

Table III. Comparison of the Energy of the First CT Band (E_{ct}) of Various Pyridinium Iodides (in CH_2Cl_2) with σ Substituent Constants and Calculated Charges (Q_N) on the Pyridinium Nitrogen

Ring substituent	$E_{ct},^a$ kcal/mol	σ_m^b	σ_p^b	σ_p^{-c}	Q_N^d
H	76.7	0	0	0	1.00
3-CN	65.6	+0.56			1.54
2-CN	60.1				1.77
4-CN	58.5		+0.66	+1.00	1.57
3-COCH ₃	70.6	+0.38			1.29
2-COCH ₃	64.7				1.31
4-COCH ₃	63.8		+0.50	+0.87	1.37
4-CH ₃	80.7 ^e		-0.17		
3-CH ₃	78.0 ^e	-0.069			
3-COOC ₂ H ₅	71.3	+0.37			
4-COOC ₂ H ₅	65.2		+0.45	+0.68	
2-COOC ₂ H ₅	67.8				

^a Reference 2. ^b J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, p 87. ^c H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953). ^d The calculated charges on nitrogen are normalized to the unsubstituted 1-methylpyridinium ion. ^e From CHCl_3 data, ref 18, as "corrected" to CH_2Cl_2 .

III are +0.48, +0.65, and +0.89, respectively. These fall in between the values of σ_p and σ^- for the corresponding para substituent.

A reasonable correlation also exists between σ values (σ_p and σ_m) and the calculated charges on the nitrogen (Q_N). However, from a plot of these data (given in Table III) and the calculated values of Q_N for the 2-substituents, σ_p for the CN appears to be larger than $\sigma_{p\text{-CN}}$ while $\sigma_{o\text{-COCH}_3}$ is less than $\sigma_{p\text{-COCH}_3}$ and approximately equal to $\sigma_{m\text{-COCH}_3}$. Though the data are inter-

esting their interpretation in terms of the various possible effects is difficult to achieve satisfactorily without additional results with more compounds.

Summary

SCEH calculations for 1-methylpyridinium ion and 2-, 3-, and 4-cyano- (and acetyl-) 1-methylpyridinium ions give data on energy differences between the lowest and next highest vacant molecular orbitals of the pyridinium ion which are in good agreement with the observed separation of the two pyridinium iodide CT bands in methylene chloride. This supports previous indications that the higher energy CT band results from charge-transfer to the second vacant molecular orbital of the pyridinium ion.

Calculated electron affinities of the pyridinium ions show expected trends in plots with the low energy pyridinium iodide CT transition. A reasonable correlation was also found to exist between σ values (σ_p and σ_m) and the calculated charges on the pyridinium nitrogen.

A possible explanation for the failure to observe three CT bands has been proposed which, if valid, allows prediction of relative intensities from simple group theoretical considerations using idealized symmetry.

Acknowledgment. The authors wish to express their appreciation to Dr. George Clarke and Dr. Barry Kalman for the use of their program and for assistance in the performance of the calculations, and to Mr. Phillip Knorr for technical assistance. Especial thanks are due to Dr. Kalman for many helpful discussions.

Unusually Weak Electronic Interaction between Two Aromatic Chromophores Less Than 10 Å Apart in a Rigid Model Molecule¹

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Abstract: *p*-Dimethoxybenzene (D) and phenanthrene (P) chromophores have been attached to an inflexible σ -bond molecular frame composed of two norbornane and one cyclopropane rings. The two π systems in the model compound have a center-to-center separation of 9 Å and their orientation is fixed, mutually perpendicular, and nearly bisecting. The energy levels of D and P are appropriate for both singlet-singlet and triplet-triplet energy transfer from D to P. Each chromophore, when separately attached to the frame, emits easily detectable and characteristic fluorescence and phosphorescence. The absorption, emission, and excitation spectra of the model molecule in dilute solution closely resembled those of an equivalent equimolar mixture of the two chromophores. Since the D-P separation is well within ranges of efficient S-S and T-T transfer, it is obvious that the D-P relative orientation in the model compound is responsible for their weak interaction. Tentative explanations related to the exchange and resonance transfer concepts are offered. Special precautions have been taken to make sure that the spectrophotofluorometric measurements were not altered by spurious light-induced reactions or eventual photo-products.

