(14) R. P. Lattimer, R. L. Kuczkowski, and C. W. Gillies, *J. Am. Chem. Soc.*, **96**, 348 (1974).
(15) R. C. Murray and A. Suzui, *J. Am. Chem. Soc.*, **93**, 4963 (1971).
(16) R. W. Murray and A. Suzui, *J. Am. Chem. Soc.*, **95**, 3343 (1973).
(17) D. P. Higley and R. W. Murray, *J. Am. Chem. Soc.*, **96**, 3330 (1974).
(18) O. Lorenz and C. R. Parks, *J. Org. Chem.*, **30**, 1976 (1965).
(19) O. Lorenz, *Anal. Chem.*, **37**, 101 (1965).
(20) J. Carles and S. Fliszar, *Can. J. Chem.*, **47**, 1113 (1969).
(21) W. R. Wadt and W. A. Goddard, III, *J. Am. Chem. Soc.*, **97**, 3004 (1975). According to this proposal the dipolar or zwitterionic state is not only unnecessary for the ozonide-forming reaction, but it is too energetic to be populated. The possibility that trioxolanes can open to give oxyperoxy diradicals was suggested earlier; S. W. Benson, *Adv. Chem. Ser.*, **No. 77**, 74 (1968).
(22) L. Salem, *J. Am. Chem. Soc.*, **96**, 3486 (1974).
(23) Subsequent to our earlier[15,16] suggestion for the mechanism of the diazo oxidation reaction, we undertook a general reevaluation of the role of diradicals in the ozonolysis reaction. This reevaluation and a consideration of the ideas of neighboring states and surface crossings expounded by Salem[22] led us to conclude that the diradical state could be involved in the decomposition of primary ozonides to give carbonyl oxides. At our request Salem applied his treatment to the ozonolysis reaction and concluded[24] that the diradical is the state of the carbonyl oxide which is initially formed from decomposition of the primary ozonide (trioxolane) and that the zwitterionic state cannot be reached without passing through the diradical state.
(24) L. Salem and P. Hiberty private communication (1974).
(25) Based on these theoretical considerations further experiments are suggested to test the involvement of the diradical state and these are in progress. It is interesting that Hamilton and Giacin preferred[26] the diradical form in interpreting their results on the oxidations of hydrocarbon solvents by a carbonyl oxide produced by photooxidizing diphenyldiazomethane.
(26) G. A. Hamilton and J. R. Giacin, *J. Am. Chem. Soc.*, **88**, 1584 (1966).
(27) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Am. Chem. Soc.*, **90**, 975 (1968).
(28) The difference between the observed labeling in this fragment and that expected (44.7%) for 100% ether bridge incorporation could be due to loss of label in the aldehyde due to the presence of small amounts of water. In the case of unsymmetrical ozonides it is not possible to accurately determine the percent label in the unobserved parent ion by analyzing the labeling in other significant ions as was done by Fliszar et. al.[4] in the case of stilbene ozonide.
(29) Fliszar and co-workers had suggested earlier[30] that the carbonyl oxide–aldehyde mechanism could operate with some exchange of oxygen atoms.
(30) S. Fliszár and J. Carles, *Can. J. Chem.*, **47**, 3921 (1969).
(31) Since this work was undertaken we have obtained the unlabeled ozonide in somewhat higher (3.5%) yield by photosensitized oxidation and in 18% yield by reaction of the diazo compound with a phosphite ozonide.[17]
(32) The method chosen for making these corrections, while not obviously more valid than several alternative approaches, gives the highest calculated percentage of ^{18}O in the M — O$_2$ fragment.
(33) G. Klopman and C. M. Joiner, *J. Am. Chem. Soc.*, **97**, 5287 (1975).
(34) R. Criegee in "Peroxide Reaction Mechanisms", J. O. Edwards, Ed., Interscience, New York, N.Y., 1962, p 29.
(35) R. W. Murray, R. D. Youssefyeh, G. J. Williams, and P. R. Story, *Tetrahedron*, **24**, 4347 (1968).
(36) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *J. Am. Chem. Soc.*, **90**, 1822 (1968); P. S. Bailey, A. Rustaiyan, and T. M. Ferrell, *J. Am. Chem. Soc.*, **98**, 638 (1976).
(37) R. A. Rouse, *J. Am. Chem. Soc.*, **95**, 3460 (1973).
(38) R. W. Murray and G. J. Williams, *J. Org. Chem.*, **34**, 1891 (1969).
(39) A. Robertson and D. G. Jones, British Patent 694 310 (1953); *Chem. Abstr.*, **49**, 11700e (1954).
(40) Labeling in slight excess of theory probably resulted from loss of a small amount of aldehyde following the first exchange, owing to its solubility in the aqueous phase.
(41) T. H. Fife and L. K. Jao, *J. Org. Chem.*, **30**, 1492 (1965).
(42) Under similar conditions the hydrolysis of benzaldehyde diethyl acetal to benzaldehyde and ethyl alcohol, using 1 equiv of unenriched H$_2$O, was shown by NMR spectroscopy to proceed to 80–85% of completion.
(43) H. Reimlinger, *Chem. Ber.*, **97**, 3493 (1964).
(44) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).
(45) G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Schechter, *J. Am. Chem. Soc.*, **87**, 935 (1965).
(46) Details of individual experiments are given in the tables.
(47) The procedure described here is obviously not ideal. A polymer-bound sensitizer[48] might be advantageously employed in this case, the gradual addition of the diazo compound during photolysis would probably minimize its direct reaction with isobutyraldehyde.
(48) A. P. Schaap, A. L. Thayer, E. C. Blossey, and D. C. Neckers, *J. Am. Chem. Soc.*, **97**, 3741 (1975).

Electronic States of Acenaphthylene. Linear Dichroism in Stretched Polyethylene and Magnetic Circular Dichroism

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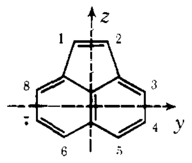
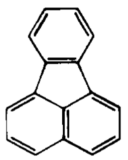
Abstract: Low-temperature absorption, linear dichroic, and magnetic circular dichroic spectroscopy of acenaphthylene (I) and five of its simple derivatives are used to confirm previous assignments of five electronic states, detect a new one, and determine the directions of magnetic dipole transition moments between excited states. Energies, intensities, polarizations, and signs of B terms are in good agreement with results of π-electron calculations. Systematic introduction of doubly excited configurations has little effect on the results for excited states assigned to the first five observed transitions. It suggests, however, that the newly observed excited state is predominantly doubly excited. The energy of the lowest triplet state of I was measured by the oxygen perturbation technique. Measurement of polarized absorption in stretched polyethylene ("stretched sheet method") yields the correct absolute polarizations even for a nearly circular molecule such as I. The expected reversal of preferred orientation on going to the 1,2-dibromo derivative is observed. The results clearly demand a two-parameter description of the orientation distribution and provide a good example for the inadequacy of one-parameter evaluation methods which are still occasionally used. A detailed discussion of the problem is given.



I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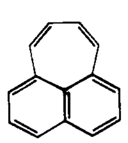
III

Acenaphthylene (I) is one of the most easily available nonalternant hydrocarbons, and the nature of its excited electronic states has been a subject of spectroscopic[1-7] and photochemical[8] as well as theoretical[1,4,9-17] interest. Also, I can be considered as a parent compound for a large number of more complex nonalternant hydrocarbons such as fluoranthene (II), benzofluoranthenes, etc., and a good understanding of its electronic states is useful for derivation of correlations between excited states within this group of compounds.

