Photodimerization and Excimer Emission in a Crystalline 1,4-Diphenylbutadiene

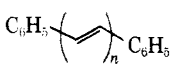
M. D. Cohen,* A. Elgavi, B. S. Green,* Z. Ludmer, and G. M. J. Schmidt[1]

Contribution from the Department of Chemistry, The Weizmann Institute of Science, Rehovot, Israel.

Received February 7, 1972

Abstract: Crystalline 1-(2,6-dichlorophenyl)-4-phenyl-*trans,trans*-buta-1,3-diene (**5**) displays excimer emission while the crystalline nonchloro analog (**2**) and solutions of both compounds exhibit only monomer emission. Solid **5**, unlike **2**, undergoes reaction on irradiation yielding only one of two topochemically-allowed, mirror-symmetric photodimers.

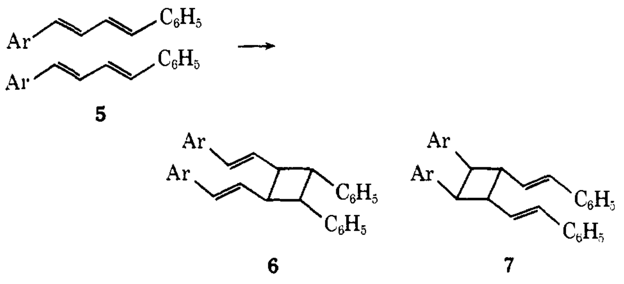
The α,ω-diphenyl all trans polyenes, **1–4**, show fluorescences which approximately mirror their long wavelength absorptions.[2-4] Furthermore, although these compounds are photoreactive in solution[2,5] they are all light stable in the crystal.[6] On the other hand, a substituted *trans*-stilbene which crystallizes in a structure with close-packed, parallel, strongly overlapped molecules (shortest unit cell axis ~4 Å) has been found to display excimer fluorescence and to undergo photodimerization in the solid, affording the topochemically expected mirror-symmetric dimer.[7] These observations indicate that the spectroscopic and photochemical properties of solid stilbenes may be determined by their crystal structures. It becomes of interest to investigate the diarylbutadienes from a similar point of view.



$n = 1$, **1** $n = 3$, **3**
$n = 2$, **2** $n = 4$, **4**

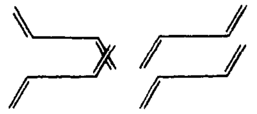
While 1,4-diphenyl-*trans,trans*-buta-1,3-diene (**2**) is light stable in the solid, its degassed solution in *n*-hexane affords on irradiation a complex mixture of dimers.[8] No dimers from the irradiation of this or other diarylbutadienes in solution[9] or in the solid have been characterized. We here report on the photochemical and spectroscopic properties of a crystalline diarylbutadiene of the same structure type (shortest unit cell axis ~4 Å) as the reactive solid stilbene referred to above.

1-(2,6-Dichlorophenyl)-4-phenyl-*trans,trans*-buta-1,3-diene (**5**) crystallizes in a structure with a unit cell axis of 4.00 Å. This material should then show excimer emission and undergo photodimerization if the molecule is intrinsically capable of participating in these processes. If dimerization occurs, then, on the basis of the crystal structure (Figure 1), the dimers expected are the two mirror-symmetric ones, **6** and **7**, which can result from interactions along the short *b* axis between the double bonds of two styryl groups and of two dichlorostyryl groups, respectively.



$Ar = 2,6\text{-}C_6H_3Cl_2$

The presence or absence of excimer emission in this system is a feature of particular interest since such emission has generally been associated only with rigid, fused-ring systems.[10] Further, it has recently been argued, on the basis of calculations,[11] that an excimer species would be expected for the approach configuration a in which there is overlap of only the central C–C bonds of two *s-trans*-butadiene molecules, one of which is excited. The arrangement of the butadiene molecules b, such as is found in **5**, was not considered; however, extension of these calculations to configuration b indicates that this arrangement is also expected to be excimer forming, the interaction of two unsubstituted butadiene molecules 4 Å apart being predicted to lead to a red shift in emission of *ca.* 4000 cm⁻¹ from that of pure monomer.[12] The presence of the aryl groups introduces differences, but to what extent this affects the argument is not yet clear.