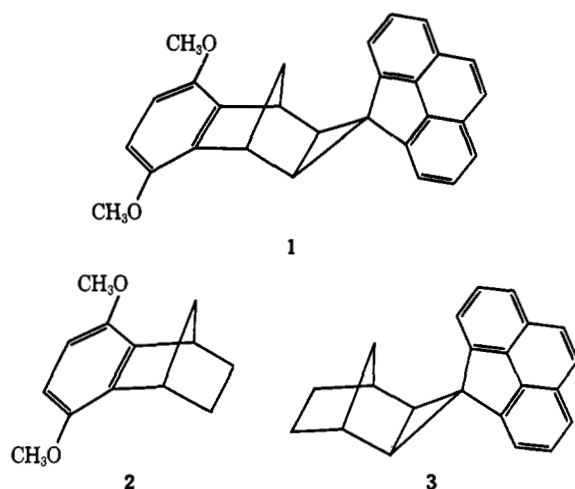
In a previous communication² we compared the absorption and emission spectra of model compound 1 with those of 3',6'-dimethoxybenzonorbornane (2) and

2,3-*exo*-(4',5'-methylenepheneanthrene-11'-spiro-1''-cyclopropane)bicyclo[2.2.1]heptane (3) which represent, respectively, the constituent *p*-dimethoxybenzene (D)

(1) Taken from the Ph.D. dissertation of D. S. C. Chang, George Washington University, 1970.

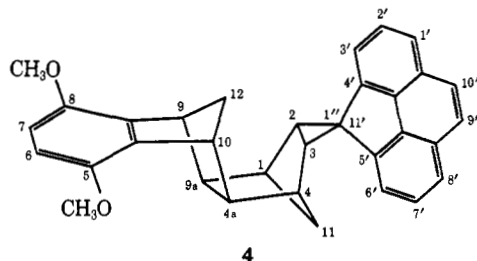
(2) (a) N. Filipescu, Symposium on Radiationless Transitions in

Molecules, Paris, France, May 1969; (b) N. Filipescu, J. R. DeMember, and G. R. Howard, *J. Chim. Phys. Physicochim. Biol.*, **67**, 84 (1970).



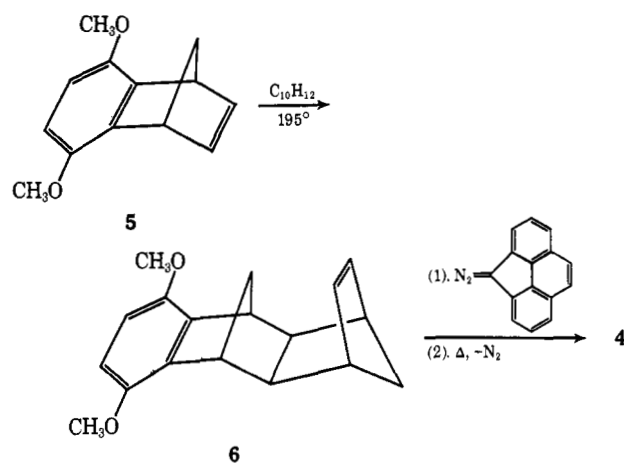
and phenanthrene (P) π chromophores of **1** separately attached to the inflexible norbornane σ -bond frame. The energy levels of the D and P chromophores lend themselves to both singlet-singlet and triplet-triplet energy transfer from D to P. Both **2** and **3** emit fluorescence and phosphorescence at different wavelengths with little spectral overlap and appropriately accurate detectability. Unlike spiro-linked fluorene,⁸ the P-on-the-frame chromophore in **1** and **3** is a very efficient emitter from both S_1 and T_1 states.

In the present paper we report on the spectrophotochemical properties of *endo,exo*-5,8-dimethoxy-1,4-methano-9,10-methano-2,3-*exo*-(4',5'-methylene)phenanthrene-11'-spiro-1'-cyclopropane)-1,2,3,4,4a,9,9a,10-octahydroanthracene, model compound **4**.

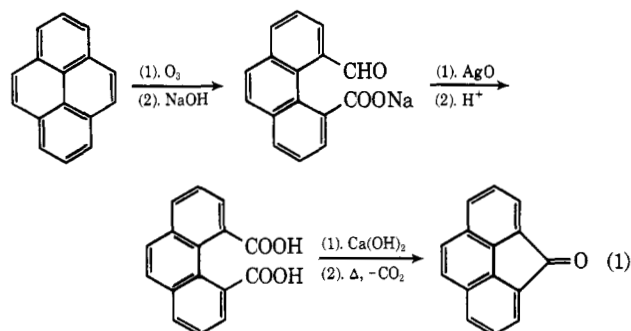


This molecule contains the same two D and P π chromophores as **1**, also in a perpendicular but somewhat different relative orientation and one norbornane unit further apart.

