

Through-space Interaction between Nonconjugated Naphthalene and Phenanthrene in a Rigid Molecule †

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The transannular interaction between naphthalene and phenanthrene in 4*H*-cyclopenta[*def*]phenanthrene-4-spiro-7'-(6*b*,7*a*-dihydro-7*H*-cyclopropa[*a*]acenaphthylene) (1) and between naphthalene and fluorene in 6*b*,7*a*-dihydro-7*H*-cyclopropa[*a*]acenaphthylene-7-spiro-9'-fluorene (2) was studied spectroscopically and photochemically. The difference between electronic absorption of these rigid model compounds and that of their component chromophores was examined by an SCF-CI-CNDO-MO procedure with partial through-space bonding of the nonconjugated π -systems. Satisfactory agreement between theoretically predicted absorption spectra and those determined experimentally was found for both (1) and (2) and their continuously conjugated photoproducts.

INTERACTION between closely spaced molecules or functional groups is of fundamental importance in virtually all problems in chemistry, photochemistry, and molecular spectroscopy. The detailed study of this interaction is carried out primarily by examination of deviations from additivity between the absorption of a mixture and that of its individual components,¹ by identification of products with the attendant limited

ability to reconstitute the original interaction,² and by detection of energy transfer by either spectrophotofluorometric or photochemical means.³ All consequences of the interaction between two species are critically dependent on their separation distance and mutual orientation. The relative spacial disposition of two molecules (or chromophores) is much better defined

† Taken in part from work done by A. V. T. in partial fulfillment of the requirements for a Ph.D. from The George Washington University, 1970.

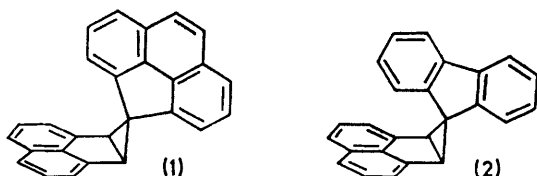
¹ See for example J. N. Murrell, 'The Theory of the Electronic Spectra of Organic Molecules,' Wiley, New York, 1963, ch. 7; Th. Förster in O. Sinanoglu, 'Modern Quantum Chemistry V. III,' Academic Press, New York, 1965.

² See, among others, E. S. Gould, 'Mechanism and Structure in Organic Chemistry,' Holt, New York, 1959; J. March, 'Advanced Organic Chemistry: Reactions, Mechanisms, and Structure,' McGraw-Hill, New York, 1968; N. J. Turro, 'Molecular Photochemistry,' Benjamin, New York, 1965.

³ For a recent review, see A. A. Lamola and N. J. Turro, 'Energy Transfer and Organic Photochemistry,' Interscience, New York, 1969, ch. II.

in rigid model compounds in which the two groups are connected to the same molecular frame⁴ than in binary mixed solutions where one can use only 'average' distances and random orientation.

Here we report the spectroscopic and photochemical study of the interaction between the naphthalene and phenanthrene chromophores in model compound (1). The fact that the two π -systems in (1) are mutually perpendicular preserves symmetry in the molecule and simplifies the interpretation of results. Furthermore, since the spectroscopic properties of chromophores naphthalene and phenanthrene have been previously studied in great detail both experimentally and theoretically, they are ideally suited for the present work. It was of interest to examine a model molecule such as (1), since the edge-to-edge interchromophoric separation of less than 3 Å places the interaction in the strong-coupling case¹ despite the absence of direct bonding.



For comparison we also include the spectral analysis of an analogous model molecule (2) in which naphthalene is paired with fluorene (F) at virtually the same separation and perpendicular orientation as the chromophores in (1).

