of Sciences, Warsaw, Poland, where the oxygen-induced singlet-triplet absorption measurements were performed some years ago, and to Dr. Andrzej Bylina for kind help with these measurements.

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

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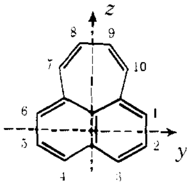
Abstract: A minimum of six and possibly seven independent electronic transitions between 15 000 and 45 000 cm^{-1} are assigned in the electronic spectrum of pleiadiene (I, cyclohepta[*de*]naphthalene) from low-temperature absorption, linear dichroic, and magnetic circular dichroic spectroscopy of I 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.

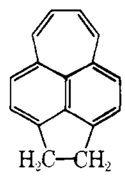
The bright red hydrocarbon, pleiadiene (I), is one of the simplest neutral nonalternants and has attracted the attention of experimental[1-4] as well as theoretical[5,6] chemists for some time. Since I is the parent of a large group of nonalternant hydrocarbons in whose excited states we have become 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 calculations of Pariser-Parr-Pople type,[6,9] but a detailed analysis of the extent of the agreement has been impossible with the limited experimental data available.

In the present paper, the techniques of absorption spectroscopy (77 K), linear dichroic spectroscopy in stretched polyethylene (77 K), and magnetic circular dichroic (MCD) spectroscopy (room temperature) are used for I and two simple derivatives to establish the presence of at least six and probably seven independent electronic transitions below 45 000 cm^{-1} for I, and to assign their polarizations and MCD signs. The spectral results are discussed in terms of semiempirical π-electron calculations. Particular attention is paid to the effect of doubly-excited configurations and to the calculation of absolute MCD signs. Intriguing problems concerning the detailed nature of the mechanism of solute orientation in polymers are posed by observation of a photochemical reaction in stretched polyethylene, during which the solute shape changes drastically.

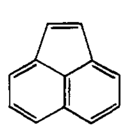
In the following paper,[11] similarities and contrasts between the electronic states of I and those of the closely related acenaphthylene[12] (III) are discussed and interpreted in terms of approximate cross-pairing between the orbitals and states of I on the one hand and III on the other. In the fourth paper of the series,[7] electronic states of a larger number of polycyclic hydrocarbons derived from I and III are discussed.



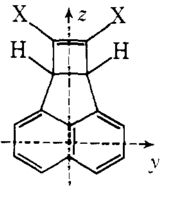
I



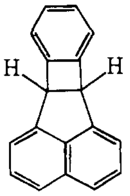
II



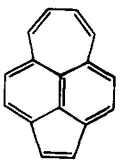
III



IV, X = Cl
V, X = H



VI



VII

Experimental Section

Materials. Samples of pure I, its 8-methyl derivative (8-Me-I), and IV were obtained from Dr. W. Hartmann and Dr. H.-G. Heine, Bayer AG, Krefeld-Uerdingen, Germany. Conversion of IV into 8,9-dichloropleiadiene (8,9-Cl$_2$-I) was effected in situ by irradiation of a solution of IV in polyethylene or of its glassy solution in 3-methylpentane (3-MP) at 77 K with light from a 200-W high-pressure mercury arc (Pyrex filter); the product was identified by its typical absorption spectrum, very close to that of I. Its isolation was not attempted. Analogous conversion of parent V into I in this fashion was first described some time ago.[3]

Chloroform and cyclohexane were spectral grade. 3-MP (Phillips Petroleum Co.) was refluxed with sodium, distilled, and passed over a Al$_2$O$_3$-AgNO$_3$ column.

Spectroscopy. Absorption and MCD spectra were measured as described in the preceding paper.[12] Linear dichroism was also measured as described there, with the following differences: The holder with the stretched sheet was immersed in liquid nitrogen in a quartz Dewar vessel with Suprasil windows as described in more detail in ref 13; ordinary (thin) stretched polymer sheets were used; the spectrophotometer was interfaced to a PDP-11/20 computer which was programmed to plot reduced absorption curves.

Our attempts to find fluorescence or phosphorescence from I failed.