Preparation and Structure of 4. By a simpler procedure, 3',6'-dimethoxybenzonorbornadiene **5** was obtained directly from the Diels-Alder cyclopentadiene-benzoquinone adduct by enolization and etherification with NaOH and $(\text{CH}_3)_2\text{SO}_4$ without going through the diacetoxystage.^{2,4} The sealed-tube reaction of **5** with dicyclopentadiene above the dissociation temperature of the latter yielded *endo,exo*-5,8-dimethoxy-1,4-methano-9,10-methano-1,4,4a,9,10,10a-hexahydroanthracene (**6**). The elemental analysis, molecular weight, and nmr spectrum of **6** confirmed that 1,4 addition of 1 mol of cyclopentadiene to **5** has taken place but provided insufficient clues as to which one of the four possible stereoisomeric adducts was formed. The *exo,endo*



conformation was established with the additional help of the ir and uv spectra of **6** and those of its photo-product.⁵ On standing for about 2 months, an ether solution of **6** and 11-diazo-4,5-methylenepheneanthrene² separated relatively pure crystals of pyrazoline adduct. Since the preparation of 4,5-methylenepheneanthrylene ketone, the precursor of the diazo compound, from tetrahydronaphthalene was long (13 steps), tedious, and of low overall yield,⁶ we have developed a shorter new synthesis which begins with the ozonolysis of pyrene as shown in eq 1. Details are given in the Experimental Section.



Thermal decomposition of the pyrazoline adduct of **6** and 11-diazo-4,5-methylenepheneanthrene yielded spirocyclopropane compound **4**.

The nmr spectrum of **4** displayed a complex pattern between δ 7.0 and 8.0 ppm which resembled that of the spirocyclopropane moiety of molecule **1**. An *exo* orientation of the cyclopropane with respect to the norbornane frame is shown not only by spectroscopic similarities with **1** but also by scale molecular models which indicate that an *endo* disposition is virtually impossible because of resulting steric interference between phenanthrene and the middle bridge carbon (C_{12}). The remainder of the nmr spectrum of **4** shows six equivalent methoxy protons, reflecting the molecular symmetry, and a complex aliphatic region. All analytical data were consistent with the designated structure of **4**.

Spectroscopy. The uv absorption spectrum of **4** is compared to those of its constituent π chromophores individually attached to a truncated norbornane frame, **2** and **3**, in Figure 1. Obviously, there is a great deal of similarity between the absorption curves of **4** and **2** + **3**.

(3) (a) J. R. DeMember and N. Filipescu, *J. Amer. Chem. Soc.*, **90**, 6425 (1968); (b) A. A. Lamola, *ibid.*, **91**, 4786 (1969).

(4) (a) J. Meinwald and G. A. Wiley, *J. Org. Chem.*, **23**, 3667 (1958); (b) N. Filipescu and J. M. Menter, *J. Chem. Soc. B*, **616** (1969); (c) J. M. Menter and N. Filipescu, *ibid.*, 464 (1970).

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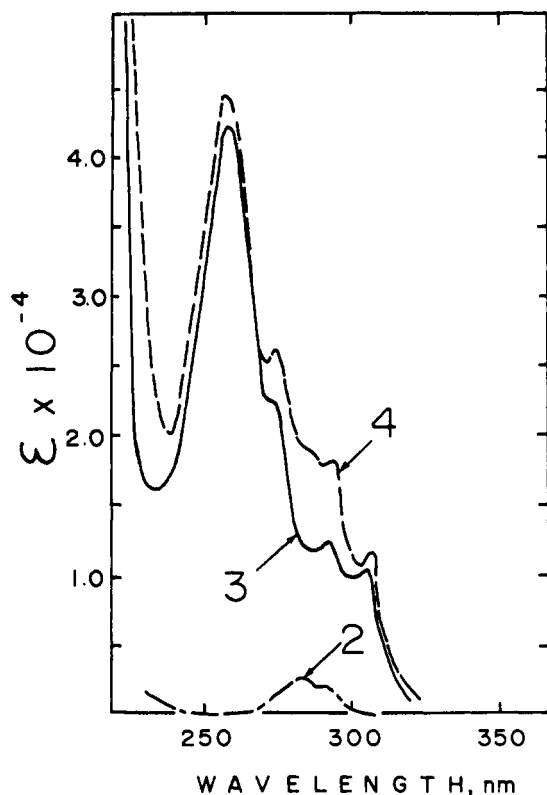


Figure 1. Absorption spectra of compounds 2, 3, and 4.