RESULTS

Model molecules (1) and (2) were prepared by addition of either the carbene derived from 4*H*-cyclopenta[*def*]phenanthrene⁴ or fluorenylidene⁵ to acenaphthylene. Molecular weight, elemental analysis, and n.m.r. and i.r. spectra were consistent with the symmetrical structures (1) and (2). The u.v. absorption spectrum of compound (1) is compared with that of an equivalent equimolar mixture of acenaphthene (3, N) and 4*H*-cyclopenta[*def*]phenanthrene (4, P) in Figure 1. In Figure 2, the near-u.v. absorption of model compound (2) is shown with that of a mixture of its component chromophores (3) and fluorene (5, F) at equivalent concentrations. Since the absorption spectra of compounds (3)—(5) are known,⁶ they will not be reproduced here. The differences in the u.v. absorptions of the two model compounds (1) and (2) and those of the mixtures are sufficiently large to suggest relatively strong mutual perturbations between the two constituent π -systems held in proximity by the rigid interconnecting σ -frame in the models. To estimate the effect of the spiro-cyclopropane link to P and F in compounds (1) and (2), respectively, we

⁴ (a) R. A. Keller, *J. Amer. Chem. Soc.*, 1968, **90**, 1940; (b) N. Filipescu in E. C. Lim, 'Molecular Luminescence,' Benjamin, New York, 1969, p. 697; (c) J. R. DeMember and N. Filipescu, *J. Amer. Chem. Soc.*, 1968, **90**, 6425; (d) A. A. Lamola, *ibid.*, 1969, **91**, 4786; (e) N. Filipescu, J. R. DeMember, and G. R. Howard, 'Proc. 20th Reunion Soc. Chim. phys.,' Paris, 1969, pp. 84—91; (f) N. Filipescu and J. M. Menter, *J. Chem. Soc. (B)*, 1969, 616; (g) J. M. Menter and N. Filipescu, *ibid.*, 1970, 484.

have compared the absorption and emission spectra of unsubstituted 4*H*-cyclopenta[*def*]phenanthrene and fluorene with those of (6) and (7). Although the norbornane frame to which P and F are connected by the spiro-cyclopropane

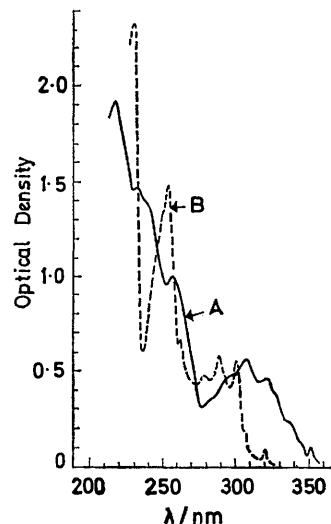


FIGURE 1 U.v. absorption spectra of model compound (1) (A, $0.25 \times 10^{-4}M$) and of an equimolar mixture of acenaphthene (3) and cyclopenta[*def*]phenanthrene (4) (B, $0.25 \times 10^{-4}M$ each) in dioxan

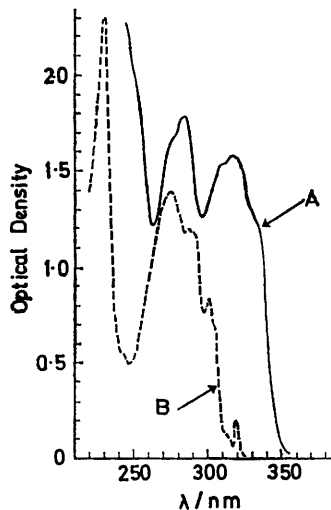


FIGURE 2 U.v. absorption spectra of model compound (2) (A, $10^{-4}M$) and of an equimolar mixture of (3) and (5) (B, $10^{-4}M$ each) in dioxan

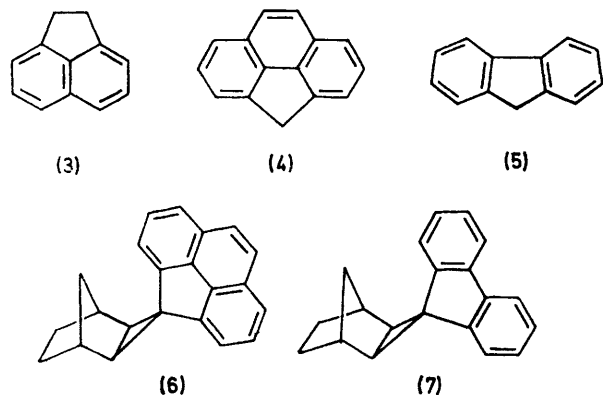
in compounds (6) and (7) is somewhat different from the 5-membered ring of acenaphthene in compounds (1) and (2), no significant differences in the u.v. absorption are expected.^{4c} In fact, the differences in absorption between (6) and (7) and P and F are sufficiently small that in the present type of analysis the effect is marginal. In any case, the cyclopropane can be considered a part of P or F chromophore in compounds (1), (2), (6), or (7). Despite the absence of large wavelength shifts in major absorption

⁵ C. D. Nenitzescu and E. Salomonica, *Org. Synth.*, Coll. Vol. II, 1948, 496.