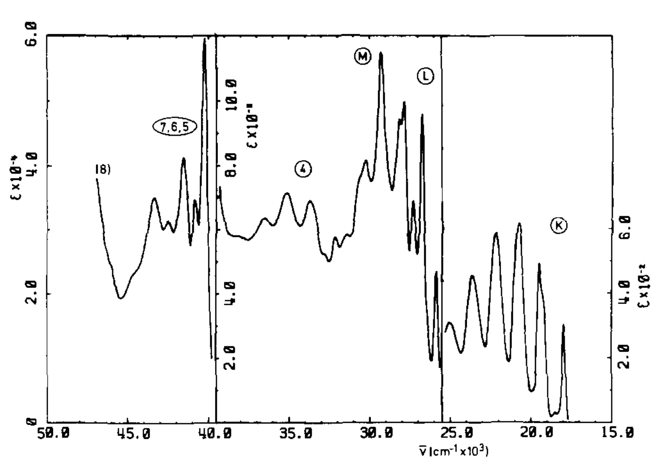


Figure 1. Absorption spectrum of pleiadiene (I) in 3-MP glass at 77 K.

Method of Calculation

Calculations were performed at the SCI and SECI-1 levels as described in the preceding article,[12] using procedures and parameters given there. Because of the larger size of I, the selection of configurations for the SECI-1 calculation was based on only 15 singly-excited configurations (selected as being the most important for the ten lowest excited states in an SCI calculation) and only the 666 doubly excited configurations which can be obtained by exciting from the highest six occupied into the lowest six empty orbitals were scanned. Thus, in a calculation using a geometry determined by the iterative SC procedure from bond orders (experimental geometry is unknown), a total of 162 configurations were selected using a diagonal cutoff limit of 8 eV and the cutoff limit 0.025 for the size of an off-diagonal matrix element divided by the energy difference of the corresponding diagonal elements.

Results

The absorption spectrum of I in 3-MP glass at 77 K is shown in Figure 1. A comparison of peak positions in I, 8-Me-I, and 8,9-Cl$_2$-I is shown in Figure 2, along with a tentative vibrational analysis and assignment of individual electronic transitions justified in detail below. This assignment was facilitated by comparison with the MCD spectrum of I, which is shown on top in Figure 3. The MCD spectrum of 8,9-Cl$_2$-I is quite similar in all respects, and the spectral curve is not shown. The signs of the individual peaks in the spectrum are given in Figure 2. Note that, by definition, a negative MCD peak corresponds to a positive B value.

The bottom of Figure 3 shows the z- and y-polarized components of the absorption spectrum of I, derived from measurements of linear dichroism. These played a major role in developing an understanding of the absorption spectrum shown in Figure 1. As could be expected from the nearly circular molecular shape of I, the degree of dichroism in stretched polyethylene is not very high. The reduction factors $d_\parallel{}^0$ and $d_\perp{}^0$ were obtained by the usual stepwise reduction procedure,[14] assuming that the first peak of the lowest transition (18 000 cm^{-1}, low dichroic ratio $E_\parallel/E_\perp$) is purely polarized, and that the sharp peaks near 26 000 cm^{-1} (high dichroic ratio $E_\parallel/E_\perp$) are purely polarized in the opposite direction. They are $d_\perp{}^0 = 0.65$, $d_\parallel{}^0 \simeq 1.00$ at room temperature, and $d_\perp{}^0 = 0.50$, $d_\parallel{}^0 = 0.98$ at 77 K. This corresponds to orientation factors[15] $K_1 = \langle\cos^2\beta\rangle_{av} = 1/(2d_\perp{}^0 + 1) = 0.435$ and $K_2 = \langle\sin^2\beta\cdot\cos^2\gamma\rangle_{av} = d_\parallel{}^0/(2 + d_\parallel{}^0) \simeq 0.333$ at room temperature (0.500 and 0.329, respectively, at 77 K), which can be compared with values for several other hydrocarbons in Figure 5 of ref 12. For a rod-shaped molecule, in which distribution of the angles γ would be uniform (γ describes rotation of the molecule along its long axis), one would expect[15] $d_\parallel{}^0 = 0.66$

