

π,π -Biradicaloid Hydrocarbons. The Pleiadene Family.

II. A Doubly Excited State of Pleiadene

Jaroslav Kolc, John W. Downing, Anthony P. Manzara, and Josef Michl*¹

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received April 11, 1975

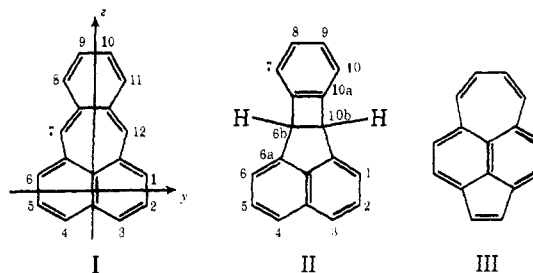
Abstract: Analysis of the electronic absorption spectra of pleiadene I, five methylpleiadenes, and two dimethylpleiadenes permits an assignment of 11 excited singlet states between 200 and 1000 nm. π -Electron calculations account satisfactorily for the results and show that the second lowest excited state is "doubly excited" (to a good approximation, the second transition involves promotion of both electrons from the highest occupied MO to the lowest unoccupied MO). Such states are of interest in correlation diagrams of the Woodward-Hoffmann type and are generally expected to lie at low energies in "biradicaloid" hydrocarbons. Pleiadene and the methylpleiadenes were prepared by photochemical ring opening of 6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (II) and its methyl derivatives in rigid glass at 77 K. The latter were synthesized by addition of benzyne and methylbenzynes to acenaphthylene and methylacenaphthylenes. Absolute polarization directions of the lowest five transitions in I were determined from photoinduced dichroism, observed when a rigid solution of II was irradiated simultaneously with two beams of plane polarized light chosen to obtain photoselection in both the singlet \rightarrow singlet and triplet \rightarrow triplet absorption steps of the two-photon transformation II \rightarrow I.

In the usual molecular orbital (MO) terminology, an electronic state is called doubly excited if it can be well described by a configuration interaction wave function in which one or several doubly excited configurations predominate. It is understood that the orbitals used for the construction of configurations are delocalized molecular orbitals, typically those obtained by diagonalization of a suitable one-electron Hamiltonian operator (Hückel orbitals, SCF orbitals, etc.) or those obtained by diagonalization of the first-order density matrix (natural orbitals).

Since the MO terminology is at present commonly used for the description of electronic states, and since, as a result, doubly excited configurations and states play a prominent role in theoretical discussions of thermal and photochemical reactions (derivation of Woodward-Hoffmann rules from correlation diagrams,² existence of "funnels" in excited state surfaces,³⁻⁵ electronic states of biradicaloid species,^{4,6} etc.), it is of interest to ask whether any such states can be observed. While experimental data can be used to establish the existence of a state and the associated transition energies, intensities, polarizations, and other characteristics, it cannot in itself prove that the state is doubly excited. This is due to the fact that the physical nature of doubly excited states is the same as that of any other excited state and, indeed, the distinction exists only if we use the MO language for description of electronic states. For instance, in the alternative valence-bond description, such a label would not be meaningful, and, instead, one will wish to classify states as covalent and zwitterionic, etc. Thus, there is no objective experimental characteristic which would in itself uniquely identify an observed transition as a transition into a doubly excited state.

To achieve such an assignment, it is necessary for an MO-CI calculation to account satisfactorily for the characteristics of a sufficient number of electronic transitions of the molecule, including those involving the presumably doubly excited state, and to result in a wave function for this particular state in which doubly excited configurations predominate. Since the calculation will be only approximate, it is also necessary to show that the assignment is independent of the approximations used. In particular, if a semiempirical calculation is used, it should be independent of the exact values of parameters. In general, the assignment can be only as reliable as the theoretical model used in the calculation, so that a future reassignment always remains a possibility.

For a long time, the best known experimentally observed molecular electronic state assigned as doubly excited was the E state of molecular hydrogen.⁷ As for organic compounds, it was suggested that a weak band in the spectrum of trifluoronitrosobenzene might correspond to a transition to a doubly excited state or a triplet state,⁸ but the former has so far not been confirmed by more detailed calculations.⁹ In 1972, the first two reasonably firm assignments of doubly excited states in organic molecules appeared.^{10,11} One was the lowest excited singlet state of 1,8-diphenyl-1,3,5,7-octatetraene observed by Hudson and Kohler¹⁰ and assigned by analogy to semiempirical calculations performed by Schulten and Karplus for 1,3,5,7-octatetraene.¹² Similar states had been predicted^{3,13} and more recently also observed in various other polyenes.¹⁴ The other observation reported in 1972 concerned the second lowest excited singlet state of pleiadene (I).¹¹ In the present paper, we



present detailed evidence for the assignment claimed in ref 11. In spite of a naturally skeptical attitude to such an unusual assignment, we feel that we can show convincingly both that the transition is authentic and that an MO-CI calculation of the usual semiempirical type which accounts for the characteristics of all observed transitions in the usual energy region leads to this assignment regardless of details of the parameter scheme used. Details of the low-temperature preparation of the highly reactive pleiadene under conditions of isolation in rigid glass, as well as proof of its structure, have appeared elsewhere.¹⁵ In the following we shall refer to substituted pleiadenes by labels such as 1-Me-I, where Me stands for methyl, and the numbering is that of formula I.

Experimental Section

Synthetic Procedures. Methyl derivatives of 6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (II), which we shall refer to by la-

bels such as 1-Me-II, specifying the position of the substituent by reference to formula II, were prepared by addition of benzyne to the olefinic bond of 3- or 5-methylacenaphthylene and addition of 3- or 4-methylbenzyne or 3,6-dimethylbenzyne to acenaphthylene. They were carefully purified, ultimately by gradient sublimation. Benzyne was prepared in situ from the corresponding anthranilic acids using a method based on the procedure described in ref 16. The anthranilic acids and acenaphthylene were commercial products. Acenaphthylene was vacuum sublimed prior to use.

A typical procedure for the preparation of a methyl derivative of II is described below. Analytical data on all products obtained are summarized in Table I.