⁶ R. A. Friedel and M. Orchin, 'Ultraviolet Spectra of Aromatic Compounds,' Wiley, New York, 1951.

bands between the models and their 'components,' the changes in the band structure suggest electronic interactions stronger than those caused simply by coupling of new vibrational modes upon adding the other chromophore.

Neither compound (1) nor (2) exhibited any measurable emission either at room temperature or in rigid matrix at 77 K. This was not entirely unexpected, since the strained



cyclopropane structure provides an easily available pathway for radiationless deactivation by means of bond dissociation.⁷ That this is the major quenching mechanism is confirmed by the photochemical reactions of the two model molecules in solution (see below).

The optical density of the u.v.-visible absorption of (1) upon successive short irradiations in dilute solution at 298 K decreased progressively with the extent of irradiation in the range 287–331 nm, while two new bands with clearly defined vibrational structure appeared at 272–287 and 331–475 nm as the solution became yellow. Three distinct isosbestic points were identified in the successive

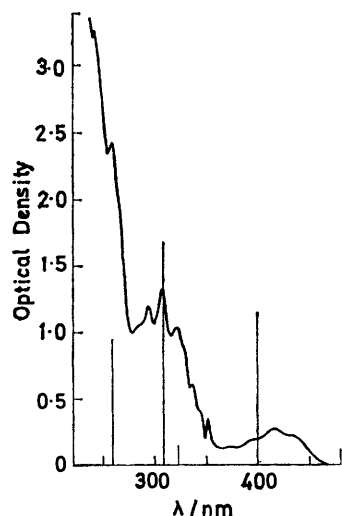
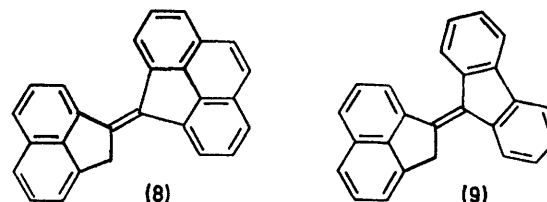


FIGURE 3 U.v. visible absorption of photoproduct (8) ($4 \times 10^{-5}M$) in cyclohexane. Bars represent calculated transitions; their height corresponds to oscillator strength in arbitrary units

spectra at 272, 287, and 331 nm. Preparative scale photochemical reactions of (1) were carried out at higher concentrations in benzene solutions. The yellow photoproduct was separated from the starting material using differences

in solubility and was purified by chromatography on silica gel. Elemental analysis, molecular weight, i.r., n.m.r., and u.v.-visible spectra were consistent with the fulvene structure (8). Figure 3 displays the u.v.-visible absorption spectrum of the photoproduct. Fulvene (8) exhibits green fluorescence in a band centred at 485 nm. The excitation spectrum exhibits the quasi-mirror-image relationship with the fluorescence band and shows vibrational structure resembling that of the absorption spectrum. The extent of the (1) \rightarrow (8) photoisomerization can be followed also



by monitoring the increase in the emission with length of irradiation of the thawed solution. The (1) \rightarrow (8) reaction takes place in rigid matrix, as well, but very inefficiently ($\Phi < 10^{-4}$) requiring prolonged irradiation.