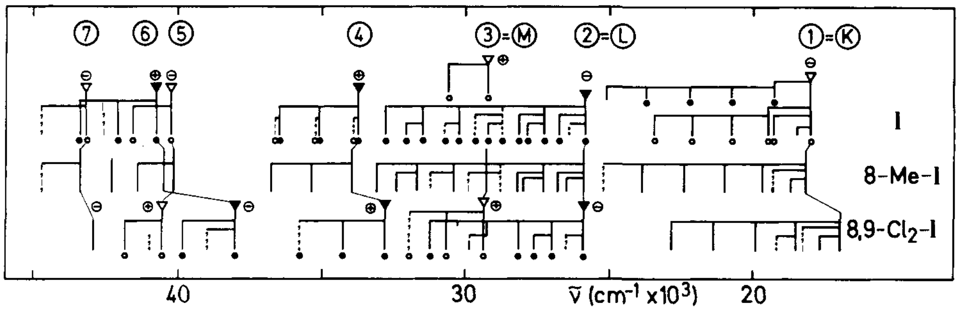


Figure 2. Effect of substitution on the absorption spectrum of I (3-MP, 77 K). Energies of peaks (full lines) and shoulders (dashed lines), their polarizations (full circles, z polarized; empty circles, y polarized in formula I), and signs in MCD spectra are indicated. Assignment to independent electronic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

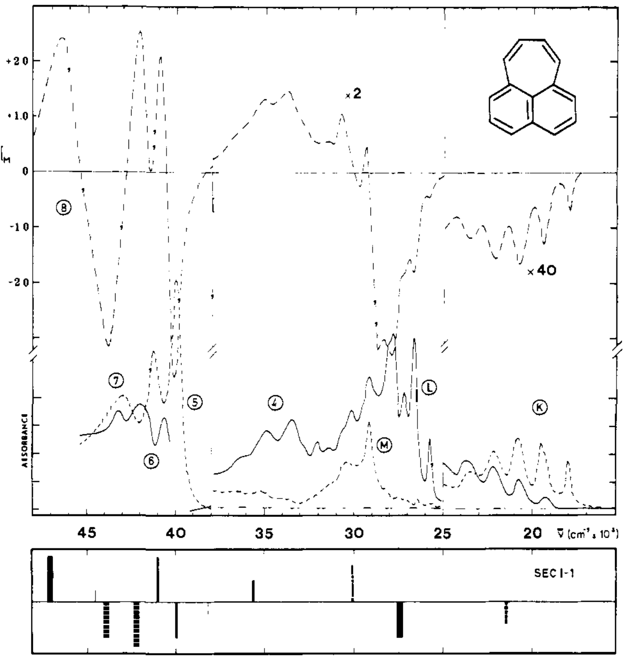


Figure 3. Top: MCD spectrum of I in cyclohexane (room temperature). Center: z-Axis (full line) and y-axis (dashed line) polarized absorption spectra of I in stretched polyethylene (77 K). Optical density in arbitrary units. Bottom: Calculated transition energies and characteristics: z polarized (full line), y polarized (dashed line); oscillator strength $f > 0.3$ (thick line), $0.3 > f > 0.01$ (medium line), $f < 0.01$ (thin line); positive MCD peak (lines in upper part), negative MCD peak (lines in lower part); MCD intensity (length of lines increasing in four steps $|B| < 1$, $|B| < 2$, $|B| < 6$, $|B| > 6$).

from $d_\perp^0 = 0.50$ and $1/d_\parallel^0 = 1/(2d_\perp^0) + \frac{1}{2}$, rather than the observed value of 0.98, but obviously, I is far from rod-shaped. For a more detailed discussion, see ref 12.

It is heartening to note that even such a small degree of dichroism permits readily the usual type of analysis leading to reduced spectra[14] $A_z(\lambda) = E_\parallel(\lambda) - 0.98E_\perp(\lambda)$ and $A_y(\lambda) = 1.49[E_\perp(\lambda) - 0.5E_\parallel(\lambda)]$, shown in Figure 1, where $E_\parallel(\lambda)$ and $E_\perp(\lambda)$ are the measured parallel and perpendicular dichroic curves after correction for baseline, respectively. The scale factor $n_0 = 1.49$ was obtained from $n_0 = (2 + d_\parallel^0)/(2d_\perp^0 + 1)$.[14,15] The large effect of temperature on the degree of dichroism is interesting, since for some other molecules (e.g., pyrene) the effect is small. A more systematic study may eventually lead to an improved understanding of the detailed mechanism of orientation.