Figure 2 shows the emission and excitation spectra of model compound 4 in ether-isopentane-ethanol (EPA) at 77°K. Each of the two chromophores emits clearly identifiable fluorescence and phosphorescence. Comparison with the individual emissions of "half"-molecules 2 and 3 reported previously² allows specific assignment to each emission in Figure 2. The intense phenanthrene fluorescence displaying characteristic vibrational progression (λ_{max} 348, 365, 385, and 404 nm, curve 1) was recorded at low amplification since it is much more intense than the partly overlapping broad phosphorescence with λ_{max} at 405 nm (see below). The typical D fluorescence centered at about 310 nm (curve 2) was also unambiguously present. Curve 3, representing total phosphorescence, was recorded through the rotating shutter phosphoroscope which removed the short-lived fluorescence. The broad structureless band centered at about 405 nm (curve 4) is characteristically associated with the $T_1 \rightarrow S_0$ emission of the D chromophore. This emission was also recorded at higher gain, curve 4. The three narrower bands in the green spectral region at 465, 502, and 543 nm represent typical P phosphorescence. The relative intensities of the four individual emissions were within 8% the same as those from an equivalent equimolar mixture of 2 and 3. The excitation spectra of P (curve 5) and D (curve 6) emissions are distinctly different and have distorted mirror image relationships with the respective fluorescences. The phosphorescence lifetimes at 400 and 500 nm were 3 and 2 sec, respectively, again close to those of the isolated chromophores. In fact, the entire emission and excitation of compound 4 are remarkably similar to those obtained from a mixture of 2 and 3 of equivalent concentrations.

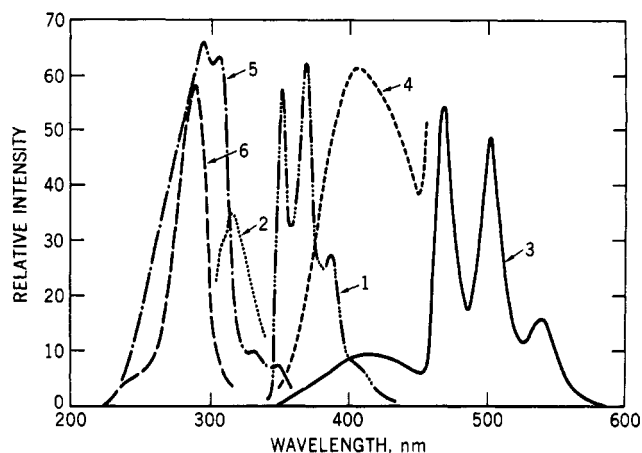
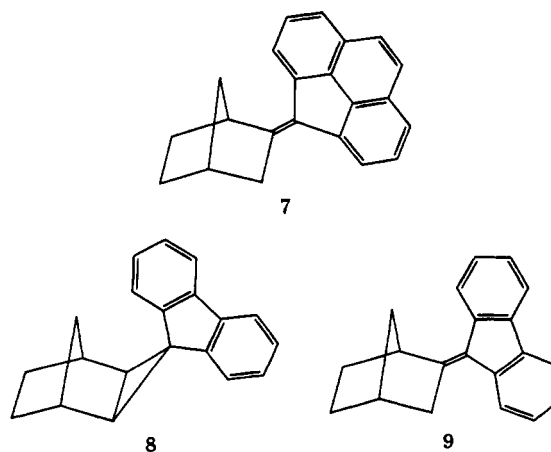


Figure 2. Emission and excitation spectra of model compound 4, uncorrected: 1, phenanthrene fluorescence; 2, *p*-dimethoxybenzene fluorescence; 3, total phosphorescence, recorded at $\times 15$ compared to curve 1; 4, *p*-dimethoxybenzene phosphorescence at $\times 5$ compared to curve 3; 5, excitation spectrum of P phosphorescence at 500 nm; 6, excitation spectrum of D phosphorescence at 400 nm; curves 3, 4, 5, and 6 were recorded while the rotating shutter phosphoroscope was on.

Photostability of 4. We gave special attention to the possibility of interference with the spectrophotofluorometric results from undesired photoproducts. Consequently we irradiated model compound 4 for extended periods of times both in frozen glass and in liquid solution. Even after exposure in EPA at 77°K to uv light of much higher intensity than in the emission spectrometer more than 20 times longer than the time required for recording, the emission and excitation spectra of 4 remained unchanged.

