should be considered only an approximate value. Metcalfe and Lee[12] estimated that the most probable excess energies of hot dimethylcyclopropanes resulting from Hg($^3P_1$) sensitization of 2,3-dimethylcyclobutanone are 90 kcal mol^{-1}. The higher dimethylcyclopropane excess energy from TDMP and CDMP is reflected by the ratio of pentenes to dimethylcyclopropanes at 1 Torr (no Ar) = 1.8, compared with 0.2 from 2,3-dimethylcyclobutanone.

From the measured molar extinction coefficients of CDMP and TDMP at 2537 Å, an estimated 3 to at most 6% of the decomposition products may be due to direct photolysis. The compounds 2M1B and 2M2B, both of which are formed in direct photolysis,[3,29] and which have a yield (Table I) of about 1% of N_2, are most likely formed in this way. The trace amounts of C2B and T2B, which we observe as stereospecific products as in direct photolysis, are also consistent with 2–3% of decomposition from a singlet pyrazoline. The correspondence between observed yields of products which arise through singlet pathways and the expected amounts of direct photolysis suggests this mechanism rather than $T_1 \rightarrow S_1$ intersystem crossing. Thus the Hg-sensitized decomposition probably proceeds entirely through triplet states, in contrast to the Hg(^3P)-sensitized decomposition of 2,3-dimethylcyclobutanone, which also yields triplet 1,2-DMTM biradicals but where 16–19% of the singlet products are formed as a direct consequence of energy transfer from Hg(^3P).[12]

Triplet biradicals react in significantly different ways than singlet biradicals. The cyclization of triplet 1,2-DMTM occurs at a slower rate than internal rotation, leading to loss of stereospecificity of dimethylcyclopropanes[3,10,11] in contrast to the predominant retention or inversion of configuration in singlet biradicals from the photolysis[3] or thermolysis,[14] respectively, of CDMP and TDMP. This result, presumably due to the slowness of triplet–singlet intersystem crossing (spin inversion) in triplet biradicals, is reconfirmed by the TDMC/CDMC values reported here. Another significant, but previously unexplained, difference is the olefin-producing reaction. Olefins are produced in the direct photolysis of cyclic azo compounds both in the gas and liquid phase, with little or no difference in their relative yields. But in the sensitized photolysis of cyclic azo compounds in solution olefin yields are greatly reduced compared with the gas phase. This difference in behavior can be understood in terms of decomposition reactions of hot triplet biradicals. In the vapor phase, hot biradicals are formed with sufficient energy to dissociate into alkyl- plus allyl-type radicals, unless collisionally deactivated, and olefin products are formed by radical–radical combination reactions. In condensed media rapid collisional deactivation processes predominate, producing triplet biradicals whose only reaction channel is cyclization (after spin inversion) to form cyclopropanes. The mechanism of olefin formation is apparently significantly different in singlet 1,3 biradicals. The formation of olefins in condensed media indicates that intramolecular rearrangements, perhaps H or CH_3 shifts, with low energy requirements, are possible in singlet species. An intramolecular migration route is absent in triplet 1,3 biradicals.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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π,π-Biradicaloid Hydrocarbons. The Pleiadene Family. I. Photochemical Preparation from Cyclobutene Precursors

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Abstract: Arynes add to acenaphthylene and give the cyclobutenes IV–VI. Irradiation of rigid dilute solutions of IV–VI gives the pleiadenes I–III, believed to have singlet ground states. Of these, I and II are stable only in rigid media, while very dilute fluid solutions of III survive brief warm-up to room temperature. The extreme ease with which I–III dimerize raises interesting questions concerning the nature of pericyclic reactions and these are discussed. It is proposed that orbital symmetry rules are of little use for the characterization of reactions of biradicaloid species. Irradiation of fluid solutions of IV–VI causes different and much slower reactions. A rationalization of this difference is proposed. Electronic absorption spectra of the pleiadenes I–III, as well as four other related hydrocarbons, are well accounted for by π-electron calculations. This gives credence to the novel yet not completely unexpected assignments of bands to doubly excited configurations in I and II, which can be described as borderline biradicaloids. The results are of potential conceptual importance not only in spectroscopy but also in photochemistry and even thermal chemistry (orbital symmetry rules). The calculations are also used as a basis for a discussion of other aspects of the electronic states of the pleiadene family of hydrocarbons.

We shall use the term *biradicaloid hydrocarbons* for those whose ground state, in the MO description, has two approximately nonbonding orbitals occupied by a total of two electrons, regardless of the details of the prevalent electron configuration in this state (singlet or triplet, etc.). The adjective, biradicaloid, is chosen so as to indicate close similarity to what is

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[1] Alfred P. Sloan Foundation Fellow, 1971–1973.

usually called biradicals without implying identity (since only one of the essential features of a biradical need be present). Since there is no clear-cut borderline between a pair of almost nonbonding orbitals on the one hand and a high-lying HOMO and a low-lying LUMO on the other, the transition from ordinary hydrocarbons, say anthracene, to biradicaloid ones, say octacene, should be continuous. Although one could draw an arbitrary dividing line, this does not appear necessary at present. We use the term *π,π-biradicaloid hydrocarbons* for those in which the two approximately nonbonding orbitals can be described as π in character (*e.g.*, planar trimethylenemethane).

The nature of low-lying electronic states of biradicaloid molecules has been discussed recently in detail.[2,3] When compared with "ordinary" species, the biradicaloid species show three main peculiarities.

(i) The lowest triplet ($^3\Phi_{1\rightarrow-1}$ in MO notation) is of comparable energy with the lowest singlet.

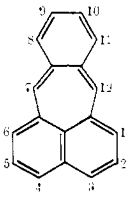
(ii) The lowest singlet is typically not as well described by a single ground-state determinant $^1\Phi_0$, as would be usual for normal molecules, but more adequately by a two-configuration function containing considerable weight of the doubly excited configuration $\Phi_{1,1\rightarrow-1,-1}$, which is rather low in energy. In this singlet, electron motions are well correlated ("covalent state").

(iii) In addition to the common low-lying "ionic" excited singlet state $^1\Phi_{1\rightarrow-1}$, there is another low-lying "ionic" (poorly correlated) singlet state, described approximately as an admixture of $^1\Phi_0$ into $^1\Phi_{1,1\rightarrow-1,-1}$. In simple language, this can be called a "doubly excited state." While states with considerable contributions from doubly excited configurations undoubtedly exist for all molecules, they are typically very high in energy. They are known in atoms and the hydrogen molecule and have only very recently been detected experimentally in an organic molecule.[4] However, they play an important role in discussions of orbital and state correlation diagrams[5] and, above all, in interpretation of photochemical reactivity.[3,6]

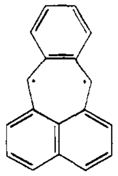
It should be noted that in the limiting case of a "perfect" biradicaloid molecule, Φ_0 and $\Phi_{1,1\rightarrow-1,-1}$ mix so strongly that both resulting states are equally "doubly excited;" indeed, in such cases it makes little sense to use the term at all and it is more meaningful to talk only of the "covalent" and "ionic" state.

Much attention is currently devoted to biradicals in connection with discussions of reactivity in cycloaddition reactions.[7] It is, at present, not clear whether such species in their singlet state indeed correspond to real minima in the ground-state potential-energy surface or if they are "twixtyls;"[8] at any rate, they seem to be difficult enough to characterize in the ground state, let alone trap and do spectroscopy on. Yet, information on their excited states might be of great help for understanding photochemical mechanisms.[3] We hope that by studying the relatively more stable π,π biradicaloids we can learn a little about the various electronic states of biradicaloid species in general. After all, much of our present understanding of the transition states of thermal pericyclic reactions can be derived from knowledge of the properties of aromatic and antiaromatic π-electron hydrocarbons with arrays of orbitals topologically equivalent to those of these transition states.[9,10]

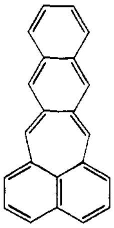
We have initiated our work by a study of hydrocarbons I–III containing the pleiadene structural unit.



