2,2′-Di(5,7-di-*tert*-pentylbenzoxazolyl) (III). This was obtained as a by-product of the attempted synthesis of 2,4,5-tri(5,7-di-*tert*-pentylbenzoxazol-2-yl)triazine from 3 mol of 2-amino-4,6-di-*tert*-pentylphenol and 1 mol of *s*-triazine-1,3,5-carbonyl chloride.

1,4-Di(benzoxazol-2-yl)buta-1,3-diene (V). Muconyl chloride (1 g) and *o*-aminophenol (1.2 g) in dioxane (14 ml) containing triethylamine (1.7 ml) were heated for 30 min on a steam bath. On cooling, the solid was collected and recrystallized from 50% aqueous pyridine to give muconoyl di(2-hydroxy)anilide (1.3 g, 57%), mp 275–276°. This compound (1 g) was added over 20 min to zinc chloride (anhydrous, 10 g) and water (0.7 ml), stirred, and heated in an oil bath at 160–170° for 1 hr. The stirring was then stopped and the heating was continued overnight. Subsequently the mixture was cooled to about 120° and water (10 ml) was added with stirring to give a smooth slurry. The mixture was cooled to 80° and poured into water (20 ml) containing concentrated hydrochloric acid (1.4 ml). After standing, with occasional stirring, for 1 hr the precipitate was collected and recrystallized from dioxane to give a pale-yellow solid (0.53 g, 60%), mp 264–266°.

4,4′-Di(5,7-di-*tert*-pentylbenzoxazol-2-yl)-1,1′:4′,1″:4″,1‴-quaterphenyl (XI). 4-Carboxy-4′-iodobiphenyl prepared from biphenyl[36–38] was converted by the standard procedure to the corresponding acid chloride, mp 149–150°.

4-Iodo-4′-(5,7-di-*tert*-pentylbenzoxazol-2-yl)biphenyl. 2-Amino-4,6-di-*tert*-pentylphenol (1.3 g) and 4-chlorocarbonyl-4′-iodobiphenyl (1.8 g) were heated under reflux for 2 hr in chlorobenzene (35 ml). The solvent was distilled off and the residue was heated under water-pump vacuum in an oil bath at 240–260° for 15 min. The product was recrystallized from petroleum ether (bp 60–80°) to give pale-yellow crystals (1.97 g, 73%), mp 171–174°.

4-Iodo-4′-(5,7-di-*tert*-pentylbenzoxazol-2-yl)biphenyl (4 g) was throughly mixed with copper powder (8 g) and plunged into an oil bath (N_2 atmosphere) at 270–280° for 15 min. The product was extracted with benzene overnight, the solvent evaporated, and the residue extracted with petroleum ether (bp 40–60°). Concentration and cooling of this solution gave pale-yellow crystals (0.76 g, 27%), mp 261–266°. A second recrystallization from the same solvent gave an analysis sample, mp 265–269°.

4,4′-Di(5,7-di-*tert*-pentylbenzoxazol-2-yl)diphenylacetylene (XIII). Diethyl diphenylacetylene-4-4′-diimidate dihydrochloride[34] (2 g) was thoroughly mixed with 2-amino-4,6-di-*tert*-pentylphenol and immersed under vacuum in a preheated oil bath at 240°. After the solid had melted and gas evolution subsided (about 10 min) the mixture was cooled to room temperature, still under vacuum. The product (2.3 g) was twice recrystallized from pyridine–water and finally from pyridine to give a white solid, mp 212–213°.

Acknowledgment. The authors wish to thank Miss P. E. Freeman and Mrs. J. Horton for carrying out the flash photolysis experiments.