a b

Experimental Section

1-(2,6-Dichlorophenyl)-4-phenyl-*trans,trans*-1,3-butadiene (5). To a solution of cinnamyltriphenylphosphonium chloride (7.1 g, 17 mmol) and 2,6-dichlorobenzaldehyde (3.15 g, 18 mmol) in 25 ml of absolute ethanol was added an ethanolic solution of lithium ethoxide (0.2 *M*, 90 ml). After standing for 1 hr at room temperature, the resulting mixture was cooled in an ice bath and the solid

---

(1) Deceased, July 12, 1971.

(2) J. H. Pinckard, B. Wille, and L. Zechmeister, *J. Amer. Chem. Soc.*, **70**, 1938 (1948).

(3) K. W. Hausser, R. Kuhn, and E. Kuhn, *Z. Phys. Chem., Abt. B*, **29**, 417 (1935).

(4) J. B. Birks and D. J. Dyson, *Proc. Roy. Soc., Ser. A*, **275**, 135 (1963).

(5) G. J. Fonken, *Chem. Ind.* (*London*), 1327 (1962).

(6) We have found that crystalline samples of compounds **1–4** are unchanged after extended periods of irradiation ($\lambda > 300$ nm).

(7) M. D. Cohen, B. S. Green, Z. Ludmer, and G. M. J. Schmidt, *Chem. Phys. Lett.*, **7**, 486 (1970).

(8) G. Aviv and A. Yogev, personal communication.

(9) C. C. Leznoff and R. J. Hayward, *Can. J. Chem.*, **48**, 1842 (1970); R. J. Hayward and C. C. Leznoff, *Tetrahedron*, **27**, 2085 (1971).

(10) Th. Foerster, *Angew. Chem., Int. Ed. Engl.*, **8**, 333 (1969).

(11) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968).

(12) L. Salem, private communication.

precipitate filtered off and washed with water. The product, 2.2 g (47% yield), was recrystallized from ethanol to give colorless needles: mp 107–108°; uv λ_{max}^{EtOH} 317 nm (ϵ ~3.6 × 10^4). Crystallographic constants are: space group $P2_12_12_1$; $a = 9.39$, $b = 4.00$, $c = 35.30$ Å; $d_c (z = 4) = 1.38$, $d_m = 1.36$ g ml^{-1}.

Anal. Calcd for $C_{16}H_{12}Cl_2$: C, 69.83; H, 4.40; Cl, 25.77. Found: C, 69.70; H, 4.36; Cl, 25.50.

The cis,trans isomer of **5**, also formed in the above reaction, could be isolated from the initial filtrate of the reaction mixture as a colorless oil by extraction with *n*-hexane and chromatography of the extract (silica gel, *n*-hexane eluent).

Photodimerization of 5. Thin layers of powdered **5** were irradiated at 5° with Westinghouse Sunlamps through 6-mm window glass (8–10 days). Alternatively, a suspension of powdered **5** was dispersed in water (*ca.* 1 g/25 ml; wetting of solid was assisted by adding a few drops of soap solution) and irradiated through Pyrex with a Wild-Heerbrugg HBO-200 apparatus while being stirred vigorously (10–15 hr); external cooling with a cold water bath or with a stream of air prevented overheating of the sample. The progress of the reaction was followed by tlc analysis (chloroform: *n*-hexane, 1:4) which revealed a single, less mobile spot, **6**, in addition to unreacted **5**. Irradiation at temperatures of *ca.* 35° or higher led to side products as a result of partial melting. Column chromatography on silica gel afforded unreacted **5**, eluted with *n*-hexane, followed by dimer **6**, eluted with 10–30% chloroform in *n*-hexane, in yields up to 80%. Crystallization of **6** from ethanol gave colorless prisms: mp 103.5–104.0°; uv λ_{max}^{EtOH} 250 nm (ϵ ~21,000); $\delta_{TMS}^{CDCl_3}$ 3.9–4.1 (4 H, m, cyclobutane hydrogens), 6.6 (4 H, m, vinyl hydrogens), and 7.15 (16 H, m, aromatic hydrogens); *m/e* (*inter alia*) 548 (M^+, Cl_4), 368 [$C_6H_3Cl_2(CH{=}CH)_3C_6H_3Cl_2$, 2.1%], 274 ($M/2^+$, Cl_2, 100%); ir ν_{max}^{KBr} 960 cm^{-1} (*trans*-CH=CH).