Previous measurements of the solution absorption spectrum,[1] substituent effect,[2] linear dichroism in stretched polyethylene,[3] polarized fluorescence,[4] vapor phase absorption,[5] polarized absorption in pure and mixed crystals,[5,6] and solution electrochromism[7] have established the location of five separate electronic transitions in the near uv spectrum of I and their absolute polarizations. These results are in good agreement with published π-electron calculations.[4,9-17]

In the present paper, we report in detail the previously only briefly mentioned[3,4] results of stretched sheet measurements on I, whose orientation axis is y in formula I, and analogous results for its 1,2-dibromo derivative (1,2-Br_2-I), whose orientation axis is z in formula I. We show that even in such nearly circular-shaped molecules this very simple experimental method[18] gives correct absolute polarization directions. I provides a good example of the inadequacy of one-parameter evaluation methods in stretched sheet spectroscopy, advocated by some authors, which are based on the assumption that all molecules behave either like rods or like disks. The problem is discussed in some detail. Second, we report the absorption spectra of I and five of its substituted derivatives in low-temperature glasses and conclude from comparison of the details of the spectra with more certainty than was possible before that a minimum of five separate electronic transitions are present below 45 000 cm^{-1}. Third, we report the magnetic circular dichroism of I and 1,2-Br_2-I, which provides further support for spectral assignments. Combined with the stretched sheet results, it establishes the location and polarization of a new transition in I near 50 000 cm^{-1}. Fourth, we confirm the previously reported[19] energy of the lowest singlet-triplet transition in I by measurement of absorption under a high pressure of oxygen.

The experimental data are compared with results of extensive π-electron calculations, with emphasis on absolute signs in the MCD spectra and on the effects of multiply excited configurations, neither of which has received attention in previous theoretical work.

In the following paper,[20] a similar spectral study is reported for pleiadiene (cyclohepta[*de*]naphthalene, III). The third paper of the series[21] compares the electronic states of I and III and correlates them with those of naphthalene. The spectra of I and III are very similar in some respects (absorption, polarization directions) and the opposite of each other in others (MCD). It is shown that the similarities and contrasts are due to a form of approximate mirror-image symmetry between I and III (approximate pairing of orbitals and states of I with those of III). This symmetry, as well as absolute MCD signs, can be derived in very simple terms. Analogous mirror-image symmetry appears in other properties of I and III, such as ^{13}C NMR spectra,[22] and is related to the usual qualitative notion that a five-membered ring will acquire excess negative charge and a seven-membered ring excess positive charge in order to "possess" a sextet of π electrons. In the fourth paper of the series,[23] electronic states of a larger number of polycyclic hydrocarbons derived from I and III are correlated, classified, related to states of naphthalene, and a simple rationalization is proposed for the unusually low energies of the first singlet-singlet transitions.

Experimental Section

Materials. Acenaphthylene was purchased (Aldrich Chemical Co.). 1,2-Dibromoacenaphthylene[24] (1,2-Br_2-I), 3-fluoroacenaphthylene[25] (3-F-I), 4-fluoroacenaphthylene[25] (4-F-I), 5-fluoroacenaphthylene[25] (5-F-I), and 5-methylacenaphthylene[26] (5-Me-I) were prepared by published procedures. They were purified by crystallization, column chromatography, and sublimation as needed. Chloroform and cyclohexane were spectral grade. 3-Methylpentane (3-MP, Phillips Petroleum Co.) was refluxed with sodium, distilled, and passed over an Al_2O_3-$AgNO_3$ column.

Spectroscopy. Absorption spectra in glassy 3-MP (77 K) were taken in 2-mm Suprasil cells immersed in a quartz Dewar vessel with Suprasil windows, filled with filtered liquid nitrogen, using a Cary 17 spectrophotometer. Oscillator strengths were obtained as $f = 4.319 \times 10^{-9} \int \epsilon \, d\nu$, correcting for band overlap by comparison with reduced polarized spectra.

MCD spectra were measured in cyclohexane as described elsewhere.[27] B terms were evaluated as $B = -(33.53\ \tilde{\nu}_0)^{-1} \int [\theta]_M \, d\tilde{\nu}$, where $\tilde{\nu}_0$ is the band center in cm^{-1} and $[\theta]_M$ is molar ellipticity per unit field in deg l. m^{-1} mol^{-1} $gauss^{-1}$, correcting visually for band overlap as much as possible.

Linear dichroism in stretched polyethylene sheets (Kordite, Mobil Chemical Corp.) was measured on a Cary 17 spectrophotometer equipped with a rotatable Glan prism. Polarization directions were 45° to the vertical, ensuring approximately equal light intensities for measurement of both dichroic curves. The sample holder was attached at the cold end of an Air Products CS 202B closed-cycle helium refrigerator held at 10 K. It was surrounded by a vacuum shroud with Suprasil windows. Polymer sheets were prepared in the usual way,[18] using chloroform solutions of the solutes for swelling. For measurement in regions of weak absorption, several sheets containing the solute were pressed together at ~100 °C and then stretched to yield a clear thick sheet of suitable optical density. This "thick sheet method" was adapted from Eggers and collaborators.[28] The dichroic absorption curves and baselines were digitized and processed on a Univac 1108 computer using procedures outlined in ref 18. Reduced absorption curves were derived assuming that out-of-plane polarized intensity was negligible.

Singlet-triplet absorption of a 2 M solution of I in benzene was measured several times in a high-pressure cell (7-cm pathlength) under 150 atm of pressure of oxygen.

Method of Calculation

Calculations were done using the semiempirical π-electron SCF-CI Pariser-Parr-Pople method at two levels of approximation, SCI (all singly excited configurations), and SECI-1 (selected[29] singly and doubly excited configurations). Geometry was either assumed to consist of two regular hexagons and a pentagon with all bond lengths $r_{\mu\nu}$ equal to 1.40 Å, or was determined in an iterative manner from calculated bond orders $p_{\mu\nu}$ ("SC procedure"), using the formulas $\beta_{\mu\nu} = \beta_0 \exp 0.335 (p_{\mu\nu} - 2/3)$ and $r_{\mu\nu} = 1.517 - 0.18 p_{\mu\nu}$, with the above geometry as the starting point (β_0 is the resonance integral for a bond 1.40 Å long, $\beta_{\mu\nu}$ the resonance integral for a bond of length $r_{\mu\nu}$). Only $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ between neighbors were adjusted in this procedure.

In SCI calculations, standard parameter values were used: $I_C = 11.42$ eV, $\gamma_C = 10.84$ eV (one-center), $\beta_{CC} = -2.318$ eV for $r_{\mu\nu} = 1.40$ Å, Mataga-Nishimoto (M-N)[30] or Dewar-Ohno-Klopman (D-O-K)[31] formulas for two-center repulsion integrals.

In SECI-1 calculations, parameters optimized[17,32] for extensive configuration interaction with multiply excited configurations on molecules with up to 12-14 π centers were used: $I_C = 11.42$ eV, $\beta_{CC} = -2.60$ eV for $r_{\mu\nu} = 1.40$ Å, $\gamma_{\mu\nu} = 14.4 [1 - 0.18 \exp(-3.2 r_{\mu\nu})]/(1.328 + r_{\mu\nu})$ eV (r in Å). The dependence of two-center electron repulsion integrals $\gamma_{\mu\nu}$ on distance $r_{\mu\nu}$ is similar to, but less steep than, that given by the M-N formula, which gives good results at the SCI level but exaggerates correlation effects when used at SECI-1 level. It was derived by adjustment of Karwowski's parameters,[33] which had been optimized for full CI on benzene.