Compound (2) undergoes a similar photorearrangement to the analogous dibenzofulvene (9). This reaction, however, is much less efficient than the similar rearrangement of

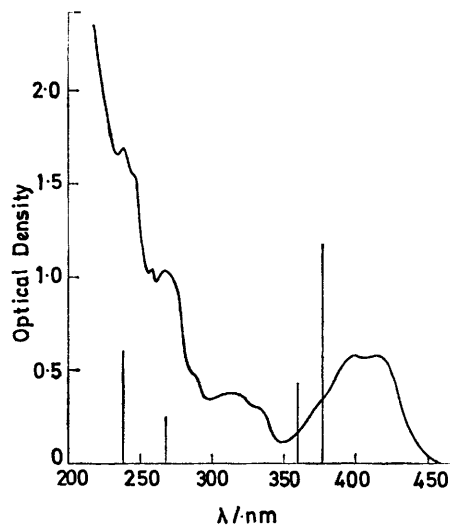


FIGURE 4 U.v. visible absorption spectrum of photoproduct (9) ($5 \times 10^{-5}M$) in cyclohexane. Bars have the same significance as in Figure 3

compound (1). Photoproduct (9) was isolated from a preparative scale experiment involving photolysis in benzene and column chromatography. Its u.v.-visible absorption spectrum is given in Figure 4. Like (8), compound (9) exhibited fluorescence, centred at 475 nm, but did not emit detectable phosphorescence.

Molecular Orbital Calculations.—Molecular orbital calculations were used to correlate the electronic absorption spectra of model compounds (1) and (2) with the through-space interaction of their two component π -systems. In addition the same general method was applied to the two

⁷ (a) J. M. Menter and N. Filipescu, *J. Chem. Soc. (B)*, 1970, 464; (b) N. Filipescu and J. R. Bunting, *ibid.*, p. 1498.

photoproducts (8) and (9), in which the same two chromophores as in (1) and (2) are coplanar and conjugated. The fact that all these molecules are inflexible makes the results more meaningful than for systems in which free rotation about single bonds connecting the two chromophores allows a variety of conformers. Electronic spectra were calculated with a semiempirical MO-SCF-CI procedure in which the π -electrons of the two component chromophores were treated as parts of a single extended system delocalized over the entire molecule rather than as individual entities. The technique includes effects of local excitations and of electron transfer in a natural way.

Since the energetic states associated with the interconnecting σ bonds are found at higher energies than those of the aromatic chromophores we neglected the electronic participation of the frame. Thus the only kind of interaction between N and P (or N and F) considered in the present treatment is a through-space mutual perturbation. The p -orbitals on the carbon cores part of aromatic nuclei were used as a basis set for an SCF calculation assuming zero differential overlap. Interactions between the two π -systems were introduced by the electrostatic repulsions between all pairs of contributing atomic orbitals and by partial bonding between the sites of the two chromophores nearest one another. Specifically, the electron-repulsion integrals γ were evaluated by the Mataga-Nishimoto formula⁸ and the non-zero intra-ring bond-resonance integrals β by a distance-dependent equation (1) whose form

$$\beta = 9.811 \exp(-1.032r) \quad (1)$$

was suggested by Pariser and Parr.⁹ This equation was constructed to give literature values for benzene and ethylene at their experimental C-C distances.⁹⁻¹¹ Ionization potentials and one-centre electrostatic repulsion

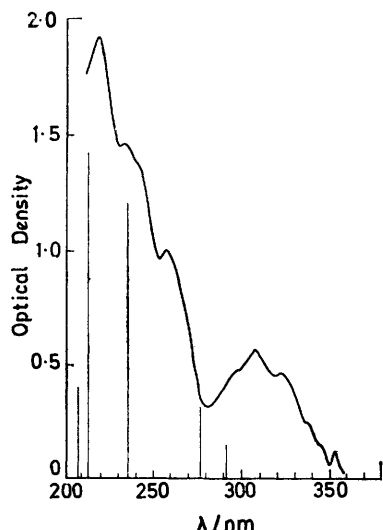


FIGURE 5 U.v. absorption of (1) ($2.5 \times 10^{-5}M$) in dioxan. Bars have the same significance as in Figure 3

integrals were taken from the literature⁹ when known: the valence-state ionization potential for fluorene was taken to be the same as that for phenanthrene. Extensive examin-

⁸ N. Mataga and K. Nishimoto, *Z. Physik.*, 1957, **13**, 140.

⁹ R. Pariser and R. G. Parr, *J. Chem. Phys.*, 1953, **21**, 767.

¹⁰ M. Klessinger, *Theor. Chim. Acta*, 1956, **5**, 236, 251.

ation of both β and γ has been done for planar systems; however, since our molecules are non-planar, an adjustment was made for the interaction of nonparallel p orbitals.