Inspection of the molecular shape of I on models shows that the axis labeled z in formula I should be the effective orientation axis, since a smaller cross-section is exposed when the molecule is viewed along this axis than when it is viewed along the y or x axis. The difference between the z and y axes is very small, and one might perhaps doubt the correctness of this assignment. It is supported by the observed increase in the observed dichroic ratio on going to 8,9-Cl_2-I, and independently confirmed by comparison with Sidman's single crystal results,[10] which showed the 0–0 transition of the first band in II to be y polarized.

The absorption spectrum of **IV** strongly resembles that of acenaphthene. In stretched polyethylene, IV aligns quite well with the y axis of formula IV along the stretching direction, as shown by the positive dichroic ratio of the naphthalene B_b band, $E_\parallel$ (228 nm)/$E_\perp$ (228 nm) = 2.85 (room temperature; the ratio in the region of the L_a band is about unity). This may be surprising at first sight, but can be understood after inspection of a model of this nonplanar molecule. A benzo analogue of related shape (VI) orients in the same manner.[16]

When an oriented sample of IV contained in a stretched polyethylene sheet is irradiated at 77 K with near uv light, its absorption spectrum changes into that of 8,9-Cl_2-I in the same way as when the experiment is performed in 3-MP glass. After less than 30 min, the conversion appears to be complete. Both in 3-MP and in stretched polyethylene, the solute molecule is apparently able to adjust its originally strongly bent shape into the equilibrium ground-state geometry of 8,9-Cl_2-I (presumably planar), the absorption spectrum showing no obvious signs of strain such as changes after annealing. The sample of 8,9-Cl_2-I thus produced in stretched polyethylene at 77 K shows virtually no dichroism. However, after warmup to room temperature and recooling to 77 K, the sample shows quite strong dichroism of the same type as I itself, only stronger, showing that the z axis is preferentially aligned in the stretching direction ($d_\perp^0 = 0.43$, $K_\parallel = 0.538$). The annealing does not change the shape of the spectrum and repeated annealing has no additional effect. In the region above 25 000 cm^{-1}, results for the polarization of absorption peaks were thus obtained and the results are shown in Figure 2. The concentrations of 8,9-Cl_2-I attained in this way did not permit measurements on the weak first band. This also made it impossible to determine a reliable value for $d_\parallel^0$, since the y-polarized peaks in the higher absorption bands overlap with strong z-polarized peaks similarly as in I itself (cf. Figure 3). Values around $d_\parallel^0 = 0.8$–1.0, expected by comparison with I and other molecules in Figure 5 of ref 12, led to quite reasonable reduced spectra.

Results of the calculations are compared with experimental data in Figure 3 and Table I.

Discussion

1. Electronic Transitions. The unpolarized low-temperature absorption spectrum (Figure 1) suggests the presence of four transitions, starting approximately at 20 000, 28 000, 34 000, and 40 000 cm^{-1}, respectively. Investigation of substituent shifts is somewhat less helpful than usual, perhaps because too

Table I. Electronic Transitions in Pleiadiene (I)

A. Experimental

Trans	K	L	M	4	5	6	7	8
E^{a}	17.94	25.84	29.28	33.73	40.27	40.82	43.05	~46.5
f^{b}	0.01[c]	0.2	0.05	0.1[d]	~0.3	0.3	~0.2	
pol[e]	*y*	*z*	*y*	*z*	*y*	*z*	*y*	
B^{f}	0.2	(4)	−(1)	−(2)	(*s*)	−(*s*)	(*s*)	−(*s*)