The selection of configurations for the SECI-1 procedure and its rationale have been described in detail elsewhere.[29] All singly excited configurations which have weight of 1% or more in at least one of the ten lowest excited states obtained in an SCI calculation with the same parameter values were identified. They, along with the ground configuration, were used for testing the probable importance of each of the 666 possible doubly excited configurations. This was achieved by computing the off-diagonal Hamiltonian matrix element of each of the latter with each of the former and dividing by the difference of the corresponding diagonal elements. If the result was 0.03 or more, the doubly excited configuration, as well as the rest of a complete set of linearly independent configurations only

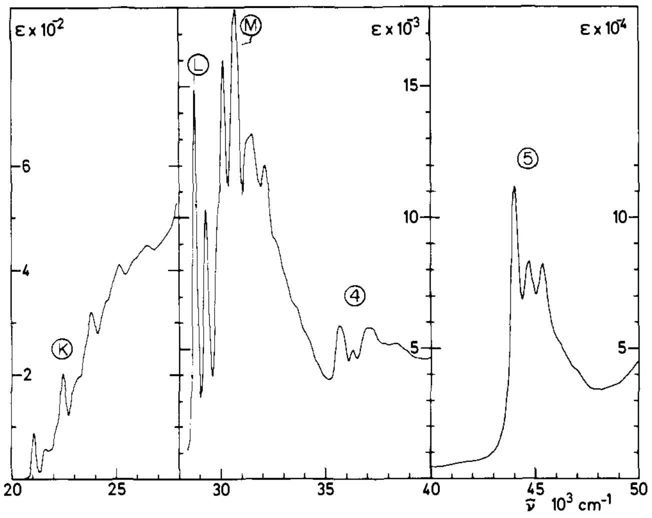

Figure 1. Absorption spectrum of 5-methylacenaphthylene (5-Me-I) in 3-MP glass at 77 K.

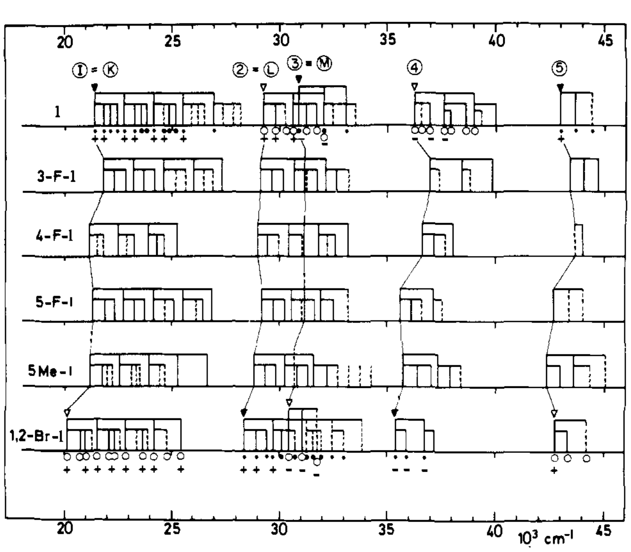

Figure 2. Effect of substitution on the absorption spectrum of 1 (3-MP, 77 K). Energies of peaks (full lines) and shoulders (dashed lines), their polarizations (full circles, long-axis polarized; empty circles, short-axis polarized), and signs in MCD spectra are indicated. Assignment to independent electronic transitions 1-5, their purely electronic polarizations (long-axis polarized, full triangle; short-axis polarized, empty triangle), and tentative analysis of vibrational structure are proposed.

differing in the spin functions, was used in the SECI-1 calculation. In addition, the ground configuration and all singly and doubly excited configurations which were less than 8 eV above it in energy were used.

For instance, in the SECI-1 calculation listed in Table I, which used a geometry determined by the SC procedure (experimental geometry is unknown), the following numbers resulted (selection of doubly excited configurations was based on matrix elements with 19 singly excited configurations). No additional singly excited configurations and five doubly excited configurations had energy less than 8 eV above that of the ground configuration, and 131 additional doubly excited configurations were added after inspection of their off-diagonal matrix elements with the 19 singly excited configurations as described above, to give a total of 156 configurations. Since in SECI-1 calculations the ground state energy is lowered out of proportion to that of singly excited states (note that triply excited configurations are missing), the energy of the ground configuration before configuration interaction is taken for the energy of the ground state of the molecule. In the case of the calculations just described, this amounts to subtracting 4450 cm^{-1} from the energy of each transition obtained by diagonalization of the CI matrix. This was done for the results listed in Table I. Other SECI-1 calculations gave similar results and these are not shown.

In all calculations, oscillator strengths were obtained using both dipole length and dipole velocity formulas. The Linderberg relation[34] was used to obtain the required matrix elements of linear momentum. The B terms in MCD spectra were calculated as described in more detail elsewhere[35] using the usual perturbation formula,[36,37] summing over all states obtained in the calculation and invoking the usual approximations of the simple PPP model.

Results

Absorption spectra of I, 1,2-Br_2-I, 3-F-I, 4-F-I, 5-F-I, and 5-Me-I in 3-MP glass at 77 K closely resemble each other. A typical example is shown in Figure 1 (5-Me-I). Positions of peaks and shoulders in the spectra of the six compounds are shown in Figure 2. The great similarity of the spectra permits a correlation of almost all the peaks from one compound to the next. Inspection of band shapes, substituent shifts, and, in the case of I and 1,2-Br_2-I, polarizations and MCD spectra permit one to distinguish between separate electronic bands and the vibrational structure of the individual bands, and the result is also shown in Figure 2. For reasons which will become apparent later,[23] the transitions are labeled K, L, M, 4, and 5. The vibrational analysis suggested there is only tentative and incomplete because of the low resolution of the data, but is in good agreement with high-resolution results where these are available.[5,6] The assignment of the origin of transition M is difficult because it lies in a region of strong absorption due to transition L. It is safe only when based on polarization measurements, i.e., for I and 1,2-Br_2-I. In the latter, the origin of M lies sufficiently higher than that of L (2000 cm^{-1}) to exclude the remote possibility that M might represent only intensity borrowed by L from some high-energy y-polarized transition.

Low-temperature polarized absorption spectra of I and 1,2-Br_2-I in the y and z directions, $A_y(\lambda)$ and $A_z(\lambda)$, respectively, are shown in Figures 3 and 4. They were obtained as linear combinations of measured linear dichroic spectra $E_\parallel(\lambda)$ and $E_\perp(\lambda)$ by the usual stepwise reduction procedure,[18] assuming that the peaks due to origins of the K band and the L band were purely polarized (the sharp origin of the latter sits on a weak diffuse background of opposite polarization, which does not disturb the reduction procedure, but would distort a simple dichroic ratio). In the spectrum of I, all peaks show positive dichroism ($E_\parallel(\lambda) > E_\perp(\lambda)$ for all λ). The degree of dichroism is higher for absorption due to transitions K, M, and 5, which just disappear in the linear combination $1.5\,E_\perp(\lambda) - E_\parallel(\lambda)$, and lower for absorption by transitions L and 4, which disappears in the linear combination $E_\parallel(\lambda) - 1.25\,E_\perp(\lambda)$. In the nomenclature of ref 18, $d_\perp{}^0 = 2/3$ and $d_\parallel{}^0 = 5/4$. Molecular models indicate that the cross-section of I perpendicular to the y axis in formula I is smaller than that perpendicular to the z axis, so that the y axis should be the molecular orientation axis. In view of the small difference of the two cross-sections, this conclusion might appear questionable, but it is confirmed by stretched sheet measurements on 1,2-Br_2-I. This molecule is extended considerably in the direction of the z axis in formula I and should orient quite unequivocally with z as its orientation axis, i.e., in a manner opposite to I. This is indeed observed. In the spectra of 1,2-Br-I, the dichroic ratio $E_\parallel(\lambda)/E_\perp(\lambda)$ for the origins of transitions K and 5 is 1.0, and they are assumed to be purely y polarized, while it is larger than one throughout most of the spectrum. The long-axis polarized absorption spectrum shown in Figure 4 is therefore given by $A_z(\lambda) = E_\parallel(\lambda) - 1.0E_\perp(\lambda)$, and $d_\parallel{}^0 = 1.0$. The short-axis polarized