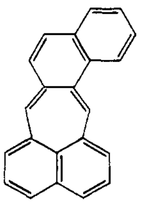
I



Ia



II



III

Already a qualitative consideration of VB structures such as those implied by Ia indicates that some biradicaloid nature can be expected for I. Indeed, MO calculations[11] predict a very high-lying HOMO and a very low-lying LUMO. Hopefully, substitution or benzoannelation can be used to manipulate the degree to which I is biradicaloid.

Pleiadene I has been of interest in itself, both to experimentalists[12–14] and theoreticians.[11] After Fieser's early unsuccessful attempts,[12] Cava and Schlessinger managed to generate I in solution as a reaction intermediate.[13] At ordinary temperatures, it proved exceedingly prone to dimerization but could be trapped as a Diels–Alder adduct with *N*-phenylmaleimide. A direct observation, even in dilute solution, appeared difficult. Additional trapping reactions were subsequently reported by Lown and Aidoo.[14]

In view of the suspected extreme reactivity of I–III, we have decided to attempt the preparation of dilute solutions in glassy matrices. The dihydrocyclobut[*a*]acenaphthylenes IV–VI appeared to represent reasonable photochemical precursors. The only authentic compounds with this carbon skeleton known at the outset of our work were the cis and trans dimers of acenaphthylene,[15] the photoadduct of duroquinone and acenaphthylene,[16] and 8b,8c,14b,14c-tetrahydroacenaphtho[1′,2′:3,4]cyclobuta[1,2-*l*]phenanthrene.[17] A 7,8-dihydro-7,8-diphenyl derivative of the parent 6b,8a-dihydrocyclobut[*a*]acenapthylene VII had been re-

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Table I. Nmr Data for Nonaromatic Protons ($CDCl_3$)

	IV	V	VI	VII	VIIIa[a]	VIIIb[b]
τ, ppm	4.72	4.52	4.40, 4.60	5.39[c]	6.86	4.87
J_{HH}, Hz	3.6 ± 0.3	4.0 ± 0.4	3.2 ± 0.3	2.5 ± 0.4	3.5[d]	
$J_{^{13}CH}$, Hz	147.2 ± 0.5	146.0 ± 0.5	147.6 ± 0.5	146.2 ± 0.5	138	

[a] In CCl_4.[30] [b] In CCl_4.[31] [c] Reported in ref 20 as 5.39. [d] Cis protons.

ported[18] but the structure assignment was later shown to be incorrect.[19] However, in recent years, there has been considerable interest in this class of compounds[20–24] and several are known now. An authentic 7,8-dihydro-7,8-diphenyl derivative of VII, as well as VII itself and its 7,8-dihydro derivative, were prepared by Meinwald and collaborators,[20] and the parent (VII) and several derivatives were also independently prepared by Plummer,[21a] Shirota,[21b] Hartmann,[22] Shields,[23] Nelsen,[24] and their respective collaborators.

We have prepared the benzo and naphtho analogs IV–VI in low-yield single-step reactions and found that their photochemical ring opening in glassy matrices indeed proceeds as desired. The preparation of stable rigid solutions of I has been reported in a preliminary communication.[25] In the present paper, we give full experimental details and also describe matrix preparation of two additional new members of the pleiadene family, II and III, characterize their properties, and compare them with those of several related previously known compounds. In the second paper of the series, we shall report the preparation of several derivatives of I and use these for a more detailed investigation of the nature of the excited singlet states. Some of the results have been briefly described elsewhere.[4,26] Finally, in a separate paper, we shall report an investigation of the unusual path followed by the photochemical electrocyclic reaction used for the preparation of matrix-isolated pleiadenes (for a preliminary communication, see ref 27).

Results

Preparation and Properties of Dihydrocyclobut[*a*]acenaphthylenes IV–VI. The cyclobutene derivatives IV–VI can be obtained by addition of benzyne, 2,3-naphthyne, or 1,2-naphthyne to acenaphthylene. The yields are 2.5–10%, comparable with yields of previously known 2 + 2 additions of benzyne to olefins.[28] Interestingly, diazotized anthranilic acid, but not *o*-fluorobromobenzene and magnesium, could be used successfully as a source of benzyne. The structures of IV–VI followed from elemental analysis and spectral properties. Since these somewhat strained compounds belong to a class with few known representatives, some of their spectral properties are briefly mentioned below.

The mass spectra of IV–VI contain very similar patterns. Each spectrum has four main groups of peaks, two due to singly and two to doubly charged fragments M, M − 2H, M − 4H, and M − C_2H_2, M − C_2H_2-2H, with their respective isotope peaks. The doubly charged fragments have quite high intensities (10–30% relative abundance). The spectrum of 6b,10b,IV-d_2[29] showed that the hydrogen and the acetylene are both lost from the aromatic rings and not from the saturated bridge. It also indicates that the weak peak at *m/e* 152 present in all spectra is most likely due to acenaphthylene molecular ion (in IV-d_2, the peak is at *m/e* 154).

A detailed discussion of the electronic absorption, fluorescence, and phosphorescence spectra of IV–VI will be reserved for a later paper describing their photochemical reactivity. The absorption spectra are close to the superimposed spectra of the two chromophores present and are shown as dashed lines in Figures 1–3.

The ^1H-nmr spectra of IV–VI correlate well with published values for structurally related systems.[30–32] They all have unexceptional aromatic regions. Nmr parameters of the bridgehead protons, obtained by analysis of ^{13}C satellites (for VI also directly from the ^1H-nmr spectrum), are collected in Table I. There seems to be a very interesting inverse relationship between the length of the unsaturated bond in the cyclobutene ring and the magnitude of the coupling constant J_{HH} between the two nonaromatic protons. This is just the opposite of the well-known correlation for the case of adjacent hydrogens on a double bond,[33] but the theoretical expressions for our case[34] are sufficiently complicated for an inverse relation to appear entirely possible. We hope to investigate this point in more detail later.

The benzylic hydrogens in IV are relatively acidic and apparently interfered with an attempt to prepare a radical anion by metal reduction in a manner reminis-

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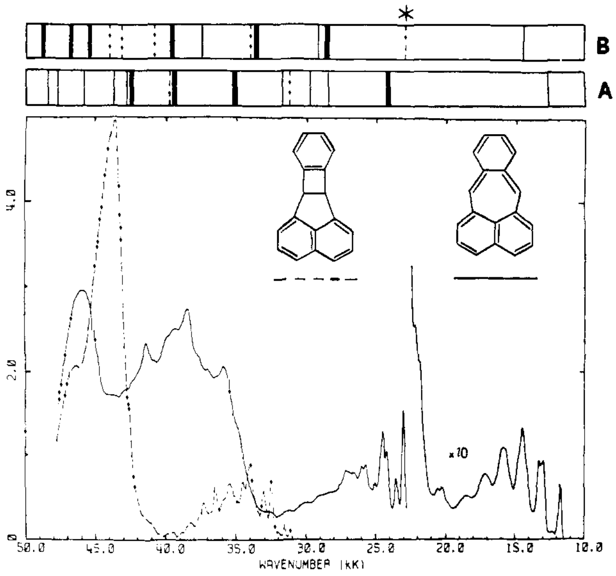

Figure 1. Absorption spectra (I, solid line; IV, dashed line) in 3-MP at −196° and calculated transitions for I (A, B; dashed lines, calculated oscillator strength below 0.02; solid thin lines, between 0.02 and 0.2; thick lines, above 0.2). The star indicates a predominantly doubly excited state.

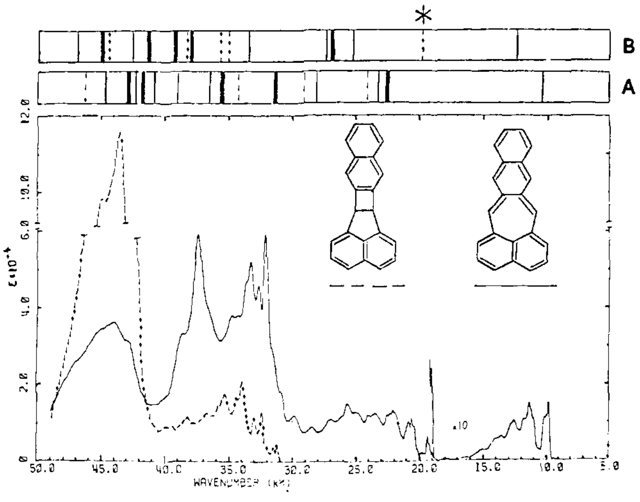

Figure 2. Absorption spectra (II, solid line; V, dashed line) in 3-MP at −196° and calculated transitions (A, B) for II (see caption to Figure 1).