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Excited Dimer Luminescence of Pairs of Phenanthrene Molecules

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Abstract: A phenanthrene sandwich dimer has been prepared by photolytic dissociation of the cis syn dimer of 9-hydroxymethylphenanthrene in a rigid matrix at 77°K. The fluorescence of this species is that of an excited dimer rather than an excimer; the phosphorescence similarly indicates a weak interaction in the triplet state. The luminescence of the partially overlapping pair formed by photolytic dissociation of the trans dimer of 4,5-methylenephenanthrene shows a very weak interaction. Previous reports of excimer luminescence for phenanthrene are suggested to be in error.

Most aromatic hydrocarbons which are not encumbered by bulky substituents have been found to form fluorescent excimers under some condition of temperature and/or concentration.[1,2] The binding energies are typically 6–10 kcal mol^{-1}. Phenanthrene is the only hydrocarbon of the four containing three or fewer rings which has not been shown unambiguously to form an excimer under any of the usual conditions. There is a brief report of what appeared to be delayed excimer fluorescence from phenanthrene in a hydrocarbon glass at 77°K[3] as well as a more recent report of luminescence in fluid solution at low temperatures which was interpreted as excimer phosphorescence.[4] It has also been said that the electrochemiluminescence spectrum of phenanthrene contained an excimer component.[5] We have examined the luminescence of a pair of phenanthrene molecules by the sandwich dimer technique[6] and found only weak interaction in both singlet and triplet states. These results suggest that the previous reports of excimer luminescence for phenanthrene are probably in error.

The determination of the fluorescence of a phenanthrene sandwich pair requires the photolytic dissociation of a phenanthrene photodimer (**1**) which must have a cis configuration. Phenanthrene itself does not photodimerize; the trans dimer (**2**, R = H; X = 2 H) has been prepared by a thermal route.[7] The failure of phenanthrene, with its stilbenoid double bond, to dimerize implies that the excimer is not long-lived at room temperature. This has also been suggested by Stevens and Dubois, who found phenanthrene to show negligible self-quenching of fluorescence at room temperature.[8]

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(3) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, 41, 3131 (1964); **42**, 1675 (1965).

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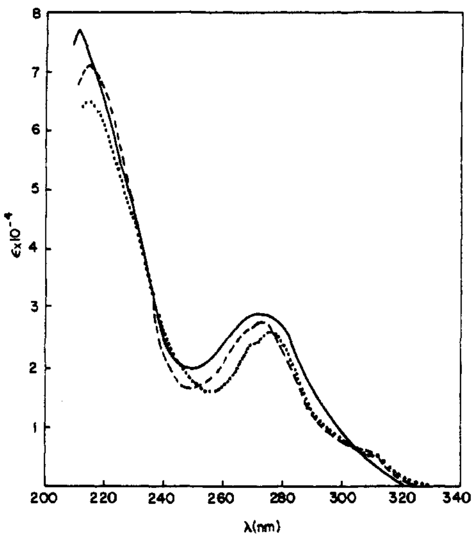
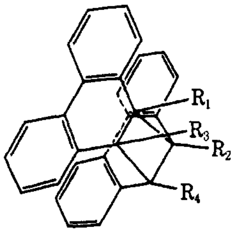


Figure 1. Ultraviolet absorption spectra of **1a** (——, CH_2Cl_2), **1b** (· · ·, EtOH) and **1c** (– – –, EtOH).

9-Cyanophenanthrene forms a photodimer which was assigned the trans configuration **2a**, implying that it does not arise from the excimer.[9] After the completion of our work, it was pointed out to us by Dr. Caldwell[10] that this assignment is incorrect and that the cyanophenanthrene dimer has the cis structure **1d**. The latter structure is in accord with our luminescence studies, whereas the trans structure is not, and we discuss our results in terms of the cis structure. 4,5-Methylenephenanthrene forms a trans photodimer;[11] its increased reactivity relative to phenanthrene is presumably due to the strain introduced by the methylene linkage. In order to prepare a cis photodimer of known structure, we irradiated the anhydride of 9-phenanthroic acid in which the anhydride linkage forces the intramolecular dimer to have the cis configuration **1a**. The photoproduct from the anhydride is assigned this structure on the basis of its ultraviolet and nmr spectra. The anhydride dimer **1a** could be hydrolyzed to diacid **1b** and it could also be reduced to diol **1c**, the cis dimer of 9-hydroxymethylphenanthrene. The latter was chosen for our fluorescence studies because we wanted the substituent to have the smallest possible effect on the phenanthrene ring system so that our results would bear on the unsubstituted hydrocarbon.