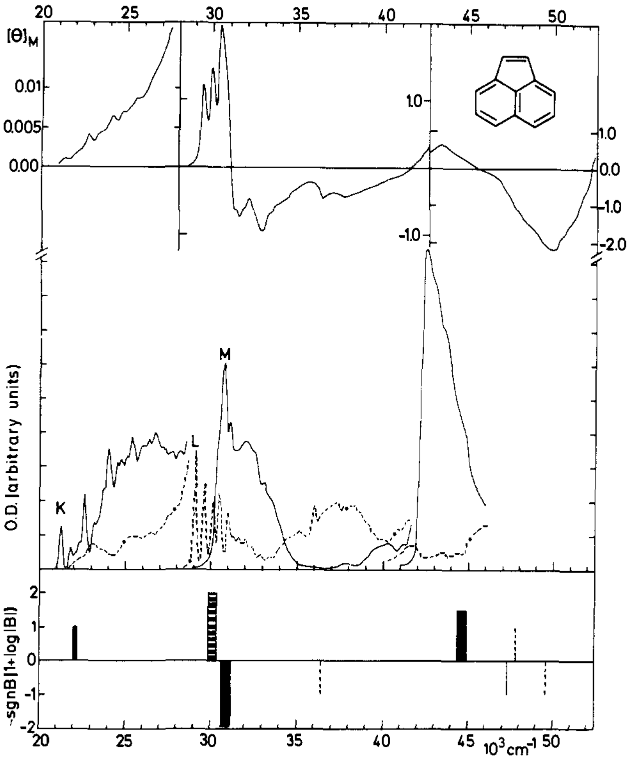

Figure 3. Acenaphthylene (I). Top: MCD spectrum in cyclohexane at room temperature. Center: Reduced low-temperature absorption curves [full line: y polarized (long axis); dotted line: z polarized]. Bottom: Calculated (SCI) transition energies, oscillator strengths (thick lines for $f_r > 0.1$, medium lines for $0.01 < f_r \leq 0.1$, thin lines for $f_r \leq 0.01$), polarizations (full lines for z-polarized, broken lines for y-polarized, see formula I) and MCD B terms in units of 10^{-3} $D^2\beta_e/\text{cm}^{-1}$ (given as $-\text{sgn } B(1 + \log|B|)$ for $|B| > 1$, otherwise $-\text{sgn } B$).

absorption curve was obtained as $E_\perp(\lambda) - 0.40E_\parallel(\lambda)$, where $d_\perp{}^0 = 0.40$ was obtained by requiring the peak due to the origin of transition L to just disappear from the linear combination.

The results permit the conclusion that transitions K, M, and 5 are y polarized and L and 4 are z polarized in both compounds. In each case, transition K borrows a substantial part of its intensity from transition M. These results are in complete agreement with other available evidence.[4-7]

Figures 3 and 4 also display the MCD spectra of I and 1,2-Br_2-I. These are in good agreement with the postulated presence of five separate electronic transitions below 45 000 cm^{-1}. Figure 3 further shows a comparison of the experimental data with the results of the calculations. A survey of measured and calculated results is given in Table I.

Finally, we wish to report the result of a measurement of oxygen-induced singlet-triplet absorption of I in benzene solution. This gave a gradually rising absorption curve similar in shape to the K band in singlet-singlet absorption of I, with an indication of poorly resolved vibrational structure. The first indistinct peak was at 16 300-16 700 cm^{-1}, in agreement with the values 16 400 and 16 700 cm^{-1} reported from heavy atom solvent-enhanced absorption measurements.[19] It is quite possible that the origin of the band is at even lower energy and is so weak that it escaped notice in these measurements. This is actually suggested by results of photosensitization experiments,[38] which led to the values 15 050-15 750 cm^{-1}. In summary, it can now be stated with reasonable confidence that the lowest triplet energy of I is bracketed by the values 15 000-16 500 cm^{-1}.

Discussion

1. Electronic Transitions. In view of all the previous studies[4-7] of polarized spectra of I, our results for the region below 45 000 cm^{-1} only serve to confirm existing assignments (Table I). In particular, there is now no doubt left that L and M are two independent electronic transitions, rather than an "intrinsic" and a "borrowed" component of the same transition, and that transition 5, whose polarization was assigned only tentatively from polarized fluorescence measurements,[4] is indeed y polarized as postulated earlier. Above 45 000 cm^{-1}, the rise in z-polarized absorption in I (Figure 3) suggests the presence of a transition 6. This is supported by the shape of its MCD curve, which gives a positive peak for transition 5, turns negative above 45 000 cm^{-1}, and gives a strong negative peak near 50 000 cm^{-1}, an order of magnitude larger than baseline and noise errors and well reproducible. The presence of a new transition in this region is not distinctly apparent in ordinary absorption spectra (Figure 1). It is confirmed conclusively by comparison with results for 1,2-Br_2-I (Figure 4). Once again, the y-polarized strong peak at 42 000 cm^{-1} is positive in MCD and is followed by a broad band of z-polarized absorption peaking near 46 000 cm^{-1}, which has a negative counterpart in MCD, assigned as transition 6. A summary of the present knowledge of the electronic transitions in I is given in Table I.

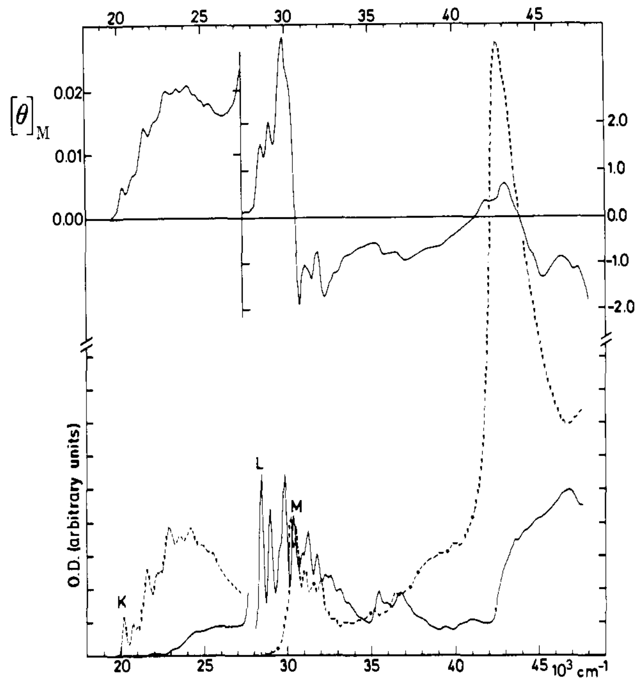

Figure 4. 1,2-Dibromoacenaphthylene (1,2-Br_2-I). Top: MCD spectrum in cyclohexane at room temperature. Bottom: Reduced low-temperature absorption curves (full line: z polarized (long axis); dotted line: y polarized, see formula I).

2. Comparison with Theory. Previous calculations of the electronic spectrum of I by π-electron methods[4,9-17] generally agree with experimental results for the lowest few electronic transitions. No previous attempts to calculate the MCD spectrum of I have been reported. Rather than discussing all the published calculations, which are in fairly good agreement with each other, we shall use our SCI results (M-N integrals, standard parameters, and all bond lengths equal to 1.40 Å) as a typical representative (Table I). Other things being equal, introduction of more realistic bond lengths by the iterative SC procedure will increase the energy of the first transition and improve numerical agreement with experiment, but the number, nature, and other important characteristics of the calculated transitions are not significantly affected, and we believe that it is reasonable to show the degree of agreement obtained with this simple version of the PPP theory.