Preparation of 8-Methyl-6b,10b-dihydrobenzo[*f*]cyclobut[*a*]acenaphthylene (8-Me-II). 5-Methylanthranilic acid (5 g) was partially dissolved in 40 ml of absolute ethanol, and concentrated hydrochloric acid (3.5 ml) was added. Another 20 ml of ethanol was added, the mixture was stirred and cooled to 5–10°, and isoamyl nitrite (6.2 ml) was added dropwise. Stirring with cooling below 10° was continued for 30 min and then ether (120 ml) was added. After stirring and cooling for another 30 min, the white solid was filtered off, washed with dry ether, and air-dried. The dry 4-methyl-2-carboxybenzenediazonium chloride (6.7 g) obtained was added to a solution of acenaphthylene (19 g) in ethylene chloride (250 ml). Propylene oxide (5 ml) was added and the mixture heated with stirring to reflux. After about 30 min, when the evolution of nitrogen had ceased, the mixture was evaporated to dryness, dissolved in a benzene-hexane mixture, filtered through a short column of silica gel, and evaporated to dryness. Excess acenaphthylene was sublimed off under reduced pressure; the dark solid residue was chromatographed on alumina, crystallized from methanol, and further purified by gradient sublimation under reduced pressure. A 200-mg sample of pure 8-Me-II was obtained (2.5% yield).

Preparation of 5-Methylacenaphthylene. 5-Bromoacenaphthene¹⁷ (17 g, containing about 15% acenaphthene) and nickel 1,2-bis(diphenylphosphino)ethane chloride¹⁸ (0.15 g) were dissolved in 1,2-dimethoxyethane (50 ml, distilled from CaH₂). This solution was added to a solution of Grignard reagent prepared from ethyl iodide (14 g) and magnesium (2.4 g) in dry ether (400 ml). The mixture was refluxed for 12 days under a capped condenser. GLC analysis showed that ca. 75% of the desired conversion had taken place. A further 0.10 g of the nickel complex was added and the mixture refluxed 2 more days; conversion was then ca. 95%. The ether solution was washed with water and evaporated; the residue was recrystallized four times from ethanol, giving 4.2 g (33%) of a solid material of mp 82–88°, which was shown by GLC analysis to be ca. 92% 5-methylacenaphthene and 8% acenaphthene.

This sample was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (6.0 g) under nitrogen in refluxing benzene (100 ml) for 4 h, at which time GLC analysis showed that nearly all of the 5-methylacenaphthene had been converted to 5-methylacenaphthylene, but that the acenaphthene was almost completely unchanged. This product was used directly for the synthesis of 3-Me-II by addition of benzyne.

Preparation of 3-Methylacenaphthylene. 1-Hydroxy-3-methylacenaphthene¹⁹ (2.65 g) was dissolved in dry pyridine (30 ml), and a solution of *p*-toluenesulfonyl chloride (2.9 g) in pyridine (30 ml) was added. The reaction mixture was kept at room temperature for 90 min, extracted first with water, then with ether. Ether extracts were evaporated and chromatographed on silica gel. The obtained yellow liquid was used directly for the preparation of 1-Me-II.

Photochemical Preparation and Spectroscopy of Pleiadenes at 77 K. Equipment, solvents, and techniques were those described in ref 15. An attempt to sharpen up spectral peaks by use of lower temperatures (20 K) yielded no improvement. A partially oriented sample of I in 3-methylpentane glass at 77 K was prepared by irradiation of a rigid solution of the cyclobutene precursor II with two collinear beams of linearly polarized light impinging on the sample from opposite directions. The first one was obtained from a 200-W high-pressure mercury arc equipped with a water filter and Balzers interference filter with maximum transmission at 302 nm (30% T) and less than 1% transmission below 270 nm and above 350 nm and was polarized by a calcite Glan prism. Absorption of light of this wavelength is photoselective and occurs preferentially by molecules oriented such that the short axis of the naphthalene chromophore is parallel, or nearly parallel, with the electric vector of the polarized light beam.²⁰ A portion of the photoselected molecules

Table I. Methyl 6b,10b-Dihydrobenzo[*f*]cyclobut[*a*]acenaphthylenes

	Elem anal ^a	NMR, ^d τ , ppm					
		Me		Mp, °C	M ⁺ ^b	Me singlet	Benzylic protons
		% C	% H				
1-Me-II	C ₁₅ H ₁₄	<i>c</i>	<i>c</i>	97	242	7.36	4.69
3-Me-II	C ₁₅ H ₁₄	94.10	5.96	134	242	7.29	4.41
7-Me-II	C ₁₅ H ₁₄	93.99	5.81	147	242	7.74	4.82
8-Me-II	C ₁₅ H ₁₄	94.11	5.80	103	242	7.78	4.82
7,10-Me ₂ -II	C ₂₀ H ₁₆	93.59	6.34	165	256	7.72	4.81

^a Calculated for C₁₅H₁₄: 94.18% C, 5.82% H; for C₂₀H₁₆: 93.71% C, 6.29% H. ^b Molecular ion, *m/e*. ^c Elemental composition verified by high-resolution mass spectroscopy (obsd molecular ion at 242.1092; calcd, 242.10955). ^d In CCl₄ with Me₄Si as internal standard.

crosses to the lowest triplet state. No ring opening to I occurs in either the singlet or the triplet states reached.¹⁵ The second light beam was obtained from a 1-kW high-pressure xenon arc equipped with a water filter, a Schott WG 345 cutoff filter ($\lambda > 320$ nm), and a Corning CS 7-59 filter (480 nm $> \lambda > 300$ nm), and was polarized by a second calcite Glan prism in a direction perpendicular to that of the polarization of the first beam. Light of these wavelengths is only absorbed by naphthalene chromophores which are in their lowest triplet state. Since this absorption is polarized predominantly along the long axis of the naphthalene moiety,²¹ additional photoselection occurs, reinforcing the first photoselective step. Absorption of the second photon is known to result in photochemical conversion to I.¹⁵ Although this involves some change in geometry and thus, probably, partial loss of orientation, at small overall conversions a quite well-oriented sample of I results, as determined by measurement of dichroic absorption on a Cary 17 spectrophotometer equipped with a Glan prism. The dichroic ratio is $E_{\parallel}/E_{\perp} \approx 1.9$ for transitions polarized along the short axis of the naphthalene chromophore, i.e., along the long axis of I (*z*), and $E_{\perp}/E_{\parallel} \approx 1.15$ for transitions polarized along the *y* axis of I.