Hydrogenation of 6. An ethanolic solution of **6** containing 5% palladium-on-carbon catalyst was treated with hydrogen at atmospheric pressure until hydrogen uptake ceased. Filtration of catalyst and evaporation of solvent left **8** as a viscous, colorless oil: uv λ_{max}^{EtOH} 253 nm (ϵ ~3600); ir ν_{max}^{KBr} 2950 (CH_2), 3050 cm^{-1}, disappearance of 960 cm^{-1} band; $\delta_{TMS}^{CDCl_3}$ 2.0 (4 H, m, $C_6H_3Cl_2CH_2CH_2$), 3.2 (6 H, m, $C_6H_3Cl_2CH_2$ and cyclobutane hydrogens adjacent to methylene), 3.75 (2 H, m, cyclobutane hydrogens adjacent to phenyl), and 7.15 (16 H, m, aromatic hydrogens); *m/e* 552 (M^+, Cl_4), 276 ($M/2^+$, Cl_2, 100%), 180 (stilbene, 6%), 179 (stilbene − 1, 12%), 178 (stilbene − 2, 10%). The stilbene peaks are absent in the mass spectrum of **6**.

Ozonolysis of 6. A solution of 100 mg of **6** in 30 ml of ethyl acetate, 10 ml of acetic acid, and 2 ml of water was cooled to −18° and treated with 1% ozone (Welsbach apparatus) for 10 min. 30% hydrogen peroxide (1 ml) was then added, the solution was allowed to stand at room temperature overnight, and the solvents were evaporated *in vacuo*. Preparative thin layer chromatography (eluent, *n*-hexane:chloroform:acetic acid:methanol, 50:45:2.5:2.5) of the residue afforded benzoic acid (identified by ir and melting point; apparently *via* oxidation of the cyclobutane ring), 2,6-dichlorobenzaldehyde (identified by ir and melting point; an authentic sample of this material was also resistant to oxidation under these conditions), and *β*-truxinic acid.[13] The latter was esterified to give dimethyl *β*-truxinate.[13]

Fluorescence Measurements. Fluorescence spectra were measured with an Aminco-Bowman spectrophotofluorimeter, modified to enable variable-temperature studies at front-face illumination. The photomultiplier was an EMI 9558B with a Fluke power supply. Samples were held in a 3-mm i.d. evacuated cylindrical cell housed in a quartz dewar. To minimize light scattering suitable Corning cut-off filters were used. Emission spectra were corrected by the method of Melhuish,[14] slightly modified by the use of barium sulfate powder in place of the mirror in the sample compartment. Relative excitation intensities were determined by use of Rhodamine-B solution.[14]

For determination of fluorescence quantum yields a 200-W mercury-xenon lamp was used, with appropriate cut-off and interference filters (Jenaer Glasswerk Schott und Gen.). The quantum yields were determined by comparison of the areas under the corrected spectra of the sample with that obtained with pyrene powder.[15]