Table I. Electronic States of Acenaphthylene (I)

	Experimental transition no.								
	1 = K			2 = L			3 = M		
	Exptl	SCI	SECI-1	Exptl	SCI	SECI-1	Exptl	SCI	SECI-1
E^a	21.39	22.11	23.99	29.31	29.98	29.89	30.95	30.32	30.35
f_r^b	0.005^e	0.04	0.03	0.1	0.30	0.20	0:2	0.20	0.13
f_p^b		0.003	0.02		0.07	0.15		0.06	0.10
pol^c	y	y	y	z	z	z	y	y	y
B^d	−0.05^e	−0.90 −0.73	(−0.31) (−0.26)	−2.2	−84.5 −86.5	(−18.2) (−18.3)	2.8	84.0 86.3	(17.9) (17.9)
Ψ		1→−1 (85%)	1→−1 (80%)		2→−1 (92%)	2→−1 (86%)		3→−1(65%) 2→−2(21%)	3→−1(62%) 2→−2(21%)

	4			–^{f}		5		
	Exptl	SCI	SECI-1	SCI	SECI-1	Exptl	SCI	SECI-1
E^a	36.27	38.21	36.86	47.23	41.92	43.00	44.55	43.83
f_r^b	0.1	0.002	0.01	0.01	0.12	1.1	1.21	0.71
f_p^b		0.002	0.01	0.01	0.09		0.53	0.59
pol^c	z	z	z	y	y	y	y	y
B^d	~0.5	0.38 0.34	(0.90) (1.13)	0.52 1.10		~−1	−3.3 −3.7	(0.36) (2.6)
Ψ		1→−2(89%)	1→−2(75%)	4→−1(83%)	4→−1(30%) 1,2→−1,−1(28%) 2→2(15%)		2→−2(72%) 3→−1(17%)	2→−2(50%) 4→−1(21%)

	–^{g}		–^{g}		6		
	SCI	SECI-1	SCI	SECI-1	Exptl	SCI	SECI-1
E^a	49.46	43.83	47.54	45.28	~49.5		48.41
f_r^b	0.01	0.001	0.01	0.0000			0.19
f_p^b	0.01	0.001	0.01	0.0004			0.17
pol^c	z	z	z	z	z		z
B^d	0.14 0.95		−0.24 −0.67		~5		
Ψ	5→−1(58%)	5→−1(39%) 2→−3(19%)	1→−4(45%) 3→−2(37%)	3→−2(39%) 1→−4(31%)			1,1→−1,−1(34%) 3→−2(13%) 2,2→−1,−1(10%)

[a] Observed energy of the 0–0 band and calculated vertical excitation energy. Units of 10^3 cm^{-1}. [b] Oscillator strength; experimental, estimating band overlap by use of polarized spectra in Figures 3 and 4; calculated, f_r from dipole length and f_p from dipole velocity. [c] Axes as in formula I. [d] B term in units of 10^{-3} D$^2 \cdot \beta_e$/cm^{-1}. The upper value was calculated with origin on top of the molecule as written in formula I, the lower value, with origin at the bottom. The values in the SECI-1 column are representative of this type of calculation but were actually obtained from a different run than the E, f, and Ψ values shown, using D-O-K parameters and 91 configurations. [e] Much of this intensity is borrowed. [f] No exptl values; part of 5? [g] No exptl values.

None of the previous work considered the effect of multiply excited configurations. These have been shown to be of considerable importance for the interpretation of low-energy transitions in some hydrocarbons, notably polyenes[39] and pleiadene.[26] On theoretical grounds,[40] they are more likely to be important in alternant than in nonalternant hydrocarbons. It seems important to find out on representative examples how justified the usual neglect of such configurations is. In Table I, we have, therefore, also included SC SECI-1 results which probably are as good an approximation to the exact (full CI) solution of the semiempirical PPP problem as can be achieved with straightforward CI on 150 configurations. If our previous experience on smaller molecules[17,29,35] is any guide, the SECI-1 energies, oscillator strengths, polarizations, and even signs of B terms of the lowest half-a-dozen transitions calculated here will be essentially the same as those which would be obtained from full CI, except for a more or less uniform shift of all excitation energies and possible misordering of almost degenerate states calculated at high energies, which may play havoc with the signs of their B terms. The uniform shift of energies has been taken into account in parameter choice and in the decision to take the energy of the ground configuration before CI to represent the ground state energy.[17,32] Nothing simple can be done to calculate reliably the B terms of a group of nearly degenerate transitions in the present approximation.

The agreement between experimental (0-0) and calculated (vertical) transition energies, relative intensities, polarizations, and signs of B terms shown in Table I is nearly perfect. The numerical values of calculated oscillator strengths (particularly for transition 4) and B terms are less satisfactory. Although the measured values of the B terms for transitions L and M are undoubtedly too small because of the large overlap of the bands, the calculated values are clearly excessive. This is at least partially due to too small a calculated difference in the excitation energies, which enters into the denominator of the expression for the contribution of their mutual mixing to their B terms as is discussed in more detail below. In the particular SECI-1 calculation listed in Table I B terms were not calculated, but we have performed other SCI and SECI-1 calculations with various modifications, and always obtained the correct signs for the lowest four transitions. One of the SECI-1 results is shown in Table I. The origin-dependence of the calculated values, although disturbing in principle, is much smaller than the uncertainties due to the freedom in parameter choice and extent of configuration interaction, and thus without practical consequence if the convention of restricting the choice of origin to the inside of the molecule is accepted. For SECI-1 calculations, the origin-dependence is generally smaller than for SCI calculations, and in the limit of full CI it disappears.[35]

Inclusion of doubly excited configurations in the CI procedure has little effect on the lowest four transitions, which can be quite adequately described successively as one-electron jumps from molecular orbitals 1, 2, and 3 to orbital −1, and from orbital 1 to orbital −2. Here, bonding MO's are numbered in the order of decreasing energy, and antibonding MO's are labeled by negative integers in the order of increasing energy. Larger modifications occur in the region above 40 000 cm^{-1} and mostly concern transitions which are so weak that they are not apparent in the spectra. No new transitions are introduced up to ca. 45 000 cm^{-1}. The lowest calculated excited state which can be identified as predominantly doubly excited lies at 48 410 cm^{-1} and is attributed tentatively to the newly observed transition 6.

3. Analysis of the MCD Spectrum. Since the calculated signs of the first four *B* terms do not depend on details of the calculation and correspond well to experimental signs (a positive *B* term implies a negative MCD peak), it appears meaningful to inquire about their origin in the sum-over-states language. The *B* term of a transition from ground state to some final state, G → F, can be written as a sum of contributions due to magnetic mixing of individual excited states I into the ground state G and of the ground state, as well as all excited states other than F into the final state F. Using the nomenclature of ref 35,

$$B(\mathrm{G} \rightarrow \mathrm{F}) = \sum_{\mathrm{I,I} \neq \mathrm{G,F}} B_{\mathrm{I,G}}{}^{\mathrm{F}} + \sum_{\mathrm{I,I} \neq \mathrm{F,G}} B_{\mathrm{I,F}}{}^{\mathrm{F}} + (B_{\mathrm{F,G}}{}^{\mathrm{F}} + B_{\mathrm{G,F}}{}^{\mathrm{F}}) \quad (1)$$

where

$$B_{\mathrm{I,G}}{}^{\mathrm{F}} = \mathrm{Im}\{(\langle \mathrm{I}|\hat{\mathcal{M}}|\mathrm{G}\rangle \cdot \langle \mathrm{G}|\hat{M}|\mathrm{F}\rangle \times \langle \mathrm{F}|\hat{M}|\mathrm{I}\rangle)/(W_{\mathrm{I}} - W_G)\} \quad (2)$$

$$B_{\mathrm{I,F}}{}^{\mathrm{F}} = \mathrm{Im}\{(\langle \mathrm{F}|\hat{\mathcal{M}}|\mathrm{I}\rangle \cdot \langle \mathrm{G}|\hat{M}|\mathrm{F}\rangle \times \langle \mathrm{I}|\hat{M}|\mathrm{G}\rangle)/(W_{\mathrm{I}} - W_{\mathrm{F}})\} \quad (3)$$

$$B_{\mathrm{F,G}}{}^{\mathrm{F}} + B_{\mathrm{G,F}}{}^{\mathrm{F}} = \mathrm{Im}\{\langle \mathrm{F}|\hat{\mathcal{M}}|\mathrm{G}\rangle \cdot \langle \mathrm{G}|\hat{M}|\mathrm{F}\rangle \times (\langle \mathrm{F}|\hat{M}|\mathrm{F}\rangle - \langle \mathrm{G}|\hat{M}|\mathrm{G}\rangle)/(W_{\mathrm{F}} - W_{\mathrm{G}})\} \quad (4)$$

In these expressions, Im stands for imaginary part of, $\hat{\mathcal{M}}$ and $\hat{M}$ are the magnetic and electric dipole moment operators, respectively, and W_A is the energy of the *A*th state.