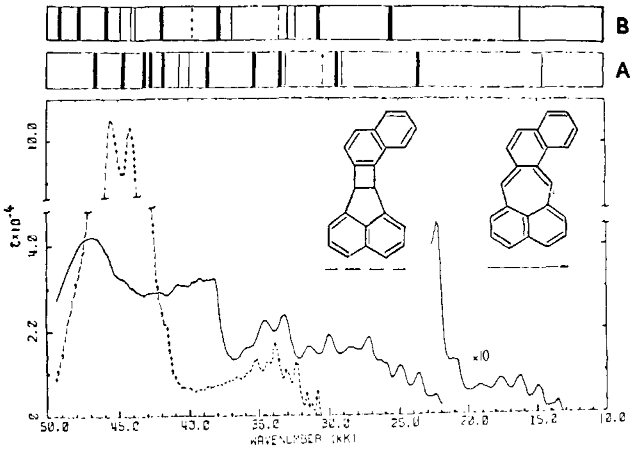

Figure 3. Absorption spectra (III, solid line; VI, dashed line) in 3-MP at −196° and calculated transitions (A, B) for III (see caption to Figure 1).

cent of the behavior of fluorene[35] and, probably, dihydropleiadene.[36] The chemistry of the single and double anions obtained by action of strong base will be reported separately.[29]

Benzocyclobutenes are known to open thermally to the very reactive *o*-quinodimethanes.[37,38] Considering their ring strain and high degree of substitution, compounds IV–VI are surprisingly stable when compared with other substituted benzocyclobutenes; *e.g.*, IV can be recovered after 6 min at 170°. At 230–240° the melts of IV–VI solidify in a few minutes. Meinwald, *et al.*,[20] report that similar treatment converts VII to IX. In our case, high-melting and sparingly soluble solids are isolated instead of the *o*-quinoid hydrocarbons I–III, which of course cannot be expected to survive under the reaction conditions. The melt of VI is at first green, possibly because of the presence of some III. The solid obtained from IV was found to be identical with the known[13] pleiadene dimer X; the rather insoluble solids from V and VI are believed to have dimeric structures as well but were not investigated in any detail.

Preparation and Properties of Pleiadenes I–III. Photochemical opening of benzocyclobutenes is well known to give *o*-quinodimethanes.[38,39] By analogy, and in view of the known propensity of pleiadene toward dimerization, irradiation of fluid solutions of the cyclobutenes IV–VI could be expected to give the pleiadenes, I–III, at sufficiently low temperatures, and their dimers, such as X, at ordinary temperatures. *This is not observed.* Slow spectral changes occurred when dilute (10^{-4} *M*) degassed fluid solutions of IV, V, and VI were subjected to very intense irradiation at room temperature, but no benzopleiadenes or their dimers were detected. Irradiation of a fluid solution of VI in 3-methylpentane at −150° gives no detectable III, although dilute solutions of III are stable apparently indefinitely at this temperature (see below).

However, in rigid solutions (glasses) the same light sources effect the desired photochemical reaction fast; the presence of I–III is easily detectable in a few minutes. The difference is quite striking: at −196°, when it is rigid, a degassed 10^{-4} *M* solution of IV in 3-methylpentane is 36% converted after 10 min of irradiation with collimated light of a 200-W high-pressure mercury arc, while the amount of IV in a degassed fluid solution of the same absorbance (room temperature) decreases only by 1% during the same irradiation period.[40a] In a cell containing a solution of IV in 3-methylpentane and half immersed in liquid nitrogen, the formation of

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colored I will proceed in the lower portion and not in the slightly warmer and much less viscous upper portion. Rigidity, and not temperature, is the dominating factor: a solution of IV in glycerol–methanol mixture (10:1), which is still rigid at −80°, can be converted to I easily at this temperature. The nature of the solvent seems to play no substantial role, and the conversions were also effected using rigid 2-methyltetrahydrofuran, EPA, and polyethylene sheet for the reaction medium.

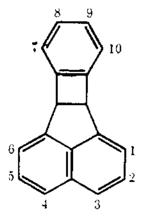
The photochemical ring opening in IV–VI in rigid media was done with filtered light (λ >280 nm). Its course is easily followed by uv–visible spectroscopy; the bands of the cyclobutene gradually disappear while bands of the product grow. Several well-defined isosbestic points are observed. All observed peaks can be assigned to either the starting material or one product throughout the reactions. Complete disappearance of the cyclobutene can be achieved if the starting solution is dilute ($\sim 10^{-4}$ *M*) and the path length short (2 mm). Further irradiation of the product with uv–visible or near-ir light produces no change. The yellow-green product from IV, the yellow one from V, and the green one from VI have reasonably similar absorption spectra (Figures 1–3), and the assignment of structures I, II, and III, respectively, is supported by their behavior upon warming the glass. This leads to a disappearance of the color of the dilute solution (10^{-4} *M*) in each case. The solution of II is least stable and I only a little more; their color disappears in a few seconds at about −150°. The dilute solution of III is considerably more stable; after warming up to room temperature (4–5 min), and subsequent recooling to −196°, the original spectrum is virtually fully restored. After hours at room temperature, the solution fades noticeably and eventually becomes colorless. More concentrated solutions fade and deposit solids already at lower temperatures, indicating that the destruction proceeds in a bimolecular manner, presumably by dimerization. None of the starting cyclobutenes (IV–VI) are re-formed in these reactions within our limits of detection.

In the case of I the warmed-up 10^{-4} *M* solution remains clear. Recooling and recording the spectrum gives a curve identical with that of the pleiadene dimer X obtained thermally. Using a vacuum-line degassed solution of IV (*ca.* 10^{-4} *M*), the resulting spectrum of X has about 80% of the intensity expected theoretically for 100% conversions in both steps, showing that side reactions are unimportant. In concentrated solutions a large degree of conversion is much harder to achieve, so that preparative work is difficult. However, after repeated irradiation and thawing X was isolated by thin-layer chromatography and identified by comparison of its uv spectrum, R_f value (tlc), and decomposition point with those of the sample prepared thermally.

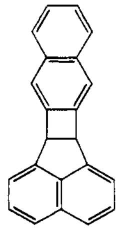
As the solutions of II and III in EPA warm up and fade, white solids precipitate out. These solids are very sparingly soluble. Unlike the dimer obtained from I, and like the dimers obtained by strong heating of V and VI, they appear to contain at least two components. In each case, one component has a uv spectrum close to that of the pleiadene dimer X while the other absorbs at longer wavelength (330–410 nm). These substances were not investigated further. Several unsuccessful attempts were made to obtain the ^{1}H-nmr spectrum of III at −80°. We were unable to find a concentration small enough to prevent excessively fast fading of the sample and yet large enough to give an acceptable nmr signal, with or without time averaging.

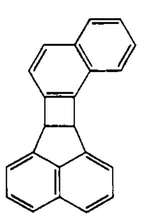
As expected for the proposed structures I–III, the rigid colored solutions give no epr signals near $g = 2.0$ (3-MP, −196°). Also a search for a half-field signal typical for triplets gave negative results. The experimental conditions of the measurement were similar to those which allow us to detect epr signals from ground-state triplets (triphenylene double anion), and it thus appears unlikely that the molecules I–III would be ground-state triplets.

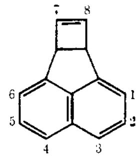
If the irradiation of the cyclobutenes IV–VI is done using light containing wavelengths shorter than about 280 nm, I–III still are the main products, but several new small peaks appear in the visible absorption spectra and a strong epr signal appears as well. When such a solution is warmed up slightly so that the glass just barely softens (*e.g.*, in 3-MP around −170°), the additional peaks in the absorption spectrum and the epr signal disappear in several seconds. Recooling to −196° at this point and recording the absorption spectrum gives a visible absorption curve identical with that obtained by irradiation with filtered light (λ >280 nm). The amount of the highly reactive radical byproduct is approximately proportional to the square of the light intensity and depends on the solvent, light source, and filter used.