Separate experiments in which 2, 3, and 4 were photolyzed for long time *in fluid solution* at 298°K showed that D attached to a saturated frame in 2 and 4 is unreactive photochemically and that spirocyclopropane-attached P in 3 (and 4) undergoes a clean photorearrangement⁷ to tribenzofulvene 7 in a manner analogous to the 8 \rightarrow 9 photoisomerization of spiro-linked fluo-



rene (F).^{2, 3, 4b} However, regarding the influence of 3 \rightarrow 7 and 8 \rightarrow 9 photoreactions on spectrofluorometric measurements, there are three major differences: (i) unlike spiro-linked F in 8, P in 3 and 4 is an intense and characteristic emitter of both fluores-

(7) N. Filipescu, F. L. Minn, and J. W. Pavlik, *Anal. Chem.*, **43**, 83 (1971).

cence and phosphorescence; (ii) the quantum yield for the $3 \rightarrow 7$ photoisomerization ($<10^{-4}$) in fluid solution is at least two orders of magnitude smaller than that for the $8 \rightarrow 9$ reaction^{4b} (0.03) and negligible in frozen glass; and (iii) fulvene 7 is a much poorer emitter (more than 100 times) than 9. We conclude, therefore, that the emission spectrum shown in Figure 2 is that of unaltered model compound 4 without interference from spurious photochemical reactions or photoproducts.

Discussion

The near identity resemblance between the uv absorptions of 4 and those of 2 + 3 strongly suggests that there is no π delocalization or even weak electronic interaction extending over both *p*-dimethoxybenzene and phenanthrene chromophores in rigid model compound 4. The very small deviations from superimposability are easily accountable by a minor perturbation of the vibronic levels of D and P brought about in 4 by the additional interconnecting σ bonds.² The lack of distortion in the emission spectra of the individual D and P chromophores of 4, when compared with those of separated 2 and 3, tends to confirm the noninteracting relationship in 4. In addition, the separate excitation spectra and the unambiguous detection of the individual $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ emissions of each chromophore in virtually the same intensity relationship and with the same decay times as in the "isolated" state established both the correctness of referring to electronic ground and excited states localized on D or on P and absence of electronic energy transfer in 4.

The energy levels and emissive properties of the D and P chromophores are ideal for spectrophotofluorometric experiments involving both singlet-singlet and triplet-triplet energy transfer. Thus, the D fluorescence ($\lambda_{\max} \sim 310$ nm) overlaps extensively with the excitation (or absorption) spectrum of P (λ_{\max} 304, 329, and 345 nm) and therefore satisfies the resonance condition for D to P S-S transfer.⁸ From spectral data one can estimate that for a random orientation of D and P chromophores ($K^2 = 2/3$) the "critical radius" R_0 would be of the order of 32 Å. In other words, at average separation distances of less than 32 Å in a random distribution the singlet energy transfer from D to P should exceed 50%. Undoubtedly, at separations of 6 Å, were it not for the special rigid orientation in compound 4, the transfer would be virtually complete.

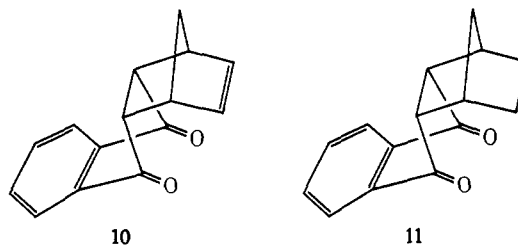
The 0-0 bands of the phosphorescence spectra place the lowest triplet states of D and P at about 23,260 (415 nm) and 21,190 cm^{-1} (473 nm), respectively, again ideally suited for T-T transfer from D to P. The fluorescence and phosphorescence of each chromophore are sufficiently intense to allow accurate measurements far from the maximum instrumental sensitivity, appear in different wavelength regions, and are characteristically different (vibrational progression for P, near structureless bands for D).

The absence of energy transfer in 4 in spite of favorable energy level and interchromophoric separation distance is quite remarkable. Thus, most previous work with either model compounds or mixtures in which appropriate donors and acceptors were brought

together at distances less than 20 Å indicated either total or very efficient singlet-singlet resonance and/or exchange transfer.⁹ No less unusual is the absence of D to P triplet energy transfer since the "edge to edge" separation between the nearest π carbon atoms is only 6 Å, less than half the distance at which T transfer was reported to have been complete from experiments with binary mixtures.¹⁰

It is quite obvious that the only possible explanation for the absence of energy transfer in 4 is related to the mutual orientation of the two-component π chromophores.