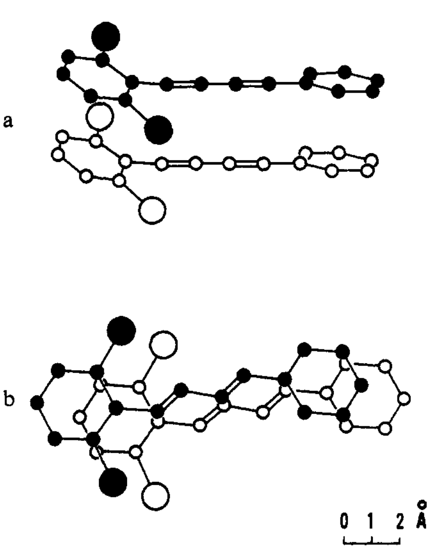
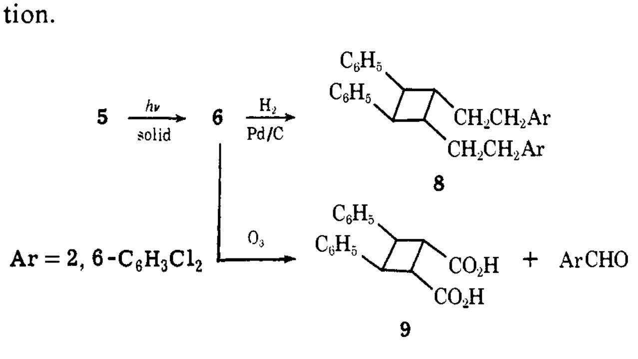


Figure 1. Packing diagram of 1-(2,6-dichlorophenyl)-4-phenyl-*trans,trans*-butadiene (**5**) seen (a) edge-on along the planar butadiene chains and (b) normal to the planar 2,6-dichlorophenyl groups.

All crystalline materials used for fluorescence measurements were center-cuts from samples extensively zone refined in vacuum.

Results and Discussion

Irradiation (λ >300 nm) of solid **5** at +5° affords a single photoproduct, characterized as **6** from the following evidence. The mass spectrum shows signals corresponding to the molecular ion (*m/e* 548) and the two possible fragmentation pathways of the cyclobutane ring [$C_6H_3Cl_2(CH{=}CH)_3C_6H_3Cl_2$ (*m/e* 368) and $C_6H_3Cl_2(CH{=}CH)_2C_6H_5$ (*m/e* 274, base peak)] all exhibiting the characteristic chlorine isotope distribution pattern. The nmr spectrum displays aromatic, vinylic, and cyclobutane resonances in the expected ratios. The uv spectrum reveals styryl absorption [λ_{max}^{EtOH} 250 nm (ϵ ~21,000)]. Catalytic hydrogenation of **6** proceeded with uptake of 2 mol of hydrogen to give **8** as a colorless oil, with diminished uv absorption and expected mass spectrum and nmr spectrum. Finally, ozonolysis of **6** and oxidative work-up afforded 2,6-dichlorobenzaldehyde and *β*-truxinic acid (**9**) which unambiguously establishes the cyclobutane configuration.



The absence of **7** as a photoproduct is unexpected since other molecules containing a double bond attached to a 2,6-dichlorophenyl group yield photodimers in the solid state.[16] The absence of reaction

---

[13] H. I. Bernstein and W. C. Quimby, *J. Amer. Chem. Soc.*, **65**, 1845 (1943).

[14] W. H. Melhuish, *J. Opt. Soc. Amer.*, **52**, 1256 (1962).

[15] J. B. Birks, A. A. Kazzaz, and T. A. King, *Proc. Roy. Soc., Ser. A*, **291**, 556 (1966).

[16] (a) 2,6-Dichloro-*trans*-cinnamic acid (M. D. Cohen, G. M. J. Schmidt, and F. I. Sonntag, *J. Chem. Soc.*, 2000 (1964); (b) methyl 2,6-dichloro-*trans*-cinnamate (B. S. Green and G. M. J. Schmidt, to be submitted for publication); (c) 2,6-dichlorochalcone (M. Luwisch, Ph.D. Thesis, Weizmann Institute of Science, 1968).