B. Calculated

	K		L		M		4		5−7		
Trans[g]	SCI	SECI-1	SCI	SECI-1	SCI	SECI-1	SCI	SECI-1	SCI	SECI-1	SCI
E^{h}	18.76	21.48	26.91	27.44	29.72	30.11	36.01	35.62	41.17	38.20	44.52
f_r^{i}	0.06	0.04	0.41	0.31	0.10	0.07	0.003	0.03	0.11	0.005	0.03
f_p^{i}	0.002	0.03	0.10	0.24	0.03	0.06	0.004	0.02	0.05	0.004	0.01
pol[e]	*y*	*y*	*z*	*z*	*y*	*y*	*z*	*z*	*y*	*y*	*z*
B_T^{j}	2.6	1.3	9.0	5.1	−7.3	−5.3	−0.6	−1.5	35	0.5	6
B_B^{j}	2.2	1.3	9.0	5.3	−7.8	−5.4	−0.5	−1.6	40	0.6	18
ψ^{k}	1→−1 (93%)	1→−1 (89%)	1→−2 (90%)	1→−2 (86%)	1→−3 (69%)	1→−3 (68%)	2→−1 (91%)	2→−1 (68%)	3→−1 (52%)	1,1→−1,2 (36%) 3→−1 (27%)	1→−4 (60%)

	5−7								8			
	SECI-1	SCI	SECI-1	SCI	SECI-1	SCI	SECI-1	SECI-1	SCI	SECI-1	SECI-1	SECI-1
E^{h}	39.95	41.44	40.99	43.28	42.22	44.57	43.91	44.52	46.96	47.02	48.67	48.72
f_r^{i}	0.07	0.52	0.10	1.13	0.59	0.07	0.30	0.0002	0.85	0.53	0.31	0.54
f_p^{i}	0.07	0.20	0.07	0.46	0.45	0.02	0.22	0.003	0.44	0.41	0.23	0.42
pol[e]	*z*	*z*	*z*	*y*	*y*	*y*	*y*	*z*	*z*	*z*	*y*	*z*
B_T^{j}	5.8	−53	−24.3	6	16.8	11	5.3	−0.4		−7.9	12.1	−11.9
B_B^{j}	5.5	−64	−23.6	17	16.7	−2	5.9	−0.5		−8.2	10.9	−12.5
ψ^{k}	1,1→−1,−1 (22%) 1→−5 (18%)	4→−1 (61%) 3→−2 (15%)	3→−2 (34%) 4→−1 (14%)	2→−2 (33%)	2→−2 (49%)	1→−5 (63%) 4→−2 (25%)	4→−2 (41%)	1,1→−1,−1 (33%)	3→−2 (47%) 4→−1 (28%)	4→−1 (32%)		

[a] Position of 0−0 transition in units of 10^3 cm^{-1}. [b] Estimated oscillator strength. [c] Plus 0.005 of borrowed intensity (*z* polarized). [d] Plus 0.03 of borrowed intensity (*y* polarized). [e] Long-axis *z* and short-axis *y* as in formula I. [f] Roughly estimated *B* term (units of $10^{-3}\beta_e \cdot D^2/\text{cm}^{-1}$). The sign is opposite to that of the MCD peak. *B* terms labeled *s* are large, probably over 5 in absolute value. [g] Assignment of calculated (SCI, SECI-1) to experimental transitions is indicated. [h] Vertical excitation energy in units of 10^3 cm^{-1}. [i] Oscillator strengths: f_r from dipole length formula, f_p from dipole velocity formula. [j] *B* term in units of $10^{-3}\beta_e \cdot D^2/\text{cm}^{-1}$: B_T, calculated with origin on top of formula I; B_B, calculated with origin at bottom of formula I. [k] Weight of the most important configurations in the excited state wavefunction. For orbital numbering, see text. The order of the almost degenerate orbitals −4 and −5 is the opposite in SCI and in SECI-1 calculations (due to differences in parameter values).

few derivatives are at hand. They would suggest the presence of the same four bands (Figure 2). A simple-minded vibrational analysis outlined in Figure 2 indicates that two separate transitions may have to be postulated in each of the 28 000 and 40 000 cm^{-1} regions, but really convincing evidence is provided only by the linear dichroic and MCD spectra (Figure 3), on which our transition assignments will rely heavily. For reasons which will become apparent later,[7] we shall use labels K, L, and M for the first three transitions.

It is interesting to note that not all of the dichloro substitution shifts are compatible with the empirical rule of thumb, which states that long-axis polarized transitions will be red-shifted more than short-axis polarized ones if a substituent is located so as to extend the long axis.