Absence of exchange transfer between D and P implies a vanishing exchange integral. Since the two chromophores are well within¹⁰ the "sphere of quenching" it is doubtful that the spatial overlap of the T_1^D and S_0^P wave functions is vanishingly small. The reason for a zero exchange integral may well be the result of symmetry properties of the product of wave functions. Thus, the plane of symmetry of the molecule which coincides with the phenanthrene group is perpendicular to the dimethoxybenzene plane. The cancellation of the exchange integral would be only natural if the ground state of P is antisymmetric with respect to the molecular plane of symmetry (as it would be in unsubstituted phenanthrene) whereas the T_1^D wave function would be symmetric. Apparently, neither the small distortions introduced by the vibrations within the interconnecting σ frame (maximum amplitude of C-C single bond ~ 0.1 Å) nor its contribution, if any, to the interchromophoric overlap are able to modify the vanishing symmetry properties of the exchange integral.⁹ⁿ Actually, the lack of triplet energy transfer between D and P in 4 at small separation is not unique; we have recently reported that the norbornylene π bond failed to quench the phosphorescence of the tetralindione chromophore in model compound 10 in spite of adequate triplet energy level energies and less than 4 Å separation.^{4b} Again, the symmetry of molecule 10 is conspicuous and may well explain why compound 10 and its norbornane analog 11 exhibit comparable phosphorescence quantum efficiencies.



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(8) For a recent review see A. A. Lamola in "Energy Transfer and Organic Photochemistry," Techniques of Organic Chemistry, Vol. XIV, Interscience, New York, N. Y., 1969.

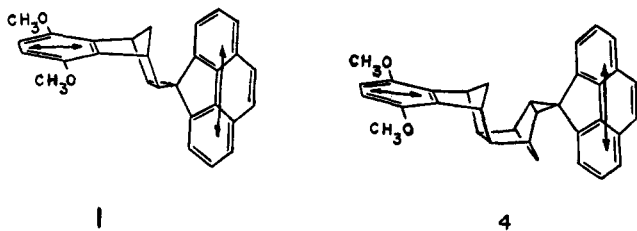


Figure 3. Orientation of $S_0 \leftrightarrow S_1$ transition vectors in P and D of model compounds 1 and 4.

The lack of resonance transfer at the singlet level in 4 in sharp contrast to the total D to P transfer in 1 is probably caused by a change in the relative orientation of the two aromatic groups rather than a change in separation distance. The centers of the two chromophores are about 9 Å apart, a distance much smaller than those found to be limiting the S-S transfer in mixed solutions.⁹ The symmetry properties considered responsible for the absence of triplet transfer are not applicable to S-S resonance transfer since, if valid here, they would have also precluded singlet transfer in 1 which has similar symmetry to 4. There is an important structural difference between model compounds 1 and 4. Scale molecular models indicate that in 4 the plane of D is approximately bisecting the phenanthrene, whereas in 1 the *p*-dimethoxybenzene plane intersects P at about C_1 . This difference in orientation may well be responsible for the absence of resonance transfer in 4. The D fluorescence at 310 nm has been found to be polarized in plane of the benzene ring, perpendicular to the line of the methoxy groups.¹¹ The absorption of P overlapping the D fluorescence around 300 nm is polarized¹² in the plane of phenanthrene perpendicular to its second plane of symmetry, from C_2 to C_7 , as shown in Figure 3. According to Förster's formulation of the inductive resonance theory,⁸ the transfer rate (or efficiency) includes an orientation factor $K = \cos \phi_{DA} - 3 \cos \phi_D \cos \phi_A$ where ϕ_{DA} is the angle between the transition vectors of the donor (D) and the acceptor (A), and ϕ_D and ϕ_A are the angles of the transition vectors of the donor and acceptor, respectively, with the line of centers of the two chromophores. Since in 4 the plane of D bisects the phenanthrene group, it is apparent that both ϕ_{DA} and ϕ_A are $\pi/2$ and therefore $K \approx 0$. In contrast, the second term of the expression for K above did not vanish for the orientation in compound 1 since $\phi_A \neq \pi/2$. We are perfectly aware of the limitations associated with extrapolation of the Förster theory to smaller donor-acceptor distances^{3b,13} and the mixed polarization character of many transitions in organic chromophores.^{3b,14} Therefore, the above interpretation of the absence of transfer in 4 represents merely a reasonable rationalization within the existing theories of electronic energy transfer. On the other hand, it seems obvious that the high symmetry and unique relative orientation of the two chromophores in 1 and 4 are responsible for lack of

triplet transfer in 1 and of both singlet and triplet transfer in 4.