Results

The absorption spectrum of pleiadene (I) in 3-methylpentane glass at 77 K is shown in Figure 1. Assignment of origins of individual electronic transitions is based on the tentative vibrational analysis shown in Figure 2, peak intensities, measured polarization directions (parallel to the long axis for transitions 2, 3, and 5, perpendicular to it for transitions 1 and 4), and analysis of the small spectral shifts due to methyl substitution in various positions (Figure 2). Polarization directions were determined from dichroism induced by partial photochemical conversion of II into I by two collinear beams of linearly polarized light of opposite polarization and wavelengths suitable for S \rightarrow S and T \rightarrow T excitation, respectively, as described in the Experimental Section. This method is easiest to use in the spectral region in which the precursor II itself does not absorb, and we have not attempted to measure the polarizations of transitions 6 and higher.

Particular attention was paid to establishing the authenticity of the very weak transition 2 near 20 000 cm⁻¹ (Figure 1). In order to show that this band is not due to traces of impurity and that it is not a part of the vibrational fine structure of one of the other transitions present, we need to consider the results obtained for the methyl derivatives of I. These were prepared by irradiation of methyl derivatives of II in a rigid glass of 3-methylpentane at 77 K as described previously for the parent I.¹⁵ Two of these (6b-Me-II, 6b,10b-Me₂-II) were available from other work;²² five others (1-Me, 3-Me, 7-Me, 8-Me, 7,10-Me₂-II) were prepared for the purpose of this study by addition of suitable benzyne to suitable acenaphthylenes. The absorption spectra of II and all of its methyl derivatives differed only by minor

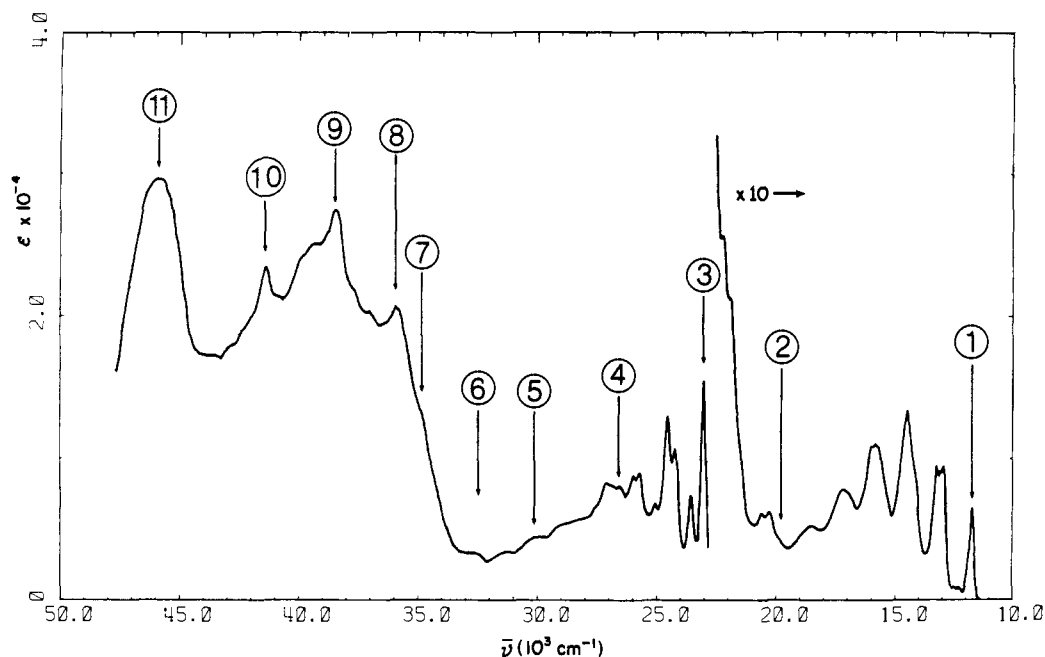


Figure 1. Absorption spectrum of pleiadene (I) in 3-methylpentane at 77 K. Assignment of band origins of individual electronic transitions is indicated (see text).

shifts, as did the spectra of I and all of its methyl derivatives, except that 7-Me-I and 7,12-Me₂-I had considerably broadened bands obscuring much of the vibrational fine structure of most bands and, unfortunately, all of the second band.

In all the other methyl derivatives of I, the weak band near 20 000 cm⁻¹ occurs with roughly the same intensity as in I itself and with similar fine structure, but is shifted to a varying degree with respect to its position in I. In view of the diverse synthetic origin of the various compounds in the series, it appears highly unlikely that the band could be due to impurities. The two starting materials used repeatedly, anthranilic acid and acenaphthylene, were obtained from several different sources but the same results were obtained. All of our spectral samples of compound II and its methyl derivatives appeared pure on thin-layer chromatographic plates and by gas-liquid chromatography. Mass spectrometry revealed no impurities of higher molecular weight. NMR and uv spectroscopic measurements also agreed with the structures assigned and showed no traces of impurities. Melting points were sharp. Use of incompletely purified synthetic samples instead of the final specimens resulted in no noticeable increase of the relative intensity of the peaks in question. All considered, we conclude that it is unlikely in the extreme that the band in question would be due to impurities in our samples of II's.