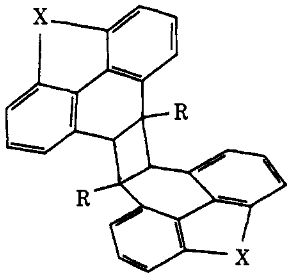
1a, $R_1 = R_2 = (\overset{\text{O}}{\overset{\|}{\text{—C—}}})_2\text{O}; R_3 = R_4 = \text{H}$

b, $R_1 = R_2 = CO_2H; R_3 = R_4 = H$

c, $R_1 = R_2 = CH_2OH; R_3 = R_4 = H$

d, $R_1 = R_4 = CN; R_3 = R_2 = H$

e, $R_1 = R_4 = CO_2H; R_2 = R_3 = H$



2a, R = CN; X = 2H

b, R = H; X = CH_2

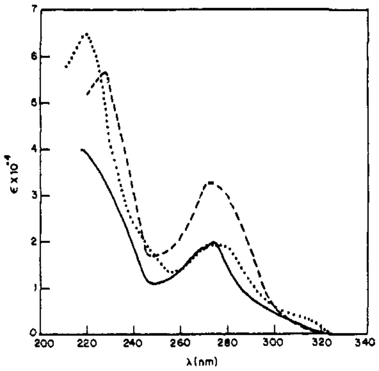


Figure 2. Ultraviolet absorption spectra of **1d** (——) and **1e** (· · ·) in ethanol and of **2c** (– – –) in methylene chloride.

The nmr spectra of the cis dimers have cyclobutyl proton resonances at higher fields than those in the trans dimers, attributable to shielding by the biphenyl system in the latter. The ultraviolet spectra of the two series (Figures 1 and 2) are also somewhat different.

Sandwich Dimer Luminescence

All of these photodimers could be converted to broken dimer[12] by irradiation with light of wavelength <~313 nm in a rigid glass at 77°K. The highest conversion to broken dimer was usually achieved with light from a 5-W low-pressure mercury lamp (predominantly 254 nm). The initial luminescence of the samples was usually weak and increased considerably with exposure to the exciting light, finally reaching a steady state.

9-Hydroxymethylphenanthrene. The luminescence spectrum of this sandwich pair in ethanol at 77°K is given in Figure 3a; the spectrum of the monomer obtained after thawing and refreezing the solution is given in Figure 3b. The spectra have been corrected for instrument sensitivity. It is obvious from the spectra that the interaction between the two phenanthrene moieties is much weaker than that expected for an excimer. Unfortunately, we were unable to determine the absorption spectrum of the broken dimer; the photodimer cannot be broken completely at 77° and the monomer absorption spectrum is not stronger

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

[9] M. V. Sargent and C. J. Timmons, *J. Chem. Soc.*, 5544 (1964).

[10] Based on a study of the nmr spectrum of the dimer, to be published by R. A. Caldwell, University of Texas at Dallas, Dallas, Texas 75230.

[11] G. Sugowdz, P. J. Collin, and W. H. F. Sasse, *Tetrahedron Lett.*, 3843 (1969).

[12] Broken dimer is defined as a pair of monomer molecules obtained by photolytic dissociation of a photodimer in a matrix sufficiently rigid to maintain the monomers in a geometry close to that which they have in the photodimer.