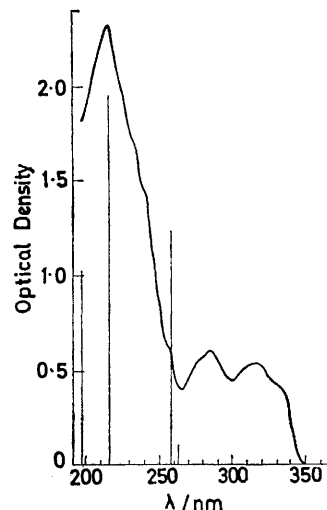


FIGURE 6 U.v. absorption of (2) ($3.5 \times 10^{-5}M$) in dioxan. Bars have the same significance as in Figure 3

Denoting the components of the unit vector between the two cores as x , y , and z , we have equations (2) and (3) for

$$\beta = x^2z^2\beta_{\sigma\sigma} + x^2z^2\beta_{\pi\pi} \quad (2)$$

$$\gamma = x^2y^2\gamma_{\sigma\sigma\sigma\sigma} + (x^2z^2 + z^4 + x^2y^2 + x^4)(x^2 + y^2)^{-1}\gamma_{\sigma\sigma\pi\pi} + y^2\gamma_{\pi\pi\pi\pi} + x^2z^2\gamma_{\pi\pi\pi'\pi'} + 4xyz(x^2 + y^2 + z^2)^{-3/2}\gamma_{\sigma\sigma\pi\pi} \quad (3)$$

noncoplanar ring systems in which one ring is in the xy plane and the other in the yz plane. The subscripts serve to denote the components which are obtained from orbitals that point directly toward one another (σ) or are parallel to each other and perpendicular to the line of centres (π). Since exact integration of the various σ and π combinations is known to give values which do not differ greatly, we took $\beta_{\sigma\sigma} = \beta_{\pi\pi}$ and $\gamma_{\sigma\sigma\sigma\sigma} = \gamma_{\sigma\sigma\pi\pi} = \dots = \gamma_{\sigma\sigma\pi\pi}$.

The SCF ground-state wave functions were allowed to interact with the first four excited-state wave functions in a CI treatment. A modification to Bloor and Gilson's closed-shell SCF-CI program¹² was used on an IBM 360/50 computer.

Obviously the energy differences will depend on the dihedral angle made by the two chromophoric planes. Since an experimental value of the angle is not available, we must estimate it from scale molecular models. These suggest 120° . Variations of this angle in the calculations allowed good correlations between experimental and theoretical spectra at 120° , as shown in Figures 3-6.

DISCUSSION

Most previous attempts to correlate electronic spectra with through-space interaction of two nonbonded chromophores were made on unsaturated polycyclic

¹¹ J. E. Bloor, B. R. Gilson, and N. Brearley, *Theor. Chim. Acta*, 1967, **8**, 35.

¹² Quantum Chemistry Program Exchange, University of Indiana, Program 71.3.

ketones¹³ and on excimers.¹⁴ Apparently the significant features in the u.v. absorption of rigid compounds containing C=C and C=O in transannular proximity are the appearance of an intense band between 220 and 250 nm and an increase in the intensity of the $n \rightarrow \pi^*$ band. The former was attributed to an intramolecular charge transfer transition; whereas the latter was assumed to be caused by overlap of the nonbonding oxygen p orbital with the ground state of the olefinic chromophore. No detailed quantum mechanical calculations have been carried out on these unsaturated carbonyl systems; most assignments were made from minor solvent effects and changes in intensity with respect to their saturated analogues. The interaction between carbonyl and olefin groups is not easily evaluated experimentally because of broad unstructured absorption.

In most recent theoretical work on the origin of excimer emission,¹⁴ the electronic states of the excited dimer were constructed by CI with neutral exciton and charge-transfer states. An alternative approach, applied to transannular interaction between identical chromophores in a sandwich configuration was used by Koutecky and Paldus^{13c,d} in a 'supermolecule' approximation which treated the π electrons in an MO-SCF calculation with limited CI. Since this method gives the best results for interpretation of electronic spectra of aromatic hydrocarbons, it was adopted in the present study. It should be pointed out that the two chromophores in compounds (1) and (2) are chemically different and are positioned at a distance smaller than van der Waals' radii in a mutually perpendicular orientation. Because of this proximity we have included partial bonding (non-zero resonance integrals) between the two chromophores in a fashion similar to that used by Longuet-Higgins and Murrell¹⁵ for conjugated 'composite' molecules such as biphenyl and styrene.