The next possibility to consider is that the samples of the II's were pure, but that the photochemical opening to the I's is not clean and gives a by-product, slightly different in each case, which is responsible for the second observed band. However, the intensity of this band was always found to be proportional to that of all the other bands of the spectrum, not only at various stages of the irradiation (conversion II → I), but also at various stages of the disappearance of the I's due to dimerization¹⁵ which occurs upon melting the glass and warming up to ca. -150°. Again, it appears extremely unlikely that a reactive side-product would in each case disappear at just the same rate as the highly reactive main product. Indeed, when short-wavelength irradiation instead of light filtered through Pyrex is used for the conversion of II to I, minute peaks of additional absorption appear in the spectrum, apparently due to a small amount

of a by-product, but upon melting they disappear at a rate much faster than the main product.¹⁵

Finally, one could argue that the band in question is a genuine band of the I's, but that it is simply a part of the vibrational fine structure of one of the neighboring bands. This appears unlikely since the vibrational structure of the first three bands is readily analyzed in terms of a few vibrational frequencies (Figure 2), and the peaks of the second band fit the vibrational analysis of neither the first nor the third band. The possibility is definitely excluded by consideration of the presently reported substituent shifts of the first three transitions (Figure 2 and Table II). Although small, the shifts are significant and show clearly that the long-wavelength region contains three independent electronic transitions. At the same time, of course, the results also help to identify electronic transitions in other spectral regions. This device for determining the number of independent transitions is well known.²³

In conclusion, there is compelling evidence that the weak band near 20 000 cm⁻¹ in the spectrum of I is an independent electronic transition inherent to the molecule. This is also true of the other transitions indicated in Figures 1 and 2, with possible exception of transition 6 (see below). We shall now briefly discuss the assignment of these transitions. Owing to the low resolution available, it should be kept in mind that the analysis of the vibrational fine structure is most likely oversimplified, particularly for higher energy transitions.

Our results for 7-Me-I and 7,12-Me₂-I, which have only poorly developed fine structure, are not shown in Figure 2. The limited amount of information they do provide is fully compatible with the assignments given below.

Transition 1. This relatively weak transition ($\epsilon \approx 1000$) at the edge of the infrared region (0-0 band at 11 710 cm⁻¹ in I) is uniformly polarized perpendicular to the long axis of the molecule (electronic symmetry of the excited state is B₂ and all active vibrations are of a₁ symmetry). Its shape is Franck-Condon forbidden. The fine structure is the same for all methyl derivatives (Figure 2) and consists of progressions in a ca. 1200 cm⁻¹ vibration built on the 0-0 band and also on each of up to four members of a progression in a ca. 1550 cm⁻¹ vibration. Some additional vibrations of

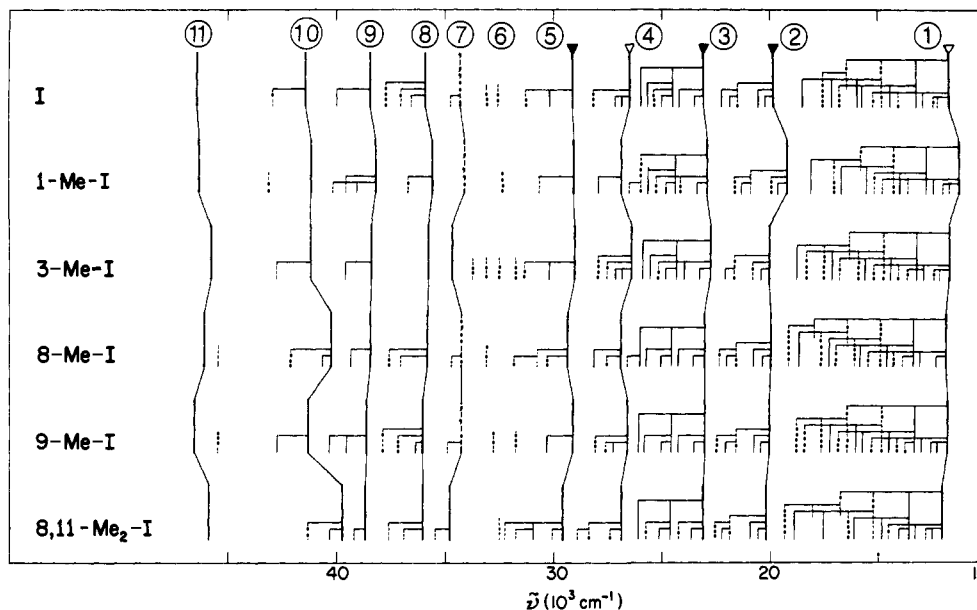


Figure 2. Positions of peaks (full lines) and shoulders (dashed lines) in the absorption spectrum of I and Me-I's, tentative vibrational analysis, and assignment of electronic transitions. Black (white) triangles indicate transitions polarized along the z (y) axis in formula I.

frequencies ca. 450 and 700 cm^{-1} can also be discerned.

Transition 2. The second absorption band is uniformly polarized along the long axis of the molecule. Its longest wavelength clearly observable feature is a weak shoulder (19 840 cm^{-1} in I), located on top of a tail of transition 1. After correction for this overlap, the molar extinction coefficient of the shoulder is only about 100. The band shape indicates strong Franck-Condon forbiddenness and/or vibronic intensity borrowing from the much stronger third transition. The fine structure of the band is the same for all compounds studied and contains, in addition to the weak origin, quanta of 380 ± 20 - and 730 ± 60 - cm^{-1} vibrations. Each of the three also occurs combined with one quantum of a 1660 ± 40 - cm^{-1} vibration. All of these vibrations are totally symmetric. If the weak first shoulder is the band origin, the symmetry of the electronic wave function of the excited state is A_1 . It is also conceivable, however, that the band origin is even weaker and is buried in the tail of the first absorption band, and that all of the observed intensity originates in vibronic borrowing from transition 3.

Transition 3. This long-axis polarized transition with origin at 23 030 cm^{-1} in I is much more intense than the first two ($\epsilon \approx 10\,000$; electronic symmetry of the excited state is A_1). It is Franck-Condon allowed, and its fine structure is easily analyzed in terms of one or two quanta of totally symmetric vibrations of frequencies 1450 ± 50 , 1200 ± 50 , and 500 ± 50 cm^{-1} in various combinations. The absorption due to this transition, located at the edge of the visible region, imparts to I its characteristic yellowish color in dilute solutions. In concentrated solutions absorption due to transition 1 becomes significant, and the combination causes the typical yellowish green hue observed.