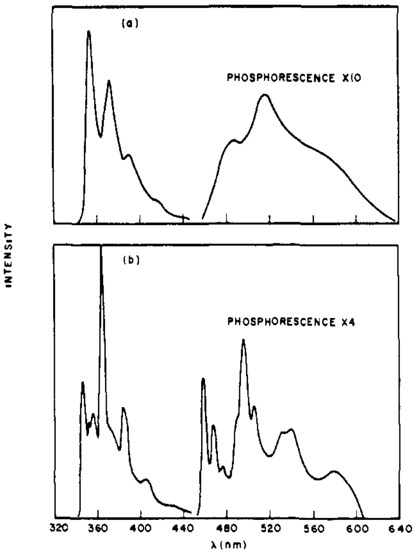

Figure 3. (a) Luminescence (corrected for instrument response) of the broken dimer derived from photodimer **1c** in ethanol at 77°K, excited with 313 nm light. (b) As above, after thawing and refreezing to give monomeric 9-hydroxymethylphenanthrene.

than that of the dimer. It is not possible to prove that we have generated a sandwich dimer rather than an offset pair or a pair separated to some extent because of the interposition of solvent between the biphenyl moieties, but, given the method of preparation and the fact that we observed similar behavior for all five cis photodimers in a variety of glasses, it seems likely that we have produced the desired sandwich pair. The hydroxymethylphenanthrene dimer experiment was done in ethanol, which forms a very rigid matrix at 77°.

The fluorescence of the 9-hydroxymethylphenanthrene sandwich pair appears to be that of an excited dimer. Relative to the monomer, there is a much greater fraction of the intensity in the O–O transition, as predicted by the vibronic coupling theory of Fulton and Gouterman.[13] The shift to lower energy for the first two bands of the dimer fluorescence is 0.65 kcm^{-1}. This corresponds to an exciton splitting of *ca.* 0.6 kcm^{-1} for the ^1L_b transition of phenanthrene in the sandwich pair configuration, larger than that observed in *absorption* for the anthracene sandwich pair (0.25 kcm^{-1}).[14] Since the phenanthrene ^1L_b transition is so much weaker than the allowed anthracene ^1L_a transition, it is probable that the interplanar spacing in the excited dimer is somewhat less than the normal van der Waals ground-state separation but not as small as that of an excimer. It is not likely that the fluorescence originates from interaction of the ^1L_a levels in the pair, as this would require an unreasonably large exciton splitting; the ^1L_a level is 5 kcm^{-1} above the ^1L_b state.

The phosphorescence of the broken dimer is markedly different from that of the monomer (Figure 3a,b). The vibrational structure is lost and there is a slight shift to lower energy. The spectrum is not the same as that reported by Langelaar, *et al.*;[4] the center of gravity of their spectrum (after approximate correction, using their curve) lies considerably to red of ours (≈2–3 kcm^{-1}). The change in phosphorescence of phenanthrene in the sandwich pair is similar to that which was recently reported for the naphthalene sandwich dimer.[15]

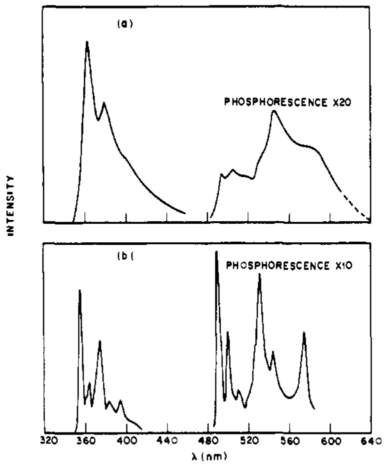

Figure 4. (a) Luminescence (corrected for instrument response) of the broken dimer derived from photodimer **1d** in methylcyclohexane glass at 77°K, excited with 313-nm light. (b) As above, after thawing and refreezing to give monomeric 9-cyanophenanthrene.