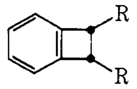
IV


V

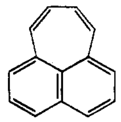

VI

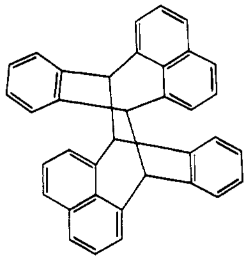


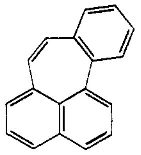
VII

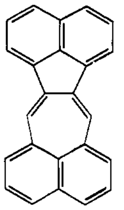


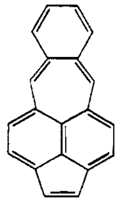
VIIIa, R = H
b, R = Ph


IX


X


XI


XII


XIII

The electronic absorption spectra of the pleiadenes I–III (Figures 1–3) were obtained from repeated measurements using a variety of path lengths and concentrations. The molar extinction coefficients shown were calculated assuming that in very dilute solutions the photochemical conversion was complete. The results for I described above indicate that the error is at most 20%.

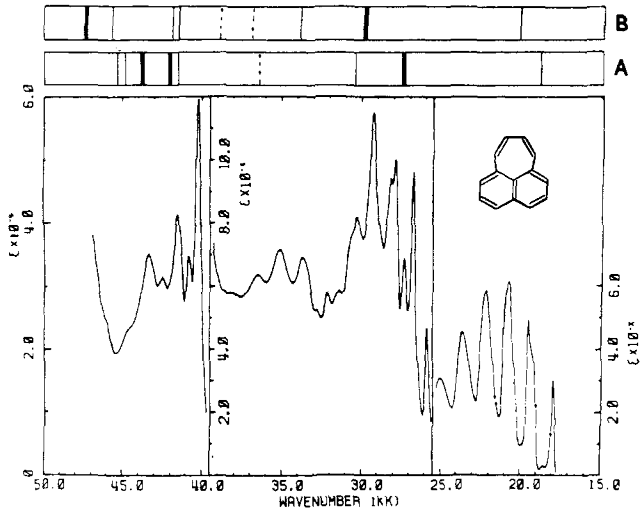


Figure 4. Absorption spectrum in 3-MP at −196° and calculated transitions for IX (A, B; see caption to Figure 1).

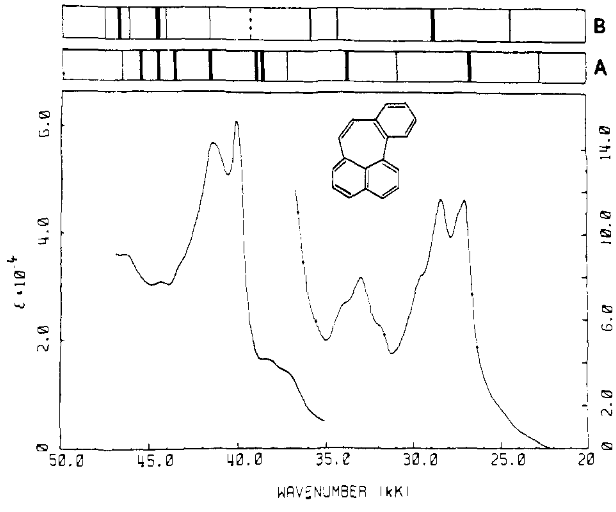


Figure 5. Absorption spectrum in 3-MP at −196° (from J. F. Muller, D. Cagniant, D. Lavalette, O. Chalvet, J. Kolc, and J. Michl, submitted for publication) and calculated transitions for XI (A, B; see caption to Figure 1).

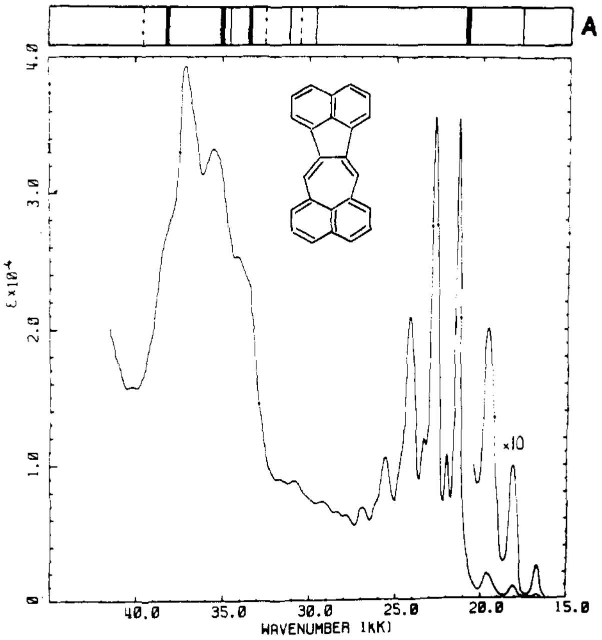


Figure 6. Absorption spectrum in 2-MTHF at −196° and calculated transitions for XII (A; see caption to Figure 1).

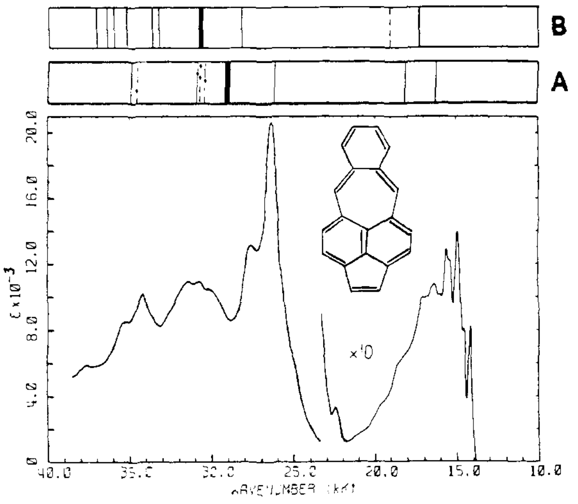


Figure 7. Absorption spectrum in 2-MTHF at −196° and calculated transitions for XIII (A, B; see caption to Figure 1).

In order to broaden the basis for the discussion of the electronically excited states of the pleiadenes I–III, we have also measured the low-temperature spectra of cyclohepta[*de*]naphthalene (IX), its benzologue XI[40b] (isomer of pleiadene I), and dinaphtho[*de*-1,2,3;*d′e′*-5,6,7]azulene XII,[41] all of which are stable at room temperature and require no special precautions. Finally, a modification of Cava and Schlessinger's procedure[42] for the preparation of solutions of acepleiadylene (XIII) at −40°, followed by cooling to −196°, permitted us to obtain the low-temperature absorption spectrum of XIII. The spectra of hydrocarbons IX and XI–XIII are shown in Figures 4–7.

Figures 1–7 and Table II also show results of semiempirical π-electron calculations of the usual PPP variety, using varying amounts of configuration interaction: set A, CI with all singly excited configurations with energies below 8 eV (Mataga repulsion integrals); set B, all singly excited configurations plus the ten doubly excited configurations corresponding to excitation from the highest two occupied to the lowest two virtual MO's (Ohno repulsion integrals); parameters were those of ref 43a; set C, triplets only, exactly as in ref 43b, except that for II, III, and XIII only the 81 configurations resulting from single excitations from the highest nine occupied to the lowest nine empty orbitals were included.

Discussion

1. Dihydrocyclobut[*a*]acenaphthylenes IV–VI. The high thermal stability of the cyclobutenes IV–VI is undoubtedly due to their cyclic structure, which prevents conrotatory ring opening so that the symmetry-forbidden high-energy disrotatory path must be followed, or a "semirotatory" path in which the motion

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[41] H. J. Bestmann and D. Ruppert, *Angew. Chem., Int. Ed. Engl.*, 7, 637 (1968).

[42] M. P. Cava and R. H. Schlessinger, *Tetrahedron*, 21, 3051 (1965).

[43] (a) J. Koutecký, J. Paldus, and R. Zahradník, *J. Chem. Phys.*, 36, 3129 (1962); (b) J. Pancíř and R. Zahradník, *J. Phys. Chem.*, 77, 107 (1973).