Transition 4. This short-axis polarized transition (B_2 excited state) is not readily apparent in the absorption curve (Figure 1) where it blends with the long-axis polarized transition 3, but the sudden change in the dichroism exhibited by a partially oriented sample clearly reveals its presence. We assign the origin at 26 530 cm^{-1} . The intensity is much higher than that of transitions 1 and 2, but does not reach that of transition 3. Because of extensive overlap with the latter, even approximate vibrational analysis is hard to perform. Frequencies needed to account for the observed peaks

are similar to those found in the fine structure of transitions 1-3 (Figure 2).

Transition 5. The dichroic spectra reveal that the medium intense indistinct peaks between 29 000 and 32 000 cm^{-1} ($\epsilon \approx 4000$) are long-axis polarized and suggest that the origin of the long-axis polarized fifth transition (A_1 excited state) lies at 29 150 cm^{-1} . Fine structure can be accounted for when several vibrations of reasonable frequencies are postulated (Figure 2).

Transition 6. The indistinct peaks in the region of lower intensity between the first five transitions and the onset of the much more intense transitions 7 and higher have shape and location which makes it hard to assign them as fine structure of any of the above transitions, particularly when behavior upon substitution is considered and make it likely though not certain that at least one separate electronic transition is present near 33 000 cm^{-1} . This is assigned tentatively as the sixth transition.

Transition 7. The region of intense absorption which sets in near 34 000 cm^{-1} begins with shoulders, which appear as peaks only in 3-Me-I and 8,11-Me₂-I. Substituent shifts (Figure 2) indicate that these belong to a separate electronic transition of medium intensity. In I, the first of these shoulders is located at 34 300 cm^{-1} .

Transitions 8, 9, and 10. We believe that this is the minimum number of transitions which must be postulated in order to account for the shape of the spectra in the region of strong absorption between 35 000 and 43 000 cm^{-1} ($\epsilon \approx 20\,000$) and for the substituent shifts (Figures 1 and 2). In I itself, the origins are assigned as (8) 35 910, (9) 38 460, and (10) 41 410 cm^{-1} . Obviously, more than three transitions may be present.

Transition 11. The strongest band in the spectrum ($\epsilon \approx 30\,000$) always appears quite isolated and very distinct and undoubtedly originates in a separate electronic transition. In I, it lies at 46 400 cm^{-1} . The shoulder which appears on its long-wavelength side in some of the spectra indicates that the band may be due to more than one transition.

Discussion

Electronic States. As discussed in detail in the preceding

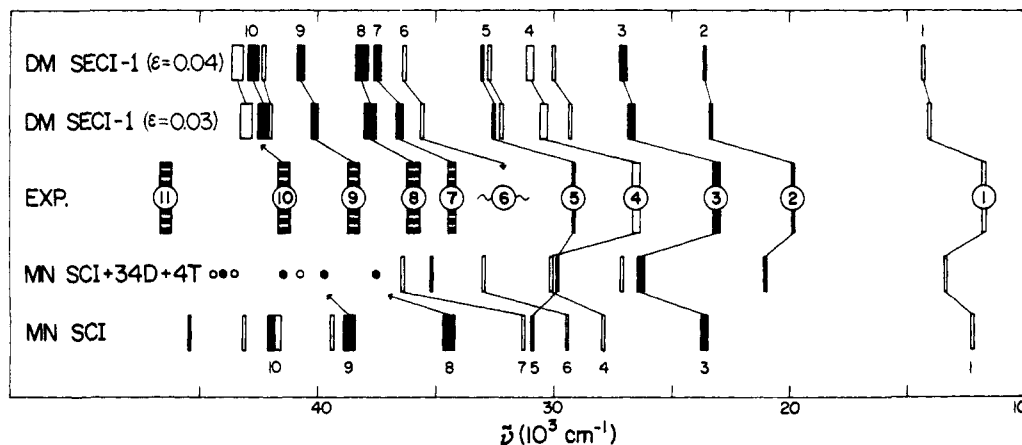


Figure 3. Electronic transition energies in I: black (white) lines, z (y) polarized transitions; striped lines, polarization unknown. For assignments see text. EXP.: observed for 0-0 transitions (77 K, 3-methylpentane). Thin, medium, and thick lines indicate weak, medium, and intense transitions, respectively. MN, DM: calculated (for details see text). Thin, medium, and thick lines indicate transitions with oscillator strengths calculated from dipole velocity formula as less than 0.1, between 0.1 and 0.3, and more than 0.3, respectively.

section, our experimental data provide strong evidence that the region of relatively weaker absorption below $34\,000\text{ cm}^{-1}$ contains at least five and, most likely, six or more electronic transitions, as well as reasonable evidence that the following region of strong absorption between $34\,000$ and $47\,000\text{ cm}^{-1}$ contains at least five additional transitions. Most important, we feel that the existence of a separate weak electronic transition near $20\,000\text{ cm}^{-1}$, labeled 2 in Figures 1 and 2, has been established beyond reasonable doubt.

It now remains to be shown that the observed transition energies, intensities, and polarizations are reasonably well accounted for by a CI-MO calculation, and that this calculation predicts a doubly excited nature for the second excited singlet state regardless of the details of the approximations made. In view of the molecular size of I, a rigorous approach is out of the question, and doubts therefore cannot be settled definitively. We use the semiempirical π -electron SCF-CI model due to Pariser, Parr, and Pople (PPP),²⁴ with the following justification.

First, molecular models indicate that pleiadene is planar. A molecule of related structure, acepleiadylene III, has been shown to be planar by x-ray diffraction.²⁵ Also, the rich spectral detail in the lowest few transitions in I is quite compatible with the postulate of planarity. Second, the transition in question is of such low energy that no assignment other than $\pi\pi^*$ seems reasonable. Third, the PPP model has been tested during the last 20 years on a bewildering variety of $\pi\pi^*$ transitions in conjugated molecules and seems to work very well, particularly for hydrocarbons. Fourth, the predicted energies and intensities of electronic transitions in a group of molecules structurally related to I have been shown to agree quite well with experiment.¹⁵