Transition K (1). This weak transition has a short-axis (*y*) polarized origin at 17 940 cm^{-1}, followed by a fairly complicated vibrational structure. Insofar as can be ascertained from our low-resolution spectra, this consists of two progressions in a 1300 cm^{-1} a_1 vibration, a short one built on the origin (not clearly seen in Figure 3, but indicated in Figure 2) and a long one built on origin plus one quantum of a 1500 cm^{-1} a_1 vibration, and of one progression in a 1500 cm^{-1} a_1 vibration built on origin plus one quantum of a 1200 cm^{-1} b_2 vibration. The b_2 vibration provides a mechanism for intensity borrowing from the oppositely-polarized second transition, clearly apparent in Figure 3. The envelope of the *y*-polarized component of the first transition has a Franck-Condon forbidden shape, magnified in the unpolarized absorption spectrum by the borrowed component, whose intensity increases toward higher energies. All of the peaks of this transition are negative in the MCD curve. Its oscillator strength can be estimated at 0.01 intrinsic plus 0.005 borrowed from transition 2. The transition corresponds to the first transition in II, which was studied at higher resolution by Sidman.[10]

Transition L (2). This is the stronger of the two oppositely polarized transitions which are jointly responsible for the band near 28 000 cm^{-1}. It is long-axis polarized and its origin lies at 25 840 cm^{-1}. Its complicated vibrational structure can be understood as a superposition of three progressions in a 1450 cm^{-1} a_1 vibration, a relatively weak one built on the origin, a stronger one built at origin plus one quantum of a 550 cm^{-1} a_1 vibration, and a strong but shorter one built on origin plus one quantum of a 900 cm^{-1} a_1 vibration, as shown in Figure 2, but a high-resolution study would probably show this to be oversimplified. The transition has Franck-Condon forbidden shape. When a correction for overlap is taken from Figure 3 and used in Figure 1, oscillator strength can be estimated at about 0.2. All peaks belonging to transition 2 are negative in the MCD curve.

Transition M (3). This somewhat weaker transition clearly stands out in Figure 3, since it is short-axis polarized and is positive in the MCD curve, both in contrast to the stronger transition 2. The origin of short-axis polarized absorption, which we assign to the 0-0 band of transition 3, lies at 29 280

cm^{-1} and thus is separated by 3400 cm^{-1} from the origin of transition 2, making it unlikely in the extreme that it could correspond to a vibronic component of the latter. Transition 3 has Franck-Condon allowed shape and very little fine structure, with only one quantum of a 1300 cm^{-1} a_1 vibration clearly visible.

Transition 4. This long-axis polarized transition is clearly present both in Figure 1 and 3, and we assign its origin at 33 730 cm^{-1}. It is Franck-Condon allowed, positive in MCD, and shows a simple progression in a 1400 cm^{-1} a_1 vibration. The oscillator strength is about 0.1. This transition seems to be weakly borrowing intensity from transition 5, using a very low frequency b_1 vibration (ca. 200 cm^{-}, borrowed oscillator strength about 0.03). Alternatively, this weak short-axis polarized absorption (Figure 3) could belong to a separate electronic transition, but our data certainly does not demand such a postulate.

Transition 5. This very intense transition with origin at 40 270 cm^{-1} appears to be a stronger replica of transition 3: it also is short-axis polarized, Franck-Condon allowed, and exhibits vibrational spacing of 1300 cm^{-1}. However, its MCD curve is negative. While the assignment of this transition presents no difficulties, and its oscillator strength can be estimated at 0.3, it is virtually impossible to derive a numerical value for its B term due to excessive overlap with the next transition. The wavenumber of this intense transition and all following transitions is lower by about 200 cm^{-1} in polyethylene than it is in 3-MP. All numbers quoted refer to 3-MP unless specified otherwise.

Transition 6. From the polarized and MCD spectra of I alone, it would be impossible to tell whether the long-axis polarized transition 6 with origin at 40 820 cm^{-1}, oscillator strength about 0.3, vibrational spacing 1300 cm^{-1}, and positive MCD sign is an independent electronic transition or whether it is a part of transition 5 resulting from vibronic intensity borrowing from some higher lying long-axis polarized transition by means of a 550 cm^{-1} b_1 vibration (Figures 1-3).