Cohen, et al. / Photodimerization of 1,4-Diphenylbutadiene

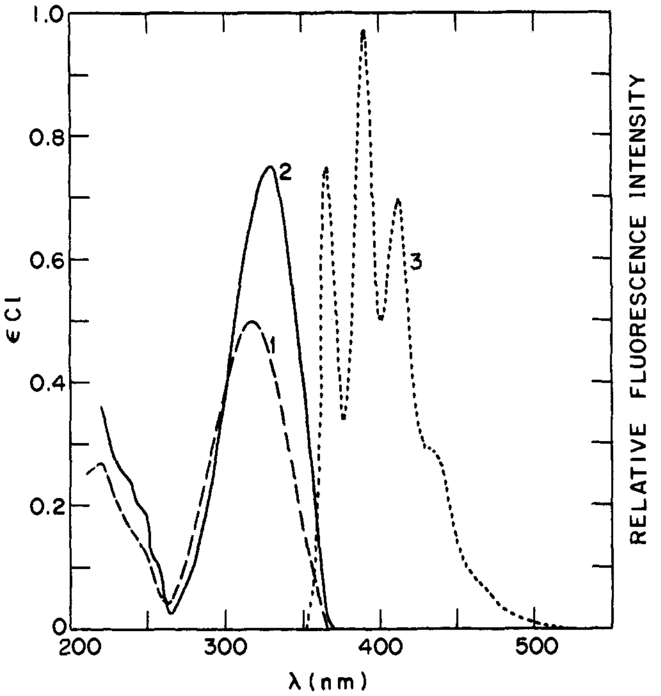


Figure 2. Absorption and fluorescence spectra of **5** in methylcyclohexane:isohexane, 2:1 solution: absorption (7.5×10^{-5} *M*; path length 0.2 cm) at 300° (curve 1) and 77°K (curve 2); fluorescence (3.5×10^{-5} *M*) at 77°K (curve 3).

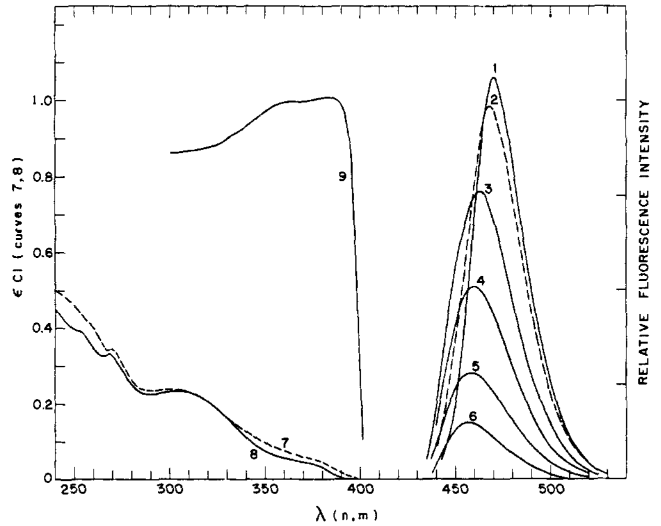


Figure 3. Absorption and emission spectra of crystalline **5**: curves 1-6, emission of crystalline powder as a function of temperature (1, 98; 2, 145; 3, 205; 4, 233; 5, 253; 6, 275°K); curves 7 and 8, absorption of polycrystalline film at 300° and 77°K, respectively; curve 9, corrected excitation spectrum of crystalline powder at 77°K.

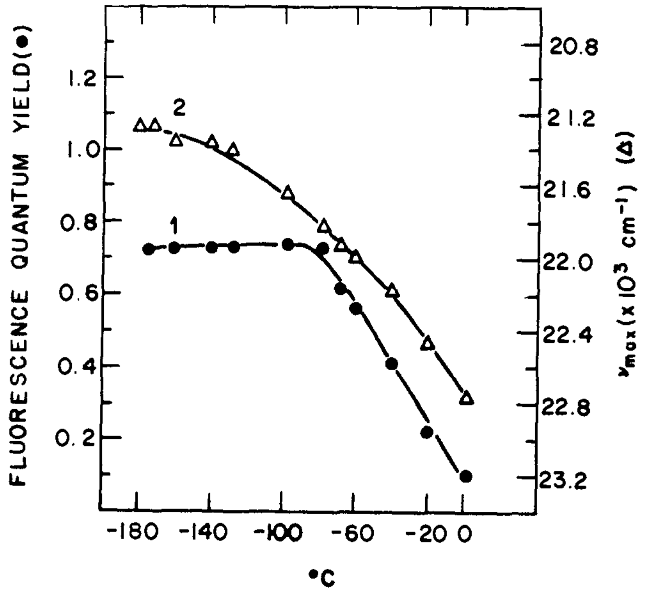


Figure 4. Fluorescence quantum yield of **5** on excitation with 365-nm light as a function of temperature (curve 1); λ_{max} of corrected excimer emission as a function of temperature (curve 2).