Although the PPP model limits attention to π electrons, and thus simplifies the problem considerably, it is usually not feasible to find exact solutions (full CI). The standard procedure is to limit configuration interaction to all singly excited configurations (SCI) or to an even smaller subset. By now, the "best" values for resonance integrals $\beta_{\mu\nu}$, one-center electron repulsion integrals $\gamma_{\mu\mu}$, and two-center electron repulsion integrals $\gamma_{\mu\nu}$ optimized for this limited extent of CI have been reasonably well established for hydrocarbons. Using $\beta_{\mu\nu} = -2.318\text{ eV}$ and assuming all bonds to be 1.40 \AA long, using $\gamma_{\mu\mu} = 10.84\text{ eV}$, and using the Mataga-Nishimoto²⁶ formula for $\gamma_{\mu\nu}$, all as in ref 27, leads to results shown in the bottom line of Figure 3 (MN SCI). Comparison with the center line which summarizes experimental re-

sults (EXP., energies correspond to band origins) permits an assignment of the individual electronic transitions as shown below the bottom line. Agreement of excitation energies, polarizations, and relative intensities is quite good, particularly considering that the calculated energies correspond to vertical rather than 0-0 transitions. The order of transitions 5 and 6 is interchanged, but this is not particularly disturbing considering the very limited experimental information available for transition 6. Two calculated transitions must be assigned to the observed transition 10, but once again, this is quite compatible with the experimental evidence. Minor variations of parameters have no profound effect. So far, the agreement appears to be at least as satisfactory as that obtained with the same method for other nonalternant hydrocarbons of this size which have been analyzed in some detail.²⁸

However, there is one fundamental flaw: the existence of the weak transition 2 is not predicted at all, and there is no reasonable way of reassigning the transitions such that transition 2 would be accounted for. This was the initial clue that led us to the present detailed investigation: if the transition is of $\pi\pi^*$ nature and is not accounted for by the SCI calculation, then either a case of significant failure of the PPP model has been found, and this would be quite interesting, or the transition is into a multiply excited $\pi,\pi \rightarrow \pi^*,\pi^*$ state. When our detailed investigation was started, this was without precedent in any organic molecule.

Actually, existence of a low-lying doubly excited state in a molecule such as I is in good agreement with physical intuition, and such states can also be expected in other "biradicaloid"¹⁵ molecules [those with small separation between the highest occupied molecular orbital (1) and the lowest free molecular orbital (-1)]. Here, and in what follows, we number bonding MO's with positive integers in the order of decreasing energy and antibonding MO's with negative integers in the order of increasing energy. The SCI calculation describes transition 1 as due predominantly to electron promotion from the molecular orbital 1 to the molecular orbital -1. The energy difference of orbitals 1 and -1 is small,¹⁵ leading to a calculated and observed excitation energy of only about 1.5 eV. Thus, very roughly, the double promotion $1,1 \rightarrow -1,-1$ should cost only about 3 eV and should introduce a new excited state of A_1 symmetry just in the region of transition 2. Its exact location might be affected by configuration interaction, but at any rate, an additional state should be present at relatively low energies. If the effect of CI were small, one could expect the additional

long-axis polarized transition to have low intensity for ordinary one-photon absorption from the ground state (zero if CI and vibronic coupling are neglected). It could be only expected to appear clearly in the ordinary absorption spectrum if it were not overlapped by strong transitions into singly excited states. In I, there is a large gap between transition 1 and the next strong transition 3. It seems intuitively reasonable that the long-axis polarized transition due to the $1,1 \rightarrow -1,-1$ excitation might be found in this gap.

Next, we have performed a series of PPP calculations which were basically SCI in nature but into which some doubly or even triply excited configurations were added as an afterthought. Indeed, as long as the doubly excited configuration $1,1 \rightarrow -1,-1$ was included in the CI procedure, the results not only accounted for the transitions already present in the SCI results, but also predicted the existence of a long-axis polarized weak transition 2 between transitions 1 and 3. The calculated weight of the $1,1 \rightarrow -1,-1$ doubly excited configuration in the wave function of the second excited singlet state depended on the details of the calculation. It ranged between 30 and 70% and was usually near 60%.

In about a dozen additional calculations, the SCI basis set was augmented more systematically by all doubly excited configurations which can be formed by exciting from orbitals 1, 2, and 3 into orbitals -1 , -2 , and -3 (except for seven which were found unimportant in a separate more extensive calculation) and by all four triply excited configurations which can be formed from the $1,1 \rightarrow -1,-1$ doubly excited configuration by a single promotion of an electron from orbital 2 or 3 into orbital -2 or -3 . Using this fixed CI basis, the value of $\beta_{\mu\nu}$ was varied between -2.2 and -2.8 eV, that of $\gamma_{\mu\mu}$ between 9.5 and 10.84 eV, $\gamma_{\mu\nu}$ was obtained from the Mataga-Nishimoto²⁶ or Dewar-Ohno-Klopman²⁹ formulas, and geometry was regular with 1.40-Å bond lengths or more realistic, taken from experimental values for naphthalene for the naphthalene moiety in I and alternating single and double bonds elsewhere as in formula I. In the calculations with unequal bond lengths, $\beta_{\mu\nu}$ was constant or was made a function of bond length in one of the usual ways.³⁰ Both Hückel MO's and SCF MO's were used as the starting point for CI.

In all of those runs which gave results anywhere near the experimental values of excitation energies, a low-lying doubly excited state was predicted and corresponded to transition 2. Results for one of the dozen runs are shown in Figure 3 (second line from the bottom, MN SCI + 34D + 4T). It used the ordinary SCI parameters, the same as the bottom line, and shows clearly the effect of introduction of 34 doubly and 4 triply excited configurations: since the Mataga-Nishimoto electron-repulsion integrals are being used, with their steep dependence on distance, the depression of the ground-state energy from its SCF value is very large, and all excitation energies are too high (see ref 13a for a discussion of the effects of the choice of electron-repulsion integrals). If the ground-state energy is assumed to be that of the SCF ground-state determinant, they are all too low. Nevertheless, for the lower energy transitions, it is possible to trace the calculated states to the SCI states shown below in Figure 3, and also to assign them to experimentally observed transitions. Note that the weak long-axis polarized transition 2 now appears where it should be (the weight of the $1,1 \rightarrow -1,-1$ configuration in it is 62%).