In our calculations on compounds (1) and (2) we varied the number of configurations, the dihedral angle between the naphthalene and cyclopropane planes, the distance-dependence of the intrachromophoric resonance integrals, and the size and number of interchromophoric values. In addition, we examined the sensitivity of the predicted absorption bands to distortions within each of the two planar chromophores.

Extending the number of configurations beyond the

¹³ (a) P. D. Bartlett and B. E. Tate, *J. Amer. Chem. Soc.*, 1956, **78**, 2473; (b) C. A. Grob and A. Weiss, *Helv. Chim. Acta*, 1960, **43**, 1390; (c) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 1956, 2302; (d) R. C. Cookson and N. Levin, *Chem. and Ind.*, 1956, 984; (e) H. Labhart and G. Wagniere, *Helv. Chim. Acta*, 1959, **42**, 2219; (f) E. M. Kosower, W. D. Closson, H. L. Goering, and J. C. Gross, *J. Amer. Chem. Soc.*, 1961, **83**, 2013; (g) S. Winstein, L. DeVries, and R. Orloski, *ibid.*, p. 2020.

¹⁴ (a) L. L. Ingraham, *J. Chem. Phys.*, 1950, **18**, 988; (b) 1957, **27**, 1228; (c) J. Koutecky and J. Paldus, *Coll. Czech. Chem. Comm.*, 1962, **27**, 599; (d) *Tetrahedron*, 1963, **19**, 201; (e) A. Ron and O. Schnepp, *J. Chem. Phys.*, 1962, **37**, 2540; (f) 1966, **44**, 19; (g) J. N. Murrell and J. Tanaka, *Mol. Phys.*, 1964, **4**, 363; (h) M. T. Vala, J. Haebig, and S. A. Rice, *J. Chem. Phys.*, 1965, **43**, 886; (i) S. Basu, *J. Chim. Phys.*, 1965, **62**, 827; (j) M. T. Vala, I. H. Hillier, S. A. Rice, and J. Jortner, *J. Chem. Phys.*, 1966, **44**, 23; (k) I. H. Hillier, L. Glass, and S. A. Rice, *ibid.*, 1966, **45**, 3015.

lowest four did not affect significantly the outcome; this is consistent with the findings of Zahradnik *et al.*¹⁶ for single planar chromophores. A change in the naphthalene-cyclopropane dihedral angle modifies the separation between the two chromophores without affecting their perpendicularity; such a distortion has substantial effect on the predicted absorption. An angle of 120°, expected from bonding considerations on a fused cyclopentadiene-cyclopropane system, gave the best spectral fit. To illustrate the sensitivity of the calculation to modifications in the relative disposition of the two chromophores, one could mention that a change of as little as 10° from the optimum 120° blue-shifted the longest wavelength absorption band by more than 30 nm and hence yielded results which could no longer be considered acceptable.

The arbitrary assumption that β is independent of separation distance leads to substantial disagreement with experiment. The distance-dependent formulation [equation (1)] is known to lead to excessively low values of β for large distances. Accordingly, adoption of equation (1) for intrachromophoric β values in connection with fixed interchromophoric β values, appropriately adjusted for orientation of p orbitals, gave satisfactory results. Like others,¹⁷ we used the non-conjugated β corresponding to *ca.* 1/4 of a bond between C-1 (or -8) of naphthalene and the nearest atom of P (or F) with the usual angular adjustment for the more distant atoms. It was apparent that bonding interaction only between the atoms on N and P closest to one another was insufficient; additional interaction with at least the next nearest atoms was necessary.

In our calculations we placed the carbon atoms of the aromatic rings at sites suggested by X-ray crystallographic studies¹⁸ on the respective chromophores. However, distortions from these co-ordinates toward a perfect hexagonal model do not affect the overall results.