adjacent to this group in **5** may be ascribed to the twist of this moiety (by 37.4°)[17] with respect to the essentially planar butadiene chain, which both hinders close approach at this end of the molecule and decreases conjugation and therefore the reactivity of the dichlorostyryl double bond. (The phenyl group is twisted out of the butadiene plane, in the same sense as the dichlorophenyl group, but by only 15.4°.)[17] Whatever the explanation the fact that there is specificity of reaction, even though the interbond distances are identical for the two double bonds, implies that in addition to the topochemical restriction to solid-state photocyclodimerization (parallel >C=C< groups separated by 4.0 ± 0.2 Å),[18] other factors are significant in determining the efficiency of reaction.

The unsubstituted butadiene derivative **2** has structured long wavelength absorption (λ_{max} 328 nm, ϵ 5.2×10^4) and emission (λ_{max} 380 nm) in solution[2-4] as well as in the crystal.[19] The dichloro derivative **5**, on the other hand, has structureless absorption in ethanol and in methylcyclohexane, both at 77° and 300°K (Figure 2). The maximum extinction coefficient (λ_{max} 317 nm, ϵ 3.6×10^4) of **5** is appreciably lower than that of **2**. These effects, too, may be associated with the nonplanarity of the molecule which would not only decrease the conjugation but would destroy the molecular pseudocenter of symmetry thus making more allowed the ^{1}C–^{1}A transition which would steal some of the intensity of the long wavelength ^{1}B–^{1}A band.[20]

In contrast to the absorption, the emission of **5** (λ_{max} 389 nm) in frozen hydrocarbon glass shows well-defined structure (Figure 2). However, the emission of a crystalline powder of **5** is structureless with λ_{max} ~470 nm at 77°K (Figure 3). The displacement of this maximum from the lowest energy vibrational sub band of the emission from solution is 6000 cm^{-1}. The lack of structure and large shift are characteristic of excimer emission.[10] Further, the shifts of the fluorescence and of the absorption with temperature are similar to those found with other excimer-emitting solids.[21] This variation and that of quantum yield with temperatures are shown in Figure 4. When a powder of **5** is irradiated at room temperature the emission, measured at low temperature, shows a decrease in the intensity of

---

[17] The crystal structure analysis of 5 was carried out in this laboratory by D. Rabinovich and Z. Shaked, who will report the details separately.

[18] G. M. J. Schmidt, "Reactivity of the Photoexcited Organic Molecule," Interscience, New York, N. Y., 1967, p 227.

[19] Unpublished results, this laboratory.

[20] H. H. Jaffe and M. Orchin, "Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 232, and references therein cited.

[21] J. B. Birks and A. A. Kazzaz, *Proc. Roy. Soc., Ser. A*, 304, 291 (1968).

the 470-nm emission and the appearance of a structured emission at higher energy which is due to monomer embedded in dimer matrix; this argues against the diffuse 470-nm band being attributed to impurity.

In stretched polyethylene film[22] the absorption of **2** shows a constant dichroic ratio throughout the long wavelength band and is interpretable as due to a single, long-axis polarized, transition. The absorption of **5**, however, shows some structure and the dichroic ratio varies continuously across the band; this may indicate the superposition of two transitions, one of which is long-axis polarized.

In conclusion, the absence of excimer emission from, and the light stability of, crystalline diphenylbutadiene are not intrinsic to the molecule but result from unsuitable packing in the crystal, as in *trans*-stilbene. Our results show that even a molecule which is distorted out of planarity in its ground state may give rise to excimer formation although, unlike previously studied fused-ring compounds, it is quite flexible in fluid media. Although the ground-state geometry of our system has been exactly analyzed by X-ray methods we can only speculate on the question of the geometry of the excimer species. Thus while the molecules are nonplanar in the ground state it is conceivable that they are planar in the excimer. This is a question of considerable interest since it relates to the possibility of using photodimerization in such crystals to generate optically active dimers, a topic which we are investigating in this laboratory.