It may be important to point out that the D and P chromophores, whether free or attached separately to the norbornane frame in 2 and 3, when used for energy transfer experiments in mixed solutions behave like any appropriate donor-acceptor pair.¹⁵ However, when the same two chromophores were incorporated in rigid model compounds 1 and 4 at close separation and distinct relative orientation they showed remarkable "anomalies." Gradual increase in the separation distance between a selected donor and acceptor by increasing the size of the interconnecting molecular frame in model compounds is a logical method of studying delocalized excitation, exchange transfer, and more distant energy migration regardless of whether the investigative method is spectroscopic⁹ or photochemical.^{4b,4c,16} Inflexibility in the model molecule is essential in determining both the separation and the relative orientation of the two chromophores, the two most important parameters governing the energy transfer process between selected donors and acceptors. This restriction is rather severe and may impose substantial hardship on the investigators who have to develop rather elaborate synthetic routes. It often happens, especially at small separation, that in some of these compounds the energy transfer from donor to acceptor is complete. The only conclusion in such cases is that there is strong interaction between the two chromophores. On the other hand, the most interesting rigid model molecules are those in which the two nonconjugated chromophores, though in close proximity, do not interact strongly and exhibit either partial transfer or no transfer at all. Compounds 1 and 4 are good examples. Spectroscopic and photochemical studies of such systems are expected to contribute not only to a better understanding of the mechanism of energy transfer but also to a more accurate description of electronically excited organic molecules.

Experimental Section

Uv and ir absorption spectra were determined in double beam mode with the Cary 15 and Beckman IR-5A spectrophotometers, respectively. Nmr spectra were recorded with a Hitachi-Perkin-Elmer spectrometer with TMS internal standard. Molecular weights were determined with the Mechrolab vapor pressure osmometer, Model 301A. Emission and excitation spectra were obtained with the Aminco-Bowman spectrophotofluorometer at 77°K. In these experiments, the EPA (ether-isopentane-ethanol) solutions were placed in 3-mm quartz tubes which were lowered in the cold finger of the dewar in liquid nitrogen.

New Preparation of 5. Cyclopentadiene-benzoquinone adduct (100 g) in 500 ml of 10% aqueous sodium hydroxide was stirred vigorously under nitrogen while 118 ml of dimethyl sulfate was added dropwise over a 0.5-hr period with cooling in an ice bath. After addition was complete, the reaction mixture was allowed to warm to room temperature, and stirred overnight. The next day an additional 250 ml of 10% NaOH was added followed dropwise by 59 ml of dimethyl sulfate with stirring and cooling. After another overnight stand, 100 ml of 10% sodium hydroxide was added to destroy any excess dimethyl sulfate. The solution was extracted with ether and the ether layer washed with aqueous NaOH

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and water. After the ether extracts were dried, evaporation and recrystallization from ethanol yielded 45 g of pure **5**, mp 76.5–77.5°. All other properties were reported.^{4a} Synthesis of **6**, the cyclopentadiene adduct of **5**, was described recently.⁵

New Preparation of 4,5-Methylenephenanthrylene Ketone. Pyrene was submitted to ozonolysis by the normal procedure except that the reaction was stopped at the sodium salt of 5-formyl-4-phenanthroic acid since the next step was run in an alkaline solution. A mixture of 18 g of silver nitrate, 8 g of sodium hydroxide, and 10.3 g of sodium 5-formyl-4-phenanthroate in 300 ml of 50% ethanol was stirred and refluxed for 4 hr. The silver and excess silver oxide were filtered off and washed with hot water. The filtrate and washings were acidified with hydrochloric acid and the precipitated phenanthrene-4,5-dicarboxylic acid was collected and recrystallized from ethanol, mp 277–278°; ir (KBr) 3250 (OH stretch) and 1680 cm⁻¹ (conjugated acid carbonyl). The calcium salt of the phenanthrene-4,5-dicarboxylic acid was prepared by boiling to dryness a mixture of equal weights of calcium oxide and acid in water. The calcium salt mixture was pyrolyzed in 30-g batches by heating the powdered solid in a beaker which was suspended inside another beaker containing boiling benzophenone (bp 306°). The subliming yellow 4,5-methylenephenanthrylene ketone was collected in a pure state on an erlenmeyer flask containing ether which kept the flask cool by refluxing from an efficient condenser attached to the flask. The average yield from 30 g of crude calcium salt mixture was 0.5 g, mp 167–170° (mixed with authentic ketone,^{2,6} 168–170°).

endo,exo-5,8-Dimethoxy-1,4-methano-9,10-methano-1,4,4a,9,10,10a-hexahydroanthracene (6). In a sealed tube were placed 11.3 g of 3',6'-dimethoxybenzonorbornadiene (**5**) and 5.6 g of dicyclopentadiene. The tube was heated at 195° for 6 hr. The resultant oil crystallized from heptane to give 8.4 g (60%) of off-white solid. Several recrystallizations from heptane gave colorless needles, mp 128–129°; ν_{KBr} 3030, 2950, 2850, 1490, 1480, 1430, 1350, 1270, 1250, 1175, 1105, 1080, 1060, 990, 910, 900, 850, 820, 795, 785, 755, 730, and 705 cm⁻¹; nmr (CCl₄) δ 6.27 (2 H, H_{6,7}, singlet), 5.98 (2 H, H_{2,3}, triplet), 3.63 (6 H, OCH₃, singlet), 3.20 (2 H, H_{9,10}, triplet), 2.90–2.57 (3 H, H_{1,4,11a}, complex), 2.19 (2 H, H_{4a,9a}, broad singlet), and 1.70–0.95 ppm (3 H, H_{11b,12a,12b}, complex).