Although the value of $B(\mathrm{G} \rightarrow \mathrm{F})$ is origin-independent in the full CI limit, the individual contributions depend on the choice of origin. In practice, like the calculated *B* terms, also the individual calculated contributions to each *B* term are almost origin-independent, and it thus makes sense to discuss the origin of the *B* values in terms of magnetic mixing of states if one is willing to agree that the origin should be somewhere inside the molecular framework.

Guided by the results of our SCI and SECI-1 calculations, both of which lead to the same conclusions, we propose the following interpretation of the origin of the *B* terms: the small negative term of transition K is due about equally to a negative contribution $B_{\mathrm{L,K}}{}^{\mathrm{K}}$ from magnetic mixing of the first (K) with the second (L) excited state and to another negative contribution $(B_{\mathrm{K,G}}{}^{\mathrm{K}} + B_{\mathrm{G,K}}{}^{\mathrm{K}})$, due to mixing of the ground with the first excited state. The much stronger negative term of transition L is due to a large negative contribution $B_{\mathrm{M,L}}{}^{\mathrm{L}}$ from mixing of the second (L) with the third (M) excited state, which overshadows all others, such as the small positive contribution $B_{\mathrm{K,L}}{}^{\mathrm{L}}$ due to mixing with the excited state *K* and the similarly small negative contribution $(B_{\mathrm{L,G}}{}^{\mathrm{L}} + B_{\mathrm{G,L}}{}^{\mathrm{L}})$. The same magnetic mixing of the second (L) with the third (M) excited state also dominates the *B* term of transition M, and, as a result, this is calculated to be approximately equal in size but of positive sign ($B_{\mathrm{L,M}}{}^{\mathrm{M}} = -B_{\mathrm{M,L}}{}^{\mathrm{L}}$). The absolute signs of the mixing terms are readily rationalized by inspection of the nodal properties of the orbitals involved in the transitions.[21] The situation is quite different for the fourth transition. Its small positive *B* term is calculated to originate about equally in small contributions from several other excited states. Still, since all of these contributions are positive, there is no doubt about the sign of the sum. This type of discussion is not possible for the higher excited states since the calculations suggest that opposing contributions from several states are important, some of these originating in rather high energy states which have not been observed experimentally. Also, in this energy region, the SCI and SECI-1 results disagree with respect to the number of states and their energies.

From the signs of the *B* terms, we can assign the sense of the direction of the magnetic transition moments in space with respect to that of two electric dipole transition moments. For instance, if the phases of the wave functions for the ground, first excited, and second excited states are chosen so as to make the electric dipole transition moment $\langle \mathrm{G}|\hat{M}|\mathrm{K}\rangle$, which lies in the *y* axis, to point to the left, and the transition moment $\langle \mathrm{G}|\hat{M}|\mathrm{L}\rangle$, which lies in the *z* axis, to point up in formula I, then the imaginary part of the magnetic dipole transition moment $\langle \mathrm{K}|\hat{\mathcal{M}}|\mathrm{L}\rangle$ points toward the viewer.

The directions found for the magnetic transition moments in this fashion are just the opposite of those found[20] for pleiadiene (III). In a following paper[21] we shall see that the similarities and differences between I and III can be easily understood in simple MO terms.

4. The Stretched Sheet Method. The well-understood polarization properties of the transitions of I, established independently by other techniques,[4-7] can serve to test various aspects of molecular orientation in stretched polyethylene. The reversal of preferred orientation on going from I to 1,2-$\mathrm{Br_2}$-I provides a nice example of the relationships between molecular shape and orientation distribution and increases one's confidence in the usefulness of the stretched sheet method for absolute polarization assignments.

An interesting aspect of the results for I is the positive value of measured dichroism $E_{\parallel}(\lambda)/E_{\perp}(\lambda)$ at all wavelengths of absorption, both at wavelengths of peaks known from other work[4-7] to be *y* polarized (λ_1), e.g., the origins of transition K and transition 5, and of those known to be *z* polarized (λ_2), e.g., the origin of transition L. This is reflected in the values $d_{\perp}{}^0 = E_{\perp}(\lambda_1)/E_{\parallel}(\lambda_1) = 0.67 < 1$ and $d_{\parallel}{}^0 = E_{\parallel}(\lambda_2)/E_{\perp}(\lambda_2) = 1.25 > 1$. Positive dichroism for long-axis (*y*) polarized transitions is, of course, no surprise and is simply a result of the definition of the long axis, but at first sight short-axis polarized transitions might be expected to always give negative dichroism $E_{\parallel}(\lambda)/E_{\perp}(\lambda) < 1$. It can be easily shown that such an expectation would indeed be correct for symmetrical top molecules with two equivalent short axes (rod-shaped molecules, for instance, 2-butyne). For such molecules, at any given inclination of the long axis from the stretching direction of the polymer (measured by angle β), all angles γ of rotation along the molecular long axis are equally probable and it can be shown[18] that $2/d_{\parallel}{}^0 = 1/d_{\perp}{}^0 + 1$. Since, by definition of the long axis, $d_{\perp}{}^0 < 1$, it then follows that $d_{\parallel}{}^0 < 1$ as well. For the purposes of stretched-sheet absorption spectroscopy, the orientation distribution of molecules of this type (rod-like) is fully described by one independent parameter, in our work chosen as $K_1 = \langle \cos^2 \beta \rangle_{\mathrm{av}}$. Obviously, the orientation of I in stretched polyethylene is not of this type, since $d_{\perp}{}^0 < 1$, $d_{\parallel}{}^0 > 1$.

The reason for this is easy to see: the two short axes of I, and most other molecules, are not equivalent. For instance, according to molecular models, the size of I measured along the in-plane short axis exceeds that measured along the out-of-plane short axis and is indeed almost equal to the length measured in the direction of the long axis. If their equivalence were complete, as it is in symmetrical-top molecules whose shape is disk-like, a constant dichroic ratio would be expected for in-plane polarized absorption at all absorbing wavelengths, i.e., $d_{\perp}{}^0 = 1/d_{\parallel}{}^0$. This other limiting type of orientation distribution has also been recognized in the literature[41,42] and can again be described by a single parameter, often taken to be

$\langle\cos^2\beta''\rangle_{av}$, where β'' is the angle formed by the out-of-plane short axis (the unique axis of the disc) and the stretching direction. Alternatively, it can still be described by $\langle\cos^2\beta\rangle_{av}$ as before if the condition $d_\perp^0 = 1/d_\parallel^0$ is specified. Now, the orientation of I in stretched polyethylene is not of this second limiting type either, since the dichroic ratio $E_\parallel(\lambda)/E_\perp(\lambda)$, although positive everywhere, is not constant ($d_\perp^0 \neq 1/d_\parallel^0$). Other examples of molecules which behave like I in this respect ($d_\perp^0 < 1$, $d_\parallel^0 > 1$ in polyethylene) have been found recently.[43,44] A large number of other cases of molecules whose orientation fulfills neither relation, $2/d_\parallel^0 = 1/d_\perp^0 + 1$, nor $1/d_\parallel^0 = d_\perp^0$, has been reported previously and it was concluded repeatedly that the assumption of rod-like behavior does not hold in general.[18,45-53] This is particularly clear in a plot of measured $d_\parallel^0$ and $d_\perp^0$ values against each other.[53] In a single case, one might perhaps have doubted the conclusion and argued against it[54] on the basis of possible inaccuracies in the measurement of the dichroic ratios, but the combined evidence seems overwhelming. Of course, it makes good physical sense that there should be a continuum of types of orientation between the two limiting cases. Also, it stands to reason that if the molecular orientation indeed originates in the tendency of molecules to expose their smallest cross-section in the direction of stretching[18] (to minimize steric repulsions and maximize van der Waals attractions), those with $\beta \neq 0$ will prefer certain values of γ over others unless they are rod-like, i.e., will expose their "edges" rather than their "flat sides". If this tendency was overwhelming (γ = 0 or 180° only), a third limiting type of orientation would result,[18] namely $d_\parallel^0 = 4\, d_\perp^0$. The observed deviations were always in this direction ($d_\parallel^0$ higher than expected for a rod-like behavior), but the limit was never reached.