---

[22] A. Yogev, L. Margulies, and Y. Mazur, *Chem. Phys. Lett.*, **8**, 157 (1971). We thank L. Margulies of this laboratory for these measurements.

Photodimerization of 9-Anthroic Acid and Sodium 9-Anthroate[1]

Dwaine O. Cowan*[2] and Walter W. Schmiegel[3]

Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. *Received February 29, 1972*

Abstract: The photodimerization and fluorescence quantum yields of 9-anthroic acid in ethanol and benzonitrile and sodium 9-anthroate in water, deuterium oxide, and benzonitrile were measured at 365 nm as a function of concentration. These efficiencies when coupled with fluorescence lifetime measurements are used to evaluate various mechanistic schemes and to determine the rate constants for the individual steps in the simplest mechanistic scheme that is consistent with our kinetic data.

Changes in substituents and solvents have been observed to produce qualitative and quantitative changes in the rates of reaction and product distributions for numerous thermal but very few photochemical reactions.[4] It has previously been shown that both heavy and light atom solvents can profoundly alter the course of the photodimerization of acenaphthylene.[5] While these solvent effects have been useful in the elucidation of the mechanism of dimerization,[6] it has not been possible to evaluate quantitatively the solvent effect on each of the reaction steps. To learn more about the reaction medium effects on the rates of radiative and nonradiative processes, we have chosen to study the photochemistry of 9-anthroic acid in ethanol and benzonitrile and sodium 9-anthroate in water, deuterium oxide, and benzonitrile.

Anthracene and its many derivatives undergo both relatively efficient dimerization (see Figure 1) and fluorescence.[7] All anthracene dimers formed in solution apparently have the head-to-tail stereochemistry[8] shown in Figure 1. To learn more about the dimerization mechanism for substituted anthracenes and to determine the effect of solvents on the various specific rate constants, we have performed the following measurements: *first*, low-conversion quantum yields of dimer formation as a function of concentration were determined; *second*, relative quantum yields of fluorescence as a function of concentration were measured over the concentration range at which the dimerization was studied; *third*, absolute fluorescence quantum yields in dilute solutions were measured; and *fourth*, the fluorescence lifetimes in dilute solutions were measured.

Results and Discussion

Absorption and Fluorescence Spectra. The absorption and uncorrected fluorescence spectra of 9-anthroic acid (9-COOH) in acidified ethanol and sodium 9-anthroate (9-COONa) in water are shown in Figure 2. The corresponding spectra of the acid and salt in benzonitrile are given in Figure 3.

Whereas a good mirror image relationship of the absorption and fluorescence spectra exists for the sodium 9-anthroate in both water and benzonitrile a very large Stokes shift and an unstructured emission band

---

[1] Photochemical Reactions. VIII. For part VII, see D. O. Cowan and W. W. Schmiegel, *Angew. Chem.*, **83**, 545 (1971).

[2] Guggenheim Fellow, 1970–1971.

[3] National Science Foundation Graduate Trainee, 1965–1969.

[4] E. M. Kosower, "Physical Organic Chemistry," Wiley, New York, N. Y., 1968; A. A. Lamola and N. J. Turro, "Technique of Organic Chemistry. XIV. Energy Transfer and Organic Photochemistry," P. A. Leermakers and A. Weissberger, Ed., Wiley, New York, N. Y., 1969.

[5] D. O. Cowan and R. L. Drisko, *Tetrahedron Lett.*, 1255 (1967); *J. Amer. Chem. Soc.*, **89**, 3068 (1967).

[6] D. O. Cowan and R. L. Drisko, *ibid.*, **92**, 6281, 6286 (1970).

[7] A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, New York, N. Y., 1968.

[8] D. E. Applequist, T. L. Brown, J. P. Kleinman, and S. T. Young, *Chem. Ind.* (*London*), 850 (1959); D. E. Applequist, E. C. Friedrich, and M. T. Rogers, *J. Amer. Chem. Soc.*, **81**, 457 (1959); R. Calas, P. Mauret, and R. Lalande, *C. R. Acad. Sci.*, **247**, 2146 (1958); O. L. Chapman and K. Lee, *J. Org. Chem.*, **34**, 4166 (1969).