Table II. PPP Calculations

	Column								
	1	2	3	4	5	6	7	8	9
		Calculation[a]							
		A	A	B	B	B	B	B	C
Compd	ΔE, β[b]	IP, eV[c]	EA, eV[d]	% ψ_0[e]	n_1[f]	n_{-1}[g]	^1E, eV[h]	$E_{1,1}{}^{-1,-1}$, eV[i]	^3E, eV[j]
XI	0.81	7.08	0.36	0.98	1.98	0.02	3.02 (0.50)	6.33	1.74
IX	0.70	6.90	0.42	0.98	1.97	0.03	2.51 (0.88)	5.63	1.33
XIII	0.60	6.86	0.36	0.95	1.94	0.04	2.14 (0.82)	4.72	0.94
XII	0.48	6.61	0.81	*k*	*k*	*k*	*k*	*k*	*k*
III	0.45	6.55	1.05	0.98	1.96	0.03	2.00 (0.88)	4.40	0.76
I	0.37	6.45	1.25	0.94	1.90	0.09	1.75 (0.87)	3.62	0.39
II	0.22	6.24	1.61	0.92	1.85	0.14	1.54 (0.84)	2.87	0.02

[a] Calculations A, B, and C; see text. [b] HMO energy difference between HOMO (1) and LUMO (−1). [c] Ionization potentials calculated from SCF orbital energies using Koopmans' theorem. A constant correction of 1.50 eV was added to all orbital energies in order to reproduce exactly the IP of anthracene (7.38 eV). Such a procedure amounts to a calculation of relative IP's only. [d] Electron affinity calculated from SCF orbital energies using Koopmans' theorem. A constant correction of 2.55 eV was added to all orbital energies in order to reproduce exactly the EA of anthracene (0.56 eV). Such a procedure amounts to a calculation of relative EA's only. [e] Weight of the SCF ground determinant ψ_0 in the CI ground state. [f] Occupation number of the least occupied natural orbital among the "occupied" ones. [g] Occupation number of the most occupied natural orbital among the "empty" ones. [h] Excitation energy of the lowest singlet state. In parentheses, weight of the $1 \rightarrow -1$ configuration in this state. [i] Energy of the $1,1 \rightarrow -1,-1$ configuration with respect to the SCF ground determinant ψ_0. [j] Excitation energy of the lowest triplet state. [k] The programs used cannot handle a 24-atom problem.

of the C–H bonds is not correlated and one turns before the other. The only really intriguing aspect of the behavior of the cyclobutenes is their relative inertness to irradiation in fluid solution, given that their ring opens readily on irradiation in rigid solutions. One might have perhaps expected the opposite, since models indicate that the change of shape from the cyclobutene structures IV–VI to the fully conjugated structures I–III is considerable and the reaction might be inhibited in media of high viscosity.

Perhaps the most obvious explanation of the observations would be to postulate that the conjugated hydrocarbons I–III undergo a fast thermal ring closure back to the cyclobutenes IV–VI, except in media of high viscosity, which makes the necessary change of shape too difficult. One would then rationalize the occurrence of the photochemical ring opening in rigid media by pointing out that some local heating and decrease of viscosity can be expected when much of the energy of the photon is dissipated as heat. However, this simple explanation cannot be correct; the ring-opening reaction refused to proceed in fluid media even at temperatures at which the product could be shown to be thermally (and light) stable, and moreover, at temperatures at which the products I–III are unstable, they react to give dimers rather than reclose to the cyclobutenes IV–VI!

A clue to an explanation which we have finally adopted[27] was provided by the observation that the reactions proceed only in those instances in which the long-lived phosphorescent emission of the cyclobutenes IV–VI is observed. It is, of course, well known[44] that the triplet lifetime of many aromatic hydrocarbons, including naphthalene, is quite long in rigid media (several seconds) and very much shorter in fluid media (~10^{-4} sec), due to triplet–triplet annihilation, impurity quenching, etc. Accordingly, in rigid solution steady illumination builds up an equilibrium concentration of molecules in the metastable triplet state which is much larger than that resulting from the same illumination in fluid solution. It is then logical to postulate that the actual substrates of the photochemical reactions are the metastable triplets of the cyclobutenes IV–VI, which are present in reasonable concentrations in rigid media but in only vanishing amounts in fluid solutions. In other words, the reaction proceeds by a two-photon mechanism (subsequent absorption of two photons). This postulate lends itself to experimental verification using a variety of standard methods. As reported in a preliminary communication,[27] it turned out to be correct. A detailed description of the study of the low-temperature reaction mechanism will be presented in a separate paper and only a few pertinent points will be mentioned here. First, it should be pointed out that biphotonic photoionization, C–H bond dissociation, and sensitized solvent decomposition are well-known phenomena in rigid media.[45–47] Ours appears to be the first reported case of a more complex photochemical reaction (electrocyclic reaction). It appears likely that many more such cases could be found. We have very recently reported the first case of the biphotonic cycloreversion reaction[48] and are presently looking for other examples. Possibly, the phenomenon is just a curiosity without any importance, but it is also possible that its study will contribute to an improved understanding of organic photochemical processes in general.

Our accidental discovery was made on the cyclobutene IV; the search for other such cases clearly required at least a crude theoretical understanding, capa-

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(44) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N. Y., 1970.

(45) For leading references see J. Moan, *Chem. Phys. Lett.*, 18, 446 (1973); J. B. Birks, Ed., "Photophysics," Vol. 1, Wiley, New York, N. Y., 1973.

(46) V. E. Kholmogorov, "Elementary Photoprocesses in Molecules," B. S. Neporent, Ed., Consultants Bureau, New York, N. Y., 1968, p 123; B. Brocklehurst, W. A. Gibbons, F. T. Lang, G. Porter, and M. I. Savadatti, *Trans. Faraday Soc.*, 62, 1793 (1966); H. S. Judeikis and S. Siegel, *J. Chem. Phys.*, 43, 3625, 3638 (1965); T. Tanei and H. Hatano, *Bull. Chem. Soc. Jap.*, 42, 3369 (1969); S. Siegel and H. S. Judeikis, "The Triplet State," Proceedings of an International Symposium held at the American University of Beirut, Lebanon, Feb 14–19, 1967, A. B. Zahlan, Editorial Board Chairman, University Press, Cambridge, 1967, p 195; S. Siegel and K. Eisenthal, *J. Chem. Phys.*, 42, 2494 (1965).

(47) P. M. Johnson and A. C. Albrecht, "The Chemistry of Ionization and Excitation," G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, London, 1967, p 91; *J. Chem. Phys.*, 48, 851 (1968); V. Zanker and D. Benicke, *Z. Phys. Chem.*, 66, 34 (1969).

(48) J. Kolc and J. Michl, Abstracts, 4th IUPAC Symposium on Photochemistry, Baden-Baden, Germany, July 1972, p 167.

ble of providing predictions. Such a theoretical aid was found in a modified version of the Woodward–Hoffmann rules.[49–51] It was predicted that V and VII should definitely behave like IV, while VI might, but should be closer to the usual behavior (photochemical reaction after absorption of a single photon). Shortly thereafter, Meinwald, *et al.*,[21] confirmed the prediction for VII, and we now find that V and VI also behave like IV. We are presently searching for instances in which a related cyclobutene is predicted to undergo a normal one-photon reaction. If the theory works even for such cases, it will be reasonable to adopt it as a general tool for further predictions. Different theoretical explanations of the reported results[27] were offered by Dewar[9] and Dougherty.[52] We shall postpone a detailed discussion of both sets of arguments for the full paper on our experimental results (see also ref 53).