Although no vibronic analysis was attempted, the agreement between predicted and detected u.v. absorption of compounds (1) and (2) is comparable to the best previously reported calculations on planar aromatic molecules.¹⁶

The principal advantage of the new photorearrangements of compound (1) and (2) in solution is that it permitted us to apply the same method of calculation to the photoproducts (8) and (9) containing continuously conjugated coplanar chromophores. As shown in Figures 3 and 4, the agreement between their predicted and experimental spectra is satisfactory. Presumably the rearrangements take place by either a homolytic or

¹⁵ (a) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, 1955, **A68**, 601; (b) J. N. Murrell, 'Electronic Spectra of Organic Molecules,' Wiley, New York, 1963.

¹⁶ (a) J. Fabian, A. Mehlhorn, and R. Zahradnik, *J. Phys. Chem.*, 1968, **72**, 3975; (b) M. Tichy and R. Zahradnik, *ibid.*, 1969, **73**, 534 and references therein.

¹⁷ (a) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, 1967, **89**, 5208; (b) R. Boschi, A. S. Dreiding, and E. Heilbronner, *ibid.*, 1970, **92**, 123.

¹⁸ (a) P. N. Skanche, *Acta Chem. Scand.*, 1965, **19**, 401; (b) B. S. Basak, *Indian J. Phys.*, 1950, **24**, 309; (c) J. A. Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375.

a heterolytic fission of the cyclopropane ring followed by hydrogen atom or proton [1, 2] shift, respectively, and recombination of the diradical or zwitterion intermediate. These photoisomerizations resemble those reported other spiro-linked fluorene compounds.⁶

EXPERIMENTAL

The u.v.-visible absorptions were determined with a Cary model 15 spectrophotometer, the emission spectra with an Aminco-Bowman spectrophotofluorimeter, and the n.m.r. spectra with a Hitachi-Perkin-Elmer R20 instrument. Elemental analysis was performed with an Aminco C-H analyser. Spectrograde solvents were used except for preparative scale photolyses. The preparation of model compound (2) from 9-diazofluorene and acenaphthylene was described previously.¹⁹

4H-Cyclopenta[def]phenanthrene-4-spiro-7'-(6b,7a-dihydro-7H-cyclopropa[a]acenaphthylene).— *4H-Cyclopenta[def]phenanthrene* was oxidized with chromic acid to the ketone, which in turn was converted to the hydrazone with hydrazine and then to the diazoalkane with mercuric oxide.^{4c} *4-Diazo-4H-cyclopenta[def]phenanthrene* (200 mg, 0.93 mmol) and acenaphthylene (400 mg, 2.62 mmol) in anhydrous ether (10 ml) were left in a stoppered flask for four weeks. The crystals formed on standing were filtered and recrystallized from benzene, m.p. 253–254° (red-brown

melt) (Found: C, 94.8; H, 4.5%; M^+ , 340. $C_{17}H_{16}$ requires C, 95.2; H, 4.7%; M , 340), ν_{\max} (KBr) 720, 741, 765, 810, 830, 862, 895, 960, and 1400 cm^{-1} , δ ($CDCl_3$) 4.4 (2H, s) and 7.6–7.9 p.p.m. (14H, m).

Photoproducts (8) and (9).—Model compound (1) (34 mg) in benzene (20 ml) was flushed with N_2 for 15 min and irradiated for 3 h with a 150 W Hg lamp. The bright yellow solution was evaporated and the residue was extracted with heptane (3×20 ml). The concentrated extract was chromatographed on silica gel with cyclohexane as eluant. Final recrystallization from ethanol gave yellow crystals of *4-acenaphthenylidene-4H-cyclopenta[def]phenanthrene*, m.p. 228–229° (Found: C, 94.7; H, 4.85%), δ (CCl_4) 4.2 (2H, s) and 7.3–7.8 p.p.m. (14H, m). Model compound (2) (31 mg) was irradiated in benzene for 24 h and treated in a similar way to give *9-acenaphthenylidenefluorene*, m.p. 233–234°.

We thank the University Computer Centre for machine time and the Atomic Energy Commission for partial support. Part of this work was carried out at Goddard Space Flight Centre, Optical Systems Branch.

[2/321 Received, 14th February, 1972]

¹⁹ A. Schönberg, A. Mustafa, and N. Latif, *J. Amer. Chem. Soc.*, 1953, **75**, 2267.