9-Cyanophenanthrene Dimer. The luminescence of the broken dimer (Figure 4) is that of an excited dimer and is remarkably similar to that of the sandwich pair derived from the cis photodimer of 9-hydroxymethylphenanthrene, in accord with the cis structure assigned by Caldwell to the photodimer. The interaction is stronger than that found for the molecular pair derived from the 4,5-methylenephenanthrene dimer. The interaction in the triplet 9-cyanophenanthrene pair is similar to that found for the other sandwich dimer, but the vibrational structure is still present in the nonsandwich species.

We also studied the photolytic dissociation of the anhydride **1a** and the cis diacids **1b** and **1e**, the former in both neutral and alkaline ethanol. The spectra were similar to those discussed above, but these species are more likely to be affected by the substituents, and we do not report these studies in any detail for this reason.

The photodissociation of the trans dimer of 4,5-methylenephenanthrene is expected to yield a molecular pair which overlaps only in the region of the phenanthrene 9,10 double bond. The exciton interaction, which varies as r^{-3}, is expected to be weak. The luminescence spectrum of the offset pair is given in Figure 5a; the monomer luminescence is given in Figure 5b. It is clear from the similarity of the spectra of both species that there is only a very weak interaction between the components of the pair. This finding supports the assignment of the cis structure to the dimer of 9-cyanophenanthrene. It is possible that, in cases such as these, the sandwich dimer technique might be of some help in assigning the structures of photodimers.

Conclusions

If our assumptions about the geometry of the sandwich pair produced by photolytic dissociation of the

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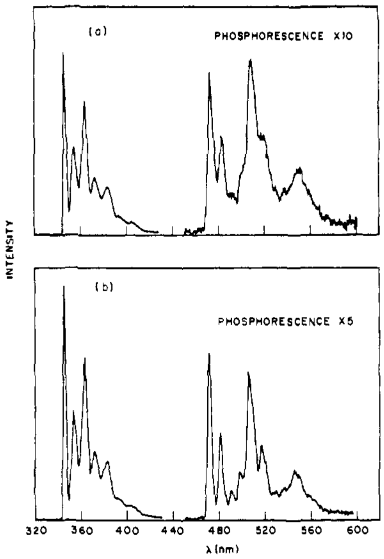

Figure 5. (a) Luminescence (uncorrected) of the molecular pair derived from the photodimer of 4,5-methylenephenanthrene in methylcyclohexane glass at 77°K, excited with 303-nm light. (b) As above, after thawing and refreezing to give monomeric 4,5-methylenephenanthrene.

cis dimers of 9-hydroxymethylphenanthrene and 9-cyanophenanthrene are correct, then it follows that phenanthrene does not form an excimer under favorable conditions. The photodimerization of 9-cyanophenanthrene may not proceed *via* an excimer; this remains an interesting question. The results of studies on anthracene[14] and naphthalene[15] sandwich dimers indicate that the activation energy involved must be small if there is any at all. It does not seem likely that the matrix would prevent excimer formation. We have no satisfactory explanation for the failure of phenanthrene to form an excimer. Various arguments involving the magnitude of the exciton splitting in sandwich dimers have been developed, but these results are sometimes inconsistent.[16] These arguments have sometimes indicated that benzene should not form an excimer because of the weakness of the ^1L_b transition and the large energy difference between this state and higher excited states having large associated transition moments. Yet benzene does form an excimer with a "normal" heat of association. We suggest that the theorists may wish to consider this problem in more detail.

Experimental Section

Melting points were determined with a heated metal block apparatus and are corrected. Nmr spectra were determined with a Varian A-60 or a Jeolco C-6OHL spectrometer in $CDCl_3$ solution with 1% TMS unless otherwise stated. Elemental analyses and the molecular weight determination were carried out by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y. Fluorescence (of solutions 10^{-3}–10^{-4} *M*) was excited with 313-nm light from a 200-W Hg–Xe lamp, passed through a pair of Jarrell-Ash 0.25-m monochromators with 2-mm slits. It was detected at right angles with a Jarrell-Ash 0.25-m monochromator (6000-Å grating, 1.6-nm slit width) and an EMI 6256S photomultiplier tube. Tuning fork choppers (200 Hz), which can be set in or out of phase, are in the excitation and emission light paths. A lock-in amplifier and *x–y* recorder coupled to the monochromator wavelength drive were used to detect and record the spectrum.