We find it necessary to discuss this matter in some detail, since the tendency to assume that all molecules can be adequately represented as either rod-like or disk-like, so that their orientation in a uniaxially stretched polymer is described by a single angle, still survives and appears even in some quite recent publications.[42,55]

A helpful way of visualizing the orientation distributions encountered in stretched sheet spectroscopy in a simple way is shown in Figure 5, where $K_2 = d_\parallel^0/(2 + d_\parallel^0)$ is plotted against $K_1 = 1/(2\,d_\perp^0 + 1)$ for several planar molecules (an alternative is to plot $d_\parallel^0$ against $d_\perp^0$ [47,53]). Here, $K_1 = \langle\cos^2\beta\rangle_{av}$ measures the deviation β of the molecular long axis from the stretching direction and $K_2 = \langle\sin^2\beta\cdot\cos^2\gamma\rangle_{av} = \langle\cos^2\beta'\rangle_{av}$ measures the deviation β' of the in-plane short axis from the stretching direction.[18] The average deviation β'' of the out-of-plane axis from the stretching direction is determined by the values of K_1 and K_2, since $K_1 + K_2 + \langle\cos^2\beta''\rangle_{av} = 1$. Although specification of K_1 and K_2 provides a complete description of all aspects of the molecular orientation distribution of the orientation axis and of the molecular plane needed in ordinary polarized absorption spectroscopy in a uniaxially stretched polymer, in planar molecules of low symmetry, in which polarization directions of $\pi\pi^*$ transitions are not restricted to the two in-plane axes y and z, an additional specification of an angle is needed to relate the polarization direction of a transition to the direction of the molecular orientation axis.[18] In liquid crystal work, it has been common to use an alternative set of orientation parameters $S_{zz} = \frac{1}{2}(3K_1 - 1)$, $S_{yy} = \frac{1}{2}(3K_2 - 1)$, $S_{xx} = -S_{zz} - S_{yy}$. With a simple change of scale and origin, Figure 5 can be equally well interpreted as a plot of S_{yy} against S_{zz}.

In Figure 5, the point $K_1 = K_2 = \frac{1}{3}$ corresponds to random orientation, the point $K_1 = 1.0$, $K_2 = 0.0$ to perfect alignment of the long axis of all molecules along the stretching direction ($\beta = 0°$, all γ's equally likely), and the point $K_1 = 0.5$, $K_2 = 0.5$ to perfect alignment of the yz plane of all molecules parallel to the stretching direction, with complete equivalence between the two in-plane axes y and z (γ = 0 or 180°, all β's equally likely). The line $K_2 = (1 - K_1)/2$ at the bottom of the triangle corresponds to orientation distributions of the rod-like limiting type, for which the γ distribution is random (all γ's equally likely), with the preference for alignment of the long axis along the stretching direction increasing gradually from left to right. The line $K_2 = K_1$ on the left-hand side of the triangle corresponds to orientation distributions of the disk-like limiting type, for which the β distribution is random and the preference of the yz plane (molecular plane) to lie parallel to the stretching direction increases gradually from bottom to top. The line $K_2 = 1 - K_1$ closing the top of the triangle corresponds to orientation distributions of the third type mentioned above, for which the yz plane of all molecules is aligned perfectly parallel to the stretching direction and the preference for alignment of the long axis with this direction grows gradually from left to right. Points inside the triangle correspond to more general types of orientation and give the possibility of continuous transitions from one limiting type of orientation distribution to another. None of the points for any of the molecules we have studied in stretched polyethylene lie outside the triangle, although this is not excluded in principle. In later publications, we plan to discuss this aspect, extend the treatment to molecules with transitions in three mutually perpendicular directions, and present data for a large number of aromatic molecules. At this time, we only illustrate our argument by a few representative points shown in Figure 5.

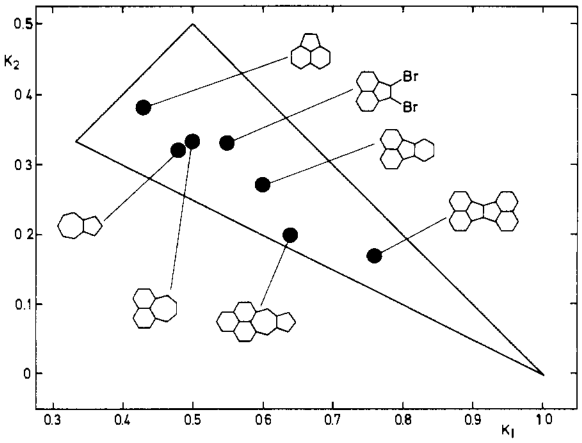

Figure 5. Orientation factors K_1 and K_2 for acenaphthacenaphthylene,[56] azulenophenalene,[50] fluoranthene,[48] pleiadiene,[20] azulene,[49] acenaphthylene (I), and 1,2-dibromoacenaphthylene (1,2-Br_2-I). The formulas are drawn so as to position the effective orientation axis in the horizontal direction.

Measurements for rod-like and disk-like molecules give points which lie on the bottom line and the left-hand side line, respectively, as expected. None of the measured points lies at the top line, which thus represents a purely hypothetical type of orientation distribution. The points shown in Figure 5 illustrate the relation between molecular shape and the values of K_1 and K_2 and make the unusual values of $d_\perp^0 < 1$ and $d_\parallel^0 > 1$ found for I appear as a natural consequence of its nearly circular shape. They also demonstrate once again that general use of assumptions which are appropriate only for rod-shaped or disk-shaped molecules is not reasonable.