2. Pleiadenes. Structure. It seems certain that the photoproduct from IV is indeed pleiadene I as expected, since the structure is secured by self-trapping to give the known dimer X in high yield. The self-trapping experiments on products obtained from V and VI are much less satisfactory since more than one product results. This is perhaps not surprising in view of the increased number of possibilities which these naphthoquinoid systems offer. The photoproducts from V and VI are assigned structures II and III by analogy to the other two cases (IV and VII) and since their thermal reactivity and absorption spectra agree well with expectations based on the properties of I, IX, and XIII. Indirect support for all three structures I–III also comes from the wealth of known examples of photochemical ring opening in substituted cyclobutenes and benzocyclobutenes.[39,54] The other precedented reaction which one can easily envisage for IV–VI, namely dissociation of the benzylic C–H bond, is excluded, since the products show no epr signal. Actually, it appears likely that the latter reaction is at the origin of the extremely reactive radical by-products formed from IV–VI with light of wavelengths shorter than about 280 nm, apparently in a two-photon process. The radical-producing photosensitized decomposition of glassy solvents by naphthalene in a two-photon process proceeding *via* its metastable triplet state is known to occur only with sufficiently energetic photons ($\lambda < 260$ nm).[46] Compounds with benzylic hydrogens are well known to give benzylic radicals in a two-photon process under similar conditions.[47] Biphotonic photoionization under these conditions is also known,[45] and the by-products could conceivably also be the radical cations of I–III or IV–VI. We consider this possibility less likely.

3. Pleiadenes. Nature of Electronic States. The simple semiempirical π-electron PPP SCF–CI model[55] has been used in view of the size of the molecules investigated. In spite of obvious shortcomings, it generally gives a satisfactory approximate description of the nature of electronic states of planar hydrocarbons. Some simple calculations with only very limited CI were performed first (results A), but since the pleiadene molecules appeared to have biradicaloid characteristics, it was considered necessary[2,3] to include some doubly excited configurations as well (results B).

In order to check the reliability of our results for the somewhat unusual molecules I–III and to provide a more comprehensive comparison with experiment, we have also performed calculations for the structurally related hydrocarbons IX and XI–XIII. The overall agreement with experimental data for lower lying transitions, such as correct prediction of shifts of the first weak transition and its separation from the first strong transition, encourages us to view with some confidence the results concerning the nature of the electronic states of pleiadenes I–III. The numerical agreement is somewhat better for results A, undoubtedly since the parameters had been optimized[43] for such an extent of CI. Of course, the doubly excited states in I and II, indicated with stars in Figures 1 and 2, are missing in A. More detailed theoretical and spectroscopic studies of some of the hydrocarbons included here, such as firmer identification of the individual electronic transitions, determination of polarization directions, and substituent effects, are under way. Particular attention is being paid to doubly excited states. Some results have already been reported[4,26] and agree with the calculations presented here.

An indication of the biradicaloid nature of hydrocarbons I–III comes already from simple Hückel calculations, which predict high-energy HOMO and low-energy LUMO, both unusually close to the Hückel zero of energy even considering the size of the molecules (Table II, column 1). Columns 2 and 3 of Table II list estimates of the gas-phase ionization potentials (IP) and electron affinities (EA), using an SCF closed-shell ground-state determinant (PPP) and Koopmans' theorem with constant additive correction terms chosen to reproduce exactly the experimental IP and EA of anthracene. The calculated IP's are indeed strikingly low, compare pentacene[56] 6.64 eV, and the EA's relatively high, compare azulene[57] 0.66 eV and fluoranthene[58] 0.63 eV. Some biradicaloid character seems indicated and single determinant calculations appear suspect. However, our more extensive CI calculations (set B and also some runs with up to 100 configurations) showed that the ground states of I–III are quite well represented by single SCF determinant (Table II, column 4), so that the predicted values of IP and EA are probably quite reasonable. The unexceptional rather than biradicaloid nature of the ground states of I–III, as well as IX and XI–XIII, is perhaps best seen in the occupation numbers of natural orbitals which were approximated crudely by diagonalization of the first-order density matrix resulting from a CI calculation of type B (Table II, columns 5 and 6). For the "occupied" orbitals, the occupation numbers are all at least 1.85; for the "empty" orbitals, they are all below 0.15. In Table II, the compounds are arranged in the approximate order of increasing "biradicaloid" character.

On the other hand, inspection of the results for low-lying excited singlet states obtained from the more exten-

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(49) J. Michl and J. Kolc, presented at the 3rd IUPAC Symposium on Photochemistry, St. Moritz, Switzerland, July 12–18, 1970.

(50) J. Michl, *J. Amer. Chem. Soc.*, **93**, 523 (1971).

(51) J. Michl, *Mol. Photochem.*, **4**, 287 (1972).

(52) R. C. Dougherty, *J. Amer. Chem. Soc.*, **93**, 7187 (1971).

(53) J. Michl, "Chemical Reactivity and Chemical Paths," G. Klopmann, Ed., Wiley, New York, N. Y., in press.

(54) R. Srinivasan, *J. Amer. Chem. Soc.*, **91**, 7557 (1969).

(55) R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York, N. Y., 1963.

(56) P. A. Clark, F. Brogli, and E. Heilbronner, *Helv. Chim. Acta*, **55**, 1415 (1972).

(57) R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966).

(58) J. Michl, *J. Mol. Spectrosc.*, **30**, 66 (1969).

sive CI results (B) reveals unusual features, attributable to the biradicaloid nature of some of these hydrocarbons (bottom of Table II). The lowest excited singlet is obtained from the ground state by one-electron HOMO → LUMO ($1 \rightarrow -1$) excitation as usual (Table II, column 7), but one or more other low-lying singlets are calculated to contain large amounts of a two-electron $1,1 \rightarrow -1,-1$ excitation (over 50%, indicated with stars in Figures 1–7). This is easily understood considering the low energy of this doubly excited configuration (Table II, column 8).

Such doubly excited configurations are normally computed to lie at rather high energies. They often interact strongly with other configurations,[59] so that no one state can be singled out as doubly excited. In our case, molecules I and II are calculated to have a low-lying predominantly doubly excited state, while in III, the $1,1 \rightarrow -1,-1$ configuration contributes almost equally to several low-lying states. As mentioned in the introduction, low-lying doubly excited singlet states should be typical of biradicaloid systems, in which the HOMO–LUMO energy difference is very small.

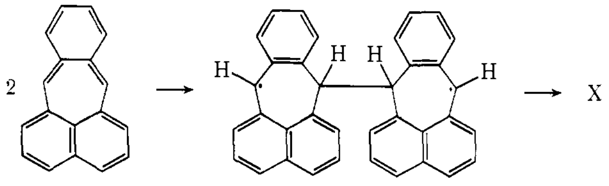
Experimentally, spectra of both I and II contain bands which correspond to the calculated transitions to the doubly excited states and which cannot be accommodated as part of the vibrational fine structure of neighboring bands. However, previous observations of doubly excited states of molecules have been extremely rare (H_2 molecule[60]), and we are not aware of another organic molecule in which an assignment of an excited state as predominantly described by one doubly excited configuration would at present be accepted, or even considered.[61] Because of the unusual nature of the assignment, we have investigated a series of substituted derivatives of I and plan to devote the next paper in this series to a detailed justification of the assignment in I (see also ref 4). Nevertheless, it is pertinent to point out here that a doubly excited configuration should have very roughly twice the energy of the corresponding singly excited configuration, so that one could actually argue that it would be surprising if weak transitions into doubly excited states could not be observed in the fortuitous absence of overlap with the more intense transitions into higher singly excited states! Weak but nonzero intensity can be expected to originate in vibronic as well as configuration mixing.

We have also calculated the energies of triplet states (set C) using parameters claimed[43b] to be suited for triplet calculations (Table II, column 9). For molecules near the bottom of Table II, the lowest triplets are only a fraction of an electron volt above the ground singlet state, as expected for biradicaloid species, and for II the lowest singlet and triplet are calculated to have the same energy. However, absence of a half-field signal in esr spectrum, agreement of observed absorption spectrum with calculated S → S spectrum, and lack of agreement with calculated T → T spectrum indicate that the lowest singlet is still significantly below the lowest triplet even for II. Calculations of T → T absorption spectra were performed for other molecules as well (set C) and in each case gave poorer agreement with observed absorption spectra than the S → S calculations shown in Figures 1–7.