In another calculation we have used the SECI-2 method of ref 31 to select configurations, but essentially the same results were obtained. We conclude that it is possible to account for transition 2 within the PPP model, but only if the $1,1 \rightarrow -1,-1$ doubly excited configuration is included in

the CI basis set, and that the second excited singlet state has partially or predominantly doubly excited nature.

It seems clear that systematic introduction of doubly excited configurations into the PPP model requires a reoptimization of parameters, in particular, a less steep dependence of the two-center electron-repulsion integrals on the distance of the centers than that provided by the Mataga-Nishimoto formula. We have recently proposed rapid methods for systematic and well-defined selection of doubly excited configurations (SECI-1, SECI-2)³¹ which permit simulation of the results of full CI with a limited size of CI matrix. They are based on inspection of the size of diagonal and off-diagonal matrix elements of the Hamiltonian (SECI-1) or of both the Hamiltonian and the dipole velocity operators (SECI-2, suitable in particular for calculation of polarization directions). The matrix elements are compared with predetermined cutoff parameters, and if they are too small, the multiply excited configuration is discarded; otherwise, it is kept. More recently, a suitable parameter set has been found which gives reasonable agreement with experiment once a sufficient number of configurations have been selected by the SECI-1 procedure by use of a sufficiently small value for the cutoff point.³² The parameters were adapted from those proposed by Karwowski.³³ As could be expected, the key to successful parameter choice lies in a suitable choice of a formula for $\gamma_{\mu\nu}$'s as a function of distance of centers μ and ν . Whether a sufficiently small cutoff value (ϵ in ref 31) has been reached and the "convergence limit" attained beyond which no further significant change in the results occurs as ϵ is lowered further is indicated explicitly by lack of further change upon further increase in the extent of CI and also by the convergence of dipole length and dipole velocity values for oscillator strengths toward each other. The extent of CI required to reach this limit increases with the size of the molecule, and with our present limitation to 175×175 CI matrices, we can reach it for 14 π -electron systems but not for larger ones. We believe that the limit corresponds closely to the results of a calculation which would include all singly and all doubly excited configurations. It has been checked on a series of smaller molecules that the effect of more highly excited configurations on the order and energies of low-lying excited states is negligible, although this is not always the case for polarization directions. Therefore, for the latter, the SECI-2 procedure is preferable.³¹ The parameter values recommended³² for SECI-1 calculations are $\gamma_{\mu\nu} = [1 - 0.18 \exp(-3.2r_{\mu\nu})]/(0.09225 + 0.06945r_{\mu\nu})$ (eV), $\beta_{\mu\nu} = -2.6 \exp[-0.335(p_{\mu\nu} - \frac{2}{3})]$ (eV). Bond lengths are obtained iteratively from SCF bond orders using the relation $r_{\mu\nu} = 1.517 - 0.177p_{\mu\nu}$. To compensate for the absence of triply and more highly excited configurations in the calculation, the SCF energy is taken for the ground-state energy.

Although one cannot reach the "convergence limit" for an 18 π -electron molecule such as I without going to CI much larger than 175×175 , it appears worthwhile to perform "unconverged" calculations for I using this method anyway, since for nonalternant hydrocarbons the convergence process is quite smooth and only rarely involves state crossings.³² This is not the case for alternant hydrocarbons, in which the energy of the covalent "minus" states decreases more rapidly than that of the zwitterionic "plus" states, so that numerous state crossings result.³⁴

Two such calculations, using cutoff parameters³¹ $\epsilon = 0.04$ (84 configurations in all) and $\epsilon = 0.03$ (119 configurations), are shown on top of Figure 3 (DM SECI-1). Except for the overall shift to higher energies, attributable to the lack of convergence, the results are in quite good agreement with experiment, and assignments are straightforward as

Table II. Methyl Substituent Shifts (cm^{-1}) for Transitions 1-3 in Pleiadene^a

	Transition			
	1		2	3
	$q^* - q^b$	$\Delta\tilde{\nu}(\text{exptl})$	$\Delta\tilde{\nu}(\text{exptl})$	$\Delta\tilde{\nu}(\text{exptl})$
1-Me-I	-0.091	-460	-570	-90
3-Me-I	-0.100	+30	+240	-250
8-Me-I	0.047	+170	+160	+10
9-Me-I	0.025	+110	+240	+10
8,11-Me ₂ -I	0.094	+360	+360	+90

^a With respect to 0-0 band energies in I: 11 710, 19 840, and 23 030 cm^{-1} . ^b Change in π -electron density on $1 \rightarrow -1$ excitation obtained from SCF molecular orbitals.

indicated on top in Figure 3. In these calculations, the $1,1 \rightarrow -1,-1$ doubly excited character is distributed about equally between transitions 2 and 3. As a result, transition 2 is calculated to be too strong (oscillator strength $f = 0.1$, compared with $f = 0.04$ for transition 1). The very weak experimental intensity of transition 2 indicates that the doubly excited nature is concentrated in it rather than shared equally with transition 3, and in this respect the "ad hoc" SCI + 34D + 4T calculation on the second line from the bottom in Figure 3 is better ($f = 0.003$). It is possible that this deficiency is due to our failure to reach the SECI-1 convergence limit for I. Nevertheless, the calculation unambiguously predicts the presence of an additional excited state in the low-energy region, due to a low-lying doubly excited configuration.

The weak short-axis polarized transition calculated to lie between transitions 3 and 4 also corresponds to a double excitation ($1,1 \rightarrow -1,-2$), $f = 0.006$. For 3 $f = 0.3$ and for 4 $f = 0.14$ are calculated, so that it is hardly surprising that the additional weak transition has not been observed. Both of the transitions whose energies correspond to that of observed transition 5 are quite weak ($f = 0.01$, $f = 0.0003$). Since the observed intensity and polarization might be due to vibronic interactions, it is hard to say which one is to be assigned as the observed transition 5. The agreement is reasonably good even at higher energies. Again, it appears that observed transition 10 corresponds to a superposition of two electronic transitions.