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References and Notes

(1) A. Pullman, B. Pullman, E. D. Bergmann, G. Berthier, E. Fischer, Y. Hirshberg, and J. Pontis, *J. Chim. Phys. Phys.-Chim. Biol.*, **48**, 359 (1951).
(2) J. Michl and R. Zahradnik, *Collect. Czech. Chem. Commun.*, **31**, 2259 (1966). In Table I of this reference (p 2261), replace A_2 and B_2 by B_1 and A_1, respectively.
(3) J. H. Eggers and E. W. Thulstrup, 8th European Congress on Molecular Spectroscopy, Copenhagen, Denmark, 1965.
(4) E. Heilbronner, J. P. Weber, J. Michl, and R. Zahradnik, *Theor. Chim. Acta*, **6**, 141 (1966).
(5) R. D. Gordon and R. F. Yang, *J. Mol. Spectrosc.*, **34**, 266 (1970).
(6) A. Bree, C. Y. Fan, and R. A. Kydd, *Spectrochim. Acta, Part A*, *25*, 1375 (1969).
(7) K. Seibold, R. Zahradnik, and H. Labhart, *Helv. Chim. Acta*, **53**, 805 (1970).
(8) For leading references, see W. I. Ferree, Jr., B. F. Plummer, and W. W. Schloman, Jr., *J. Am. Chem. Soc.*, **96**, 7741 (1974); J. M. Labrum, J. Kolc, and J. Michl, *ibid.*, **96**, 2636 (1974); J. E. Shields, D. Gavrilovic, J. Kopecky, W. Hartmann, and H. G. Heine, *J. Org. Chem.*, **39**, 515 (1974), D. O. Cowan and J. C. Koziar, *J. Am. Chem. Soc.*, **97**, 249 (1975).
(9) J. Koutecky, P. Hochman, and J. Michl, *J. Chem. Phys.*, **40**, 2439 (1964).
(10) R. Zahradnik, *Angew. Chem., Int. Ed. Engl.*, **4**, 1039 (1965), *Fortschr. Chem. Forsch.*, **10**, 1 (1968); in "Nonbenzenoid Aromatics", Vol. II, J. P. Snyder, Ed., Academic Press, New York, N.Y., 1971, p 53.
(11) A. J. Sadlej, *Acta Phys. Pol.*, **27**, 859 (1965).
(12) G. Leroy and S. Jaspers, *J. Chim. Phys. Phys.-Chim. Biol.*, **64**, 463 (1967).
(13) J. E. Bloor, B. R. Gilson, and N. Brearley, *Theor. Chim. Acta*, **8**, 35 (1967).
(14) P. Hochmann, R. Zahradnik, and V. Kvasnicka, *Collect. Czech. Chem. Commun.*, **33**, 3478 (1968).
(15) G. Tröger and J. Fabian, *Z. Phys. Chem.* (*Leipzig*), **247**, 139 (1971).
(16) V. N. Poltavets and M. M. Mestechkin, *Opt. Spectrosc.*, **31**, 460 (1971).
(17) J. W. Downing, Ph.D. Dissertation, University of Utah, 1974.
(18) E. W. Thulstrup, J. Michl, and J. H. Eggers, *J. Phys. Chem.*, **74**, 3868 (1970).
(19) R. Zahradnik, I. Tesarova and J. Pancir, *Collect. Czech. Chem. Commun.*, **36**, 2867 (1971).
(20) J. Kolc and J. Michl, *J. Am. Chem. Soc.*, **98**, 4540 (1976).
(21) J. Michl, *J. Am. Chem. Soc.*, **98**, 4546 (1976)
(22) A. J. Jones, P. D. Gardner, D. M. Grant, W. M. Litchman, and V. Boekelheide, *J. Am. Chem. Soc.*, **92**, 2395 (1970); D. Wendisch, W. Hartmann, and H.-G. Heine, *Tetrahedron*, **30**, 295 (1974); H. Günther and H. Schmickler, *Pure Appl. Chem.*, in press.
(23) J. Michl and J. F. Muller, *J. Am. Chem. Soc.*, **98**. 4550 (1976).
(24) D. A. Herold, M.S. Thesis, University of North Carolina, Chapel Hill, N.C., 1972.
(25) M. J. S. Dewar and J. Michl, *Tetrahedron*, **26**, 375 (1970).
(26) J. Kolc, J. W. Downing, A. P. Manzara, and J. Michl, *J. Am. Chem. Soc.*, **98**, 930 (1976).
(27) D. J. Shieh, S. H. Lin, and H. Eyring, *J. Phys. Chem.*, **77**, 1031 (1973).
(28) J. H. Eggers, private communication.
(29) J. W. Downing, J. Michl, P. Jørgensen, and E. W. Thulstrup, *Theor. Chim. Acta*, **32**, 203 (1974).
(30) N. Mataga and K. Nishimoto, *Z. Phys. Chem.* (*Frankfurt am Main*), **13**, 140 (1957).
(31) M. J. S. Dewar and N. L. Hojvat (Sabelli), *J. Chem. Phys.*, **34**, 1232 (1961); *Proc. R. Soc. London, Ser. A*, **264**, 431 (1961); K. Ohno, *Theor. Chim. Acta*, **2**, 219 (1964); G. Klopman, *J. Am. Chem. Soc.*, **86**, 4450 (1964).
(32) J. W. Downing and J. Michl, unpublished results.
(33) J. Karwowski, *Chem. Phys. Lett.*, **18**, 47 (1973).
(34) J. Linderberg, *Chem. Phys. Lett.*, **1**, 39 (1967).
(35) S. M. Warnick and J. Michl, *J. Am. Chem. Soc.*, **96**, 6280 (1974).
(36) P. N. Schatz and A. J. McCaffery, *Q. Rev., Chem. Soc.*, **23**, 552 (1969).
(37) P. J. Stephens, *Annu. Rev. Phys. Chem.*, **25**, 201 (1974).
(38) D. O. Cowan and R. L. E. Drisko, *J. Am. Chem. Soc.*, **92**, 6286 (1970).
(39) B. Hudson and B. Kohler, *Annu. Rev. Phys. Chem.*, **25**, 437 (1974).
(40) J. Cizek. J. Paldus, and I. Hubac, *Int. J. Quant. Chem.*, **8**, 951 (1974).
(41) B. Norden, *Chem. Scr.*, **1**, 145 (1972).
(42) A. Yogev, L. Margulies, B. Strasberger, and Y. Mazur, *J. Phys. Chem.*, **78**, 1400 (1974).
(43) 2,7-Diazapyrene: E. W. Thulstrup, J. W. Downing, and J. Michl, unpublished results.
(44) Dicyclopenta[*ef,kl*]heptalene: J. Michl, unpublished results.
(45) J. Michl and J. H. Eggers, *Tetrahedron*, **30**, 813 (1974).
(46) J. Kolc and J. Michl, *J. Mol. Spectrosc.*, **51**, 298 (1974).
(47) J. Michl, E. W. Thulstrup and J. H. Eggers, *Berg. Bunsenges. Phys. Chem.*, **78**, 575 (1974).
(48) J. Kolc, E. W. Thulstrup, and J. Michl, *J. Am. Chem. Soc.*, **96**, 7188 (1974).
(49) E. W. Thulstrup, P. L. Case, and J. Michl, *Chem. Phys.*, **6**, 410 (1974).
(50) E. W. Thulstrup, J. Michl, and C. Jutz, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1618 (1975).
(51) J. Kolc, J. Michl, and E. Vogel, *J. Am. Chem. Soc.*, **98**, 3935 (1976).
(52) C. C. Bott and T. Kurucsev, *J. Chem. Soc., Faraday Trans. 2*, **71**, 749 (1975).
(53) E. W. Thulstrup, M. Vala, and J. H. Eggers, *Chem. Phys. Lett.*, **7**, 31 (1970).
(54) A. Yogev, L. Margulies, and Y. Mazur, *Chem. Phys. Lett.*, **8**, 157 (1971).
(55) E.g., B. Nordén, *Chem. Phys. Lett.*, **23**, 200 (1973); Q. Chae and P.-S. Song, *J. Am. Chem. Soc.*, **97**, 4176 (1975); R. T. Ingwall, C. Gilon, and M. Goodman, *Ibid.*, **97**, 4356 (1975).
(56) E. W. Thulstrup and J. Michl, *J. Mol. Spectrosc.*, in press.

Electronic States of Pleiadiene (Cyclohepta[*de*]naphthalene). Linear Dichroism in Stretched Polyethylene and Magnetic Circular Dichroism

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Abstract: A minimum of six and possibly seven independent electronic transitions between 15 000 and 45 000 cm^{-1} are assigned in the electronic spectrum of pleiadiene (I, cyclohepta[*de*]naphthalene) from low-temperature absorption, linear dichroic, and magnetic circular dichroic spectroscopy of I and two simple derivatives. Even for such a nearly circular molecule, the "stretched sheet method" yields correct absolute polarizations. The combined data are used to derive directions of magnetic dipole transition moments between excited states. Energies, intensities, polarization, and signs of B terms of the lowest four transitions agree well with results of π-electron calculations. Systematic introduction of doubly excited configurations in the calculation has little effect on the transitions. In the course of this work, a photochemical reaction which changed the shape of a molecule and thus rotated its preferred orientation axis by 90° was performed in stretched polyethylene at 77 K. An unoriented sample resulted, which then oriented spontaneously on warming.

The bright red hydrocarbon, pleiadiene (I), is one of the simplest neutral nonalternants and has attracted the attention of experimental[1-4] as well as theoretical[5,6] chemists for some time. Since I is the parent of a large group of nonalternant hydrocarbons in whose excited states we have become interested,[7] and at least one of which shows interesting absorption due to a transition to a doubly excited state,[8,9] an analysis of the electronic absorption spectrum of I appeared desirable. Previously, only the room[1] and low[9] temperature solution absorption curve of I and polarized absorption spectra of the first absorption band in a simple derivative,[10] II, have been published. These seem to be in accord with π-electron calcu-