9-Cyanophenanthrene Dimer (1d). The nitrile (5 g) in toluene (30 ml, degassed) was irradiated for 2 days in a Rayonet reactor with long-wavelength lamps (λ 300–400 nm). The colorless crystalline product (2.9 g) precipitated directly. It had mp 213.5–214.5° (lit.[9] 214–216°). The nmr spectrum has peaks at τ 2.33–3.77 (16 H, aromatic) and 4.84 (2 H, cyclobutyl, lit.[9] 4.84).

The dimer **1d** was hydrolyzed to diacid **1e** by the method of Sargent and Timmons.[9] The nmr spectrum (acetone-d_6) shows signals at τ 2.31–3.80 (16 H, aromatic) and 5.10 (2 H, cyclobutyl, lit.[9] 4.96). The diacid decomposes slowly on standing.

9-Phenanthrenoic Anhydride Dimer (1a). 9-Bromophenanthrene (mp 64–65°) was treated with *n*-butyllithium in ether and then carbonated. The crude alkali-soluble product (95%) was recrystallized from glacial acetic acid and then from chloroform to give colorless needles (10%), mp 257.5–259.5°. The acid was converted to the anhydride by heating with acetic anhydride for 1 hr while slowly distilling part of the latter. The remainder was removed under reduced pressure and the residue crystallized from chloroform and then from acetone to give colorless crystals (60%), mp 197.5–199°, whose nmr spectrum exhibited a complex pattern from τ 0.66 to 2.70.

A solution of the anhydride (3.1 g) in toluene (1.5 l.) was deaerated by heating and bubbling with a nitrogen stream. After irradiation (5 hr) as above, the toluene was evaporated and the residue crystallized from chloroform to give colorless crystals (0.92 g), mp 260–262°. The nmr spectrum of the photoproduct has signals at τ 2.33–2.70 (16 H, aromatic) and 5.26 (2 H, cyclobutyl). *Anal.* Calcd for $C_{30}H_{18}O_3$: C, 84.49; H, 4.25. Found: C, 84.07; H, 4.19.

The anhydride dimer **1a** was hydrolyzed to the diacid **1b** by treatment with a dilute solution of sodium hydroxide in 20% aqueous dioxane. The diacid was crystallized from ethanol and had mp 256–261°, nmr τ 2.42–3.45 (16 H, aromatic) and 5.34 (2 H, cyclobutyl). *Anal.* Calcd for $C_{30}H_{20}O_4$: C, 81.07; H, 4.54. Found: C, 81.56; H, 4.78. This compound decomposes slowly on standing.

9-Hydroxymethylphenanthrene Dimer (1c). A solution of the anhydride **1a** (220 mg) and $LiAlH_4$ (*ca.* 40 mg) in ether was stirred for 2 hr. After treatment with water and extraction with chloroform, the crude product was recrystallized from aqueous ethanol (200 mg, mp 230–231°). Recrystallization raised the melting point to 232–233°, nmr (dimethylformamide) τ 2.33–3.33 (16 H, aromatic), 5.04 (2 H, cyclobutyl), and 5.62 (4 H, hydroxymethylene). *Anal.* Calcd for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81; mol wt, 417. Found: C, 86.71; H, 6.00; mol wt, 406 (osmometric, $CHCl_3$).

4,5-Methylenephenanthrene Dimer (2c). This dimer was prepared as described by Sasse.[11]

Acknowledgment. We thank Miss C. A. Pryde for performing the experiments on the dimer of 4,5-methylenephenanthrene.

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[16] J. B. Birks, *Chem. Phys. Lett.*, 1, 304 (1967), and references therein.