It is worth noting that the extensive inclusion of doubly excited configurations has little effect other than introducing transition 2. The relative energies and intensities of the other transitions change only little and so does the nature of their wave functions. Thus, in the SCI as well as SECI-1 calculation, transition 1 corresponds approximately to the one-electron jump $1 \rightarrow -1$, transition 3 to the jump $1 \rightarrow -2$, transition 4 to the jump $1 \rightarrow -3$, etc. The correlation of these three transitions with the first three transitions of other molecules of the pleiadene series,^{28a} based on comparison of shapes of molecular orbitals and of the one-electron jumps involved, remains valid even in the SECI-1 picture.

Substituent Shifts. If the perturbation caused by methyl substitution were small enough, and if transition 1 and transition 2 corresponded to pure $1 \rightarrow -1$ and $1,1 \rightarrow -1,-1$ excitations, respectively, the substituent shifts exhibited by the second band should be in the same direction and just twice those shown by the first band. It is encouraging to note that the effect of two equivalent methyls is approximately equal to twice the effect of one of them (compare 8-Me-I with 8,11-Me₂-I in Table II), so that use of first-order perturbation theory appears appropriate. On the other hand, according to the calculations, the weight of the $1,1 \rightarrow -1,-1$ configuration in the second excited state is only about 60-70% and possibly even less. Inspection of Table II

shows that the shifts of the first and second transitions are always in the same direction, the shift being larger for transition 2, but usually not by a factor of 2. Substitution in positions 8 and 11 is exceptional in that it leads to equal shifts for both transitions.

It is well known that shifts upon methyl substitution can generally be expected to be larger in nonalternant hydrocarbons than in alternant ones. The π -electron density distribution is often quite non-uniform in the former and liable to change upon excitation. To the first approximation, consideration of the electron-donating inductive effect of the methyl group gives $\Delta E = \Delta\alpha_C(q^* - q)$, where ΔE is the substituent shift, $\Delta\alpha_C$ is the change in the Coulomb integral of a carbon atom due to the methyl substituent it carries, and q^* and q are π -electron densities on that carbon in the excited and ground states, respectively. The methyl shifts of the first band of azulene were rationalized on this basis a long time ago using π -electron densities obtained from Hückel MO's.³⁵ Application of this approximation to the first transition of pleiadene gives disappointing results. Primarily because of the larger size of the molecule, the predicted changes in π -electron density in any one position are relatively small by comparison with azulene, and, as a result, the predicted shifts are small. Although a certain degree of agreement is obtained, at least for the direction of most of the shifts of transition 1, the effects are apparently too small to be reproduced adequately by this first-order method (Table II).

Conclusions

To summarize, we feel that we can account reasonably well for the electronic spectrum of I, that we have shown beyond reasonable doubt that the weak second transition in the absorption spectrum is authentic, and that the corresponding excited state is doubly excited in the usual MO-CI description.

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Ionization Potentials, Electron Affinities, and Reactivities of Cyanoalkenes and Related Electron-Deficient Alkenes. A Frontier Molecular Orbital Treatment of Cyanoalkene Reactivities in Cycloaddition, Electrophilic, Nucleophilic, and Radical Reactions

K. N. Houk* and Linda L. Munchausen

Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803. Received June 17, 1975

Abstract: The He(I) photoelectron spectra of nine cyanoalkenes (acrylonitrile, α -methylacrylonitrile, crotononitrile, vinylidene cyanide, tetracyanoethylene, 1,2-bis(trifluoromethyl)fumaronitrile, methyl α -cyanoacrylate, α -acetoxyacrylonitrile, α -chloroacrylonitrile) and two models (vinyl acetate and isopropenyl acetate) are reported. The experimental ionization potentials of these compounds and of fumaronitrile and maleonitrile have been used to estimate electron affinities of all the cyanoalkenes. The electron affinities calculated in this way correlate with other theoretical and experimental electron affinity estimates. The nature of the cyano substituent effect on π orbital energies is discussed, and correlations between frontier orbital stabilization energies and rates of Diels-Alder reactions (measured by Sauer et al.) are demonstrated. Whereas these reactions involve the partial formation of two bonds in the transition state, attack on cyanoalkenes by simple nucleophiles will involve formation of only one bond in the transition state. The calculated relative reactivities of cyanoalkenes toward "two-bond" nucleophiles is markedly different from the calculated relative reactivities with "one-bond" nucleophiles. The "one-bond" reactivities are in agreement with the available qualitative data on reactions of cyanoalkenes with nucleophiles such as amines and water. "One-bond" and "two-bond" nucleophilicities of cyanoalkenes are approximately the same. These reactivity indexes are also of use in the prediction of rates of radical addition to, and excited state quenching by, cyanoalkenes.

Introduction

Substituent effects on chemical reactivity are valuable probes of reactivity. Quantification of substituent effects in organic reactions has been achieved with varying degrees of success through use of Hammett- or Taft-type relationships, where rates or equilibria of standard reactions are used to define the magnitude and mechanism of electron withdrawal or release by substituents. Photoelectron spectroscopy provides a physical means to evaluate substituent effects, where the reference process is ionization of the neutral molecule. A comparison of the vertical ionization potentials (IP) of an unsubstituted molecule with a substituted molecule gives a direct measure of the influence of the substituent on the relative energies of the ground state and the radical cation in the ground state geometry. In the context of a charge-transfer (CT) or configuration interaction (CI) model of reactivity,¹⁻³ the IP's and electron affinities (EA) of molecules are partial indexes to the reactivity of a molecule with electrophiles, or with nucleophiles, respec-

tively. Thus, changes in IP's (EA's) of molecules induced by substituents are not only valuable measures of substituent effects, but will have a direct relationship to the reactivity of a molecule.

Frontier molecular orbital treatments of reactivity,^{1,2} in which the energies and shapes of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of a molecule dictate the reactivity of that molecule toward electrophiles or nucleophiles, respectively, provide a useful, if not rigorous, language in which to discuss chemical reactivity. Frontier molecular orbital treatments are a first approximation to a complete perturbation treatment of chemical reactivity.^{1,2,4-6} By application of Koopmans' theorem,⁷ where the negatives of the SCF orbital energies of a molecule are equated to the IP's of the molecule, the frontier molecular orbital method becomes equivalent to the CT or CI models of reactivity.² Furthermore, the use of orbital language is so convenient that it outweighs the opprobrium heaped by referees on those who pretend that orbitals, rather than states, have any reality.