Anal. Calcd for C₁₈H₂₀O₂: C, 80.60; H, 7.46. Found: C, 80.16; H, 7.55.

endo,exo-5,8-Dimethoxy-1,4-methano-9,10-methano-2,3-exo-(4',5'-methylenephenanthrene-11'-spiro-1''-cyclopropane)-1,2,3,4,4a,9,9a,10-octahydroanthracene (4). A mixture of 4 g of 4,5-methylenephenanthrylene ketone, 6 ml of 95% hydrazine, and 100 ml of absolute alcohol was refluxed with stirring for 16 hr. The reaction mixture was then cooled and the 11-hydrazo-4,5-methylenephenanthrene product collected, mp 214–215°, yield 3 g; ir (KBr pellet) 3400 and 3325 cm⁻¹ (N–H stretch). 11-Diazo-4,5-methylenephenanthrene was prepared by reaction of 0.3 g of 4,5-methylenephenanthrene-11-hydrazone with 0.6 g of yellow mercuric oxide and 0.2 g of anhydrous sodium sulfate in 50 ml of ether and several drops of saturated alcoholic potassium hydroxide solution. After the mixture was shaken for 30 min in the dark, the solution was filtered and the precipitate washed several times with ether. Into the combined ether solution of 11-diazo-4,5-methylenephenanthrene and washings was dissolved 0.4 g of **6** and the solution was set aside in the dark. After 2 months at room temperature, the reaction mixture had lost most of its color and the crystalline pyrazoline had precipitated. Nmr spectrum of the crude precipitate in deuteriochloroform showed δ 7.0–8.0 (8 H, H_{1'-3'}, H_{6'-10'}, complex), 6.43 (2 H, H_{6,7}, singlet), 5.6 (1 H, H₂, complex doublet), 3.76 (3 H, OCH₃, singlet), 3.59 (3 H, OCH₃), 3.2 (2 H, benzylic H, complex), and 1.5–3.0 ppm (9 H, complex).

The entire solution was evaporated to dryness and the powdered residue covered with decalin. The solution was heated slowly to 160°, at which temperature the evolution of nitrogen ceased. Removal of the decalin under vacuum resulted in a red oil which was decolorized with charcoal in ethanol and recrystallized once from heptane and once from chloroform–alcohol yielding colorless cubic crystals, mp 210–211°; nmr (CDCl₃) δ 7.0–8.0 (8 H, H_{1'-3'}, H_{6'-10'}, complex), 6.54 (2 H, H_{2,3}, singlet), 3.78 (6 H, OCH₃, singlet), 3.63 (2 H, H_{9,10}, complex), and 1.0–3.0 ppm (10 H, complex).

Anal. Calcd for C₃₃H₂₈O₂: C, 86.84; H, 6.14. Found: C, 86.62; H, 6.23.

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Rates of Termination of Radicals in Solution. VI.¹ Ketyl Radicals Derived from Methyl-Substituted Phenylglyoxylic Acids

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Abstract: Phenylglyoxylic acid and five of its C-methylated derivatives have been studied by irradiation of isopropyl alcohol solutions of these compounds in the cavity of an electron paramagnetic resonance spectrometer. Ketyl radicals are produced when the aromatic ring has no ortho substituents or when both ortho positions are occupied by methyl groups. A single *o*-methyl group prevents the formation of a detectable concentration of radicals, presumably because of a competitive photoenolization reaction. Hyperfine coupling constants and rates of bimolecular radical decay are reported.

In previous papers in this series we have described our studies of structure–reactivity relationships of ketyl radicals, demonstrated by the rates of radical termination as measured by the esr-light intermittency technique.^{1–4} We have now extended these studies to

include the effect of methyl substituents on the photochemistry of the phenylglyoxylic acids, **1a–f**, and ketyl radicals, **2a–f**, derived from some of them.

Experimental Section

Materials. Phenylglyoxylic acid (Aldrich) was commercial material. Methyl-substituted phenylglyoxylic acids were prepared

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