In summary, the results indicate that hydrocarbons I and II, and to a lesser degree III, show some but not all of the expected biradicaloid properties and apparently lie on the borderline. As outlined in the introduction, π,π-biradicaloid systems, in addition to their intrinsic interest, also provide models for less accessible biradicaloids of other kinds. Biradicaloid geometries are believed to be reached by excited molecules during pericyclic and other photochemical reactions, and some recent attempts at detailed descriptions of the photochemical process emphasize their importance.[3,6,62] The role played in these arguments by doubly excited configurations in molecules at such geometries is well known, but their so far purely hypothetical nature has sometimes been considered a weakness.[52] Doubly excited configurations also play an important role in the construction of Woodward–Hoffmann-type correlation diagrams for pericyclic reactions.[5] Accordingly, we believe that our results for the doubly excited states of pleiadenes are more than just a spectroscopic curiosity.

4. Pleiadene (I). The Dimerization Reaction. Although all three pleiadenes investigated, I–III, as well as acepleiadylene XIII,[42] apparently dimerize with great ease, only the dimerization of I will be discussed here since the structures of the products from II and III have not been established.

The geometrical restrictions imposed by the ring structure limit the likely mechanisms to two possibilities: a two-step cycloaddition with a biradical intermediate (such as XIV) and a concerted "forbidden" 4s + 4s cycloaddition. The extreme ease of the dimerization appears to be equally well explained by either mechanism and we are presently not able to decide between them. In the first step of the nonconcerted mechanism, two essentially localized C=C double bonds are lost in exchange for a C—C single bond, twice the benzene resonance energy, and twice the additional delocalization energy of an α-naphthylphenylmethyl radical. Using Dewar's values for π-electron energies and additive σ-bond energies,[63] it would appear that this step is thermoneutral or even slightly exothermic. It is then not surprising that the activation energy should be very low. The second step



XIV

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[59] (a) J. Koutecký, *J. Chem. Phys.*, 47, 1501 (1967); (b) K. Schulten and M. Karplus, *Chem. Phys. Lett.*, 14, 305 (1972); B. S. Hudson and B. E. Kohler, *ibid.*, 14, 299 (1972), and references therein.

[60] O. W. Richardson, "Molecular Hydrogen and Its Spectrum," Yale University Press, New Haven, Conn., 1934; G. H. Dieke, *Phys. Rev.*, 76, 50 (1949); G. H. Dieke and S. P. Cunningham, *J. Mol. Spectrosc.*, 18, 288 (1965).

[61] The lowest excited singlet of 1,8-diphenyloctatetraene appears to have partially doubly excited character.[59b] Similar states have been calculated for *o*-xylylene[59b] and butadiene [T. H. Dunning, Jr., R. P. Hosteny, and I. Shavitt, *J. Amer. Chem. Soc.*, **95**, 5067 (1973)]. In these, singly excited configurations still represent over 50% of total weight. A weak band observed in CF_3NO might be due to transition into a doubly excited state or a triplet state: K. L. McEwen, *J. Chem. Phys.*, 34, 547 (1961).

[62] J. Michl, *Top. Current Chem.*, in press.

[63] M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, 90, 1953 (1968); C. R. deLlano, Dissertation, University of Texas at Austin, Texas, 1968; M. J. S. Dewar and C. R. deLlano, private communication.

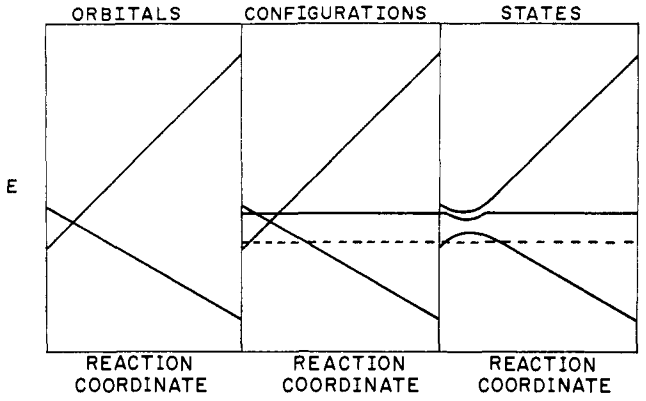
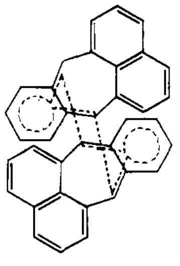


Figure 8. Correlation diagrams for a pericyclic reaction of a biradicaloid molecule (left-hand side of diagrams) to a normal product (right-hand side of diagrams), *e.g.*, 2I → X. Schematic. Solid line, singlet; dashed line, triplet.

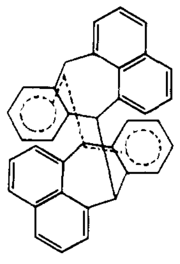
is undoubtedly exothermic and most likely even faster, although it involves a symmetry-imposed barrier of the type encountered in the stepwise dimerization of ethylene.[8]

At first sight, the concerted 4s + 4s process may appear less appealing, since it is "symmetry forbidden." However, all this means is that the transition state is biradicaloid in nature and has two approximately nonbonding electrons.[64] Since the two electrons in the HOMO of I are largely nonbonding anyway, this is not much of a sacrifice. Clearly, the concepts of symmetry-"allowed" and -"forbidden" reaction paths inevitably lose much of their significance when applied to reactions of a species which is biradicaloid to start with. Since the symmetry-imposed barriers then are very small, and moreover the reactions are likely to be very exothermic, normally secondary considerations, such as configuration interaction with a low-lying doubly excited configuration, may become important. The argument can be seen clearly from correlation diagrams of the usual type drawn for a reaction of a biradicaloid species (Figure 8). When the doubly excited configuration involved in the crossing is only a little above the ground-state configuration, the correlation-imposed barrier diminishes, and after introduction of CI it may disappear entirely. In the case of I, the doubly excited configuration is only about 3 eV above the ground configuration,[4] instead of the usual 6–10 eV or so, and the Woodward–Hoffmann concept of forbiddenness could well become meaningless. This should be even more so in a truly biradicaloid species with an even smaller HOMO–LUMO separation. These arguments have appeared in our preliminary communications[4,25] and in the work of Schmidt.[65]

Whether the reaction proceeds in two steps *via* XIV with a finite lifetime or in one step *via* XV is probably determined primarily by the energies of XIV and XV, since at the low temperatures used the entropy factor is likely to play only a secondary role (it would be expected to favor XIV). The "tight" geometry XV probably derives a certain degree of stabilization from cyclic delocalization (*cf.* ref 7a, 62, 66, and 67); on the other hand, one can argue that electron repulsion is minimized at the "loose" geometry XIV (*cf.* ref 3, 62, and 68). If the latter effect prevails, the species would spend awhile at loose geometries such as XIV before gathering enough energy to go through a transition-state geometry such as XV or XVI to form the product X. This seems to be the case in ordinary two-step cycloadditions which lead to partial or complete loss of stereochemistry.[69]



XV



XVI

Whether the reaction is one step, using XV, or two step, *via* XIV and then XV or XVI, simple considerations of secondary orbital interaction indicate that the head-to-tail dimer rather than the head-to-head dimer should be formed, as is indeed observed.

Experimental Section

Analytical samples were dried over phosphorus pentoxide at 105° and 0.001 Torr for 24 hr. Melting points were determined in capillary. The nmr spectra were measured on Varian XL-100-12, mass spectra on Perkin-Elmer 270, and electronic absorption spectra on Cary 17 instruments.

Low-temperature spectra were mostly taken in 3-methylpentane (3-MP), 2-methyltetrahydrofuran (2-MTHF), and EPA. 3-MP (Phillips 66, pure grade) was purified by refluxing with metallic sodium, distillation through a column, and passage through an alumina–silver nitrate column. 2-MTHF (Matheson Coleman and Bell, chromatoquality reagent) was purified in a similar way and passed through an alumina column. EPA mixed solvent (American Instrument Co.) was used without further purification. Quartz cells of 2-mm path length (volume *ca.* 0.5 ml) immersed in a quartz dewar equipped with flat windows and containing liquid nitrogen were used for photochemistry and spectroscopy at −196°. All quartz in the optical path was Suprasil. For weak absorption bands in the visible and near-ir regions, a Pyrex cell of 30-mm path length in one direction (for absorption measurements) and 5-mm path length in the other direction (for irradiation) was used. The photochemistry and spectroscopy between −196° and room temperature were done by using the same dewar and nitrogen gas from liquid nitrogen as a coolant, employing an apparatus constructed in this laboratory, and using a thermoelement, temperature controller (Capacitrol, Barber-Colman Co.), and cartridge heater.

