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(2) Its exclusive use for presentation of bonding in current general monographs on organotransition metal chemistry serves as a measure of its acceptance. Cf. (a) M. L. H. Green, "The Transition Elements, Vol. 2 of Organometallic Compounds," Methuen, London, 1968; (b) R. B. King "Transition Metal Organometallic Chemistry, An Introduction," Academic Press, New York, N. Y., 1969; (c) M. Tsutsui, M. N. Levy, A. Nakamura, M. Ichikawa, and K. Mori, "Introduction to Metal π -Complex Chemistry," Plenum Press, New York, N. Y., 1970.

(8) Reference 7, p 110.

(9) J. K. McVey, unpublished result.

(10) W. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).

(11) The relative intensity of the anthracene emission to the naphthalene-like emission from **1** does increase slightly upon thorough degassing; therefore, the partial contribution of T–T annihilation in the formation of S_1 of anthracene may not be excluded.

(12) P. Lechtken, R. Breslow, A. H. Schmidt, and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3025 (1973).