A 200-W high-pressure mercury arc with $f = 1.5$ quartz optics (PEK, Inc.), water heat filter (10-cm path length), and glass cut-off filters was used to achieve photochemical conversions.

6b,10b-Dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (IV). To a stirred refluxing solution of 45.6 g (0.3 mol) of acenaphthylene and 15 ml (0.11 mol) of freshly distilled isopentyl nitrite in 1000 ml of dry methylene chloride, 13.7 g (0.1 mol) of anthranilic acid in 60 ml of tetrahydrofuran was added dropwise over 4 hr. The stirring and reflux were continued for 2 additional hr. The reaction mixture was evaporated to dryness and dissolved in benzene-petroleum ether mixtures, extracted with 5% aqueous sodium bicarbonate and 5% HCl, dried over anhydrous sodium sulfate, and filtered through a short column of activated neutral alumina. The filtrate was evaporated to dryness and the major part of the acenaphthylene removed by sublimation under vacuum. Crystal-

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(64) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(65) W. Schmidt, *Helv. Chim. Acta*, **54**, 862 (1971); *Tetrahedron Lett.*, 581 (1972); K. A. Muszkat and W. Schmidt, *Helv. Chim. Acta*, **54**, 1195 (1971).

(66) J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972).

(67) H. E. Zimmerman and G. A. Epling, *ibid.*, **94**, 8749 (1972).

(68) J. Michl, "Physical Chemistry," Vol. 7, H. Eyring, W. Jost, and D. Henderson, Ed., Academic Press, New York, N. Y., in press.

(69) W. C. Herndon, *Chem. Rev.*, **72**, 157 (1972).

lizations from cyclohexane and benzene–hexane afford 2.1 g of white crystals, mp 130–132° (9.2% yield).

The sample was crystallized three times from cyclohexane: mp 133–134°; uv max (3-MP), 291 nm (ϵ 8000), 226 (43,000), 213 (32,000).

Proton nmr spectra in acetone-d_6 (60, 100, 200 MHz) show an ABC system integrating for 6 H (approximately τ_1 2.45, τ_2 2.53, τ_3 2.37, J_{12} = 7 Hz, J_{23} = 8 Hz), an AA′BB′ system centered at τ 2.84 (4 H), and a broad singlet at τ 4.67 (2 H,half-width 1.7 Hz). Decoupling showed that a broadening is due to unresolved long-range coupling between the aliphatic protons and both aromatic systems. Mass spectrum showed molecular ion at *m*/*e* 228. *Anal.* Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 94.94; H, 5.29.

6b,10b-Dihydronaphtho[2,3-*j*]cyclobut[*a*]acenaphthylene (V). 3-Amino-2-naphthoic acid (7.5 g (0.04 mol)) was used to prepare 3-diazonium naphthalene-2-carboxylate employing the procedure described in ref 70. The diazonium carboxylate was decomposed by refluxing in a solution of 30 g (0.2 mol) of acenaphthylene in 600 ml of 1,2-dimethoxyethane for 12 hr under nitrogen. The product was isolated as described above for IV. Crystallization from benzene–petroleum ether afforded 0.45 g of white crystals (4% yield).

Mp 195–196°; uv max (3-MP), 291 5 nm (ϵ 11,000), 288 (71,500), 222 (69,000). Proton nmr spectra in chloroform-*d* (100 MHz) show an aromatic multiplet between τ 2.21 and 2.83 (12 H) and a singlet at τ 4.52 (2 H). Mass spectrum showed molecular ion at *m*/*e* 278. *Anal.* Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 95.00; H, 5.02.

6b,12b-Dihydronaphtho[2,1-*j*]cyclobut[*a*]acenaphthylene (VI). 1-Amino-2-naphthoic acid was used in the same way as described in the preparation of V to prepare VI with a yield of 2.5% crystallized from benzene–petroleum ether.

Mp 185–186°; uv max (3-MP) 294.5 nm (ϵ 13,300), 224 (92,000), 218.5 (91,000). Proton nmr spectra in chloroform-*d* (100 MHz) show an aromatic multiplet between τ 2.02 and 2.86 (12 H) and a pair of doublets at τ 4.40 and τ 4.60 (1 H each). Mass spectrum showed molecular ion at *m*/*e* 278. *Anal.* Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 94.97; H, 5.04.

Pleiadene and Benzopleiadenes (I–III). A dilute solution (10^{-4}–10^{-5} *M*, depending on the particular absorption band studied) of IV in 3-MP in a quartz cell was cooled to the liquid nitrogen temperature in a quartz dewar and irradiated with a collimated beam of light from a 200-W source, using a Corning CS 0-53 glass cut-off filter (2 mm thickness) for 40 min. After this time the conversion of IV to I was 100%. I was prepared also using 2-methyltetrahydrofuran, EPA, or polyethylene at −196° and glycerol–methanol (10:1) at −78° as matrices. The electronic spectrum was the same except for small shifts and more blurred vibrational structure.

The benzopleiadenes II and III were prepared in the same way using the precursors V and VI. Attempts were made to obtain an nmr spectrum of III. A degassed 10^{-4} *M* solution (15 ml) of VI in Et_2O–CH_3COOCH_3 (9:1) in a flat Pyrex cell (5 mm inside) was cooled to −196° to make a glass and irradiated with a 200-W lamp for 3 hr. The solvent was then removed at −80° under vacuum (10^{-6} Torr) and the dark green colored III extracted from unconsumed starting VI with several drops of diisopropyl ether. Six runs prepared in this way were then combined and concentrated at −80° to fit the volume of a 5-mm thin wall nmr tube, and an attempt was made to observe the nmr spectrum at −80° using CAT. Despite its dark green color, the concentration of III in the solution was not sufficient to get a satisfactory spectrum in 3 hr. During this time, the solution faded appreciably, and the solid precipitate (probably dimer) formed made further measurement impossible.

Pleiadene Dimer X. (a) By Thermal Dimerization of IV. I (45 mg) was sealed under nitrogen into an ampoule and heated to 230–240° for 15 min. The sample melted and after *ca.* 5 min solidified. Two crystallizations from toluene gave 29 mg of white crystals: melting point, above 370° dec (reported[13] for pleaidene dimer: 350–370° dec); uv max (dioxane), 317.5 nm (ϵ 17,500), 304.5 (19,200), ϵ at 214 nm: 77,700 (no maximum); (reported[13] for pleiadene dimer: 318 (17,000), 304 (18,800), 214 (90,500)); nmr in $CDCl_3$ τ 4.89 (4 H), 3.29 (4 H), 2.27–2.67 (16 H)); (reported[13] for pleiadene dimer: τ 4.83 (4 H); 3.22 (4 H); 2.3–2.7 (16 H)).

(b) By Dimerization of Photochemically Formed Pleiadene I. IV (3 mg) in 10 ml of 3-MP was placed into two 5-ml quartz cells (optical path 1 cm). The samples were degassed in the usual way (freeze–pump–thaw cycles) and then irradiated using a 1-kW Hg–Xe arc (Pyrex filter) at −196° for 20 min, warmed to room temperature, recooled to −196°, and irradiated for another 20 min, etc. After ten such cycles, the solid formed on the walls of the cells was dissolved in chloroform, chromatographed on a thin layer of silica gel (chloroform eluent), and found to have an identical R_f value with the dimer obtained by thermal dimerization of IV (*vide supra*). Pure dimer was isolated from several tlc plates; its uv spectrum and decomposition points were also the same as obtained in procedure a.

Acepleiadylene XIII. A solution of 5,10-dihydroacepleiadene-5,10-diol[42] in dioxane is known to afford unstable blue acepleiadylene (XIII) when treated with concentrated hydrochloric acid.[42] We have modified this procedure by using a dilute (10^{-3} and 10^{-4} *M*) solution of the diol in 2-MTHF, which was placed in a spectroscopic low-temperature Suprasil cell; HCl gas was bubbled gently through the solution at −40° for 3 min and the intensely blue solution obtained was immediately cooled to −196° and a spectrum recorded.

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(70) H. E. Zimmerman and C. O. Bender, *J. Amer. Chem. Soc.*, **92**, 4366 (1970).