The fact that in 8-Me-I the separation of the origin of the transition 6 from the origin of transition 5 is only 320 cm^{-1} suggests that it is more likely that we indeed deal with two separate transitions, since the introduction of a methyl into a molecule of the size of I usually does not change frequencies of skeletal vibrations by this much. Also, the very high intensity of absorption of both polarizations makes it somewhat unlikely that we are only dealing with one electronic transition. A definitive proof that the long-axis polarized origin at 40 820 cm^{-1} is not a false origin is obtained from the results of polarization measurements on 8,9-Cl_2-I (Figure 2). In this derivative, the long-axis polarized origin is shifted to 38 000 cm^{-1}· while the short-axis polarized origin of transition 5 remains almost unchanged (40 680 cm^{-1}). This reversal shows that we are indeed dealing with two independent electronic states.

Transition 7. The intense short-axis polarized peak at 43 050 cm^{-1} (stretched polyethylene) does not fit into the structure of transition 5 nor transition 6. Moreover, it is separated from the nearest short-axis polarized peak by 1700 cm^{-1}, and also the negative MCD peak which corresponds to it appears to be much too strong for assignment to transition 5, considering that the 43 050 cm^{-1} peak lies on top of a quite strong positive contribution to the MCD due to transition 6 (cf. the much smaller negative dip in the MCD curve caused by the second vibrational component of transition 5, located at 41 350 cm^{-1} in polyethylene). These factors lead us to suspect that the 43 050 cm^{-1} peak corresponds to a separate electronic transition. Its oscillator strength is of the order of 0.2, its B term is positive, but its magnitude cannot be estimated.

2. Comparison with Theory. It appears reasonable to assume that I and its simple derivatives are planar in view of its close relation to acepleiadylene (VII), which is known to be planar from an x-ray analysis.[17] This assumption is supported by the recently published analysis[18] of NMR data for I.

Previous calculations of the electronic spectrum of I by PPP-type methods all used configuration interaction with singly excited configurations or equivalent techniques[6] or only a few doubly excited configurations.[9] They are in quite good mutual agreement and we shall not discuss them here. As a typical representative of this type of calculation, we shall use our SCI calculation, performed as described in detail in the preceding paper.[12] A calculation of the MCD spectrum of I has previously not been attempted. For reasons likewise outlined previously,[12] Table I also presents the results of a SECI-1 calculation employing selected doubly excited configurations.

Up to about 40 000 cm^{-1} (first four transitions), 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 of B terms are less satisfactory. Of course, the experimental values of the B terms for transitions L and M are quite inaccurate and only indicate orders of magnitude. The origin-dependence of the calculated B terms of low-energy transitions is insignificant compared with the uncertainties due to the freedom in the choice of parameters and in the extent of CI, as long as one assumes that the origin is somewhere inside the π-electron framework of the molecule.

When doubly excited configurations are included in the calculation (SECI-1), the results change little. The lowest four transitions can still be quite adequately described, successively, as one-electron jumps from molecular orbital 1 to orbitals −1, −2, and −3, and from orbital 2 to −1 (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).

Between 40 000 and 45 000 cm^{-1}, a large number of nearly degenerate intense transitions is predicted. Our experimental results show that three are present and do not exclude the presence of more than three. It is not obvious which three calculated transitions should be assigned to the observed ones. It is possible that the weak y-polarized absorption between experimental transitions 4 and 5, assigned here as a part of transition 4, in reality corresponds to the weak fifth calculated transition of significant doubly excited character.

The eighth experimental transition, tentatively identified by its positive MCD peak (Figure 3) and the rise of absorption near 46 000 cm^{-1}, seems to correspond to the strong transition calculated at 47 000 cm^{-1}.

3. Analysis of the MCD Spectrum. The calculated signs of the first four B terms do not depend on details of the calculation and are in good agreement with experimental signs. This encourages us to attempt their interpretation in terms of magnetic mixing of states similarly as done for III previously.[12] As outlined there, and using nomenclature of ref 19, the contribution $B_{\mathrm{I,F}}{}^{\mathrm{F}}$ to the B term of the transition from the ground state G to an excited state F, which is due to magnetic mixing of another excited state I into the excited state F, can be written as

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

where 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 Ath state.

As in the case of III,[12] we find that the calculated contributions $B_{\mathrm{I,F}}{}^{\mathrm{F}}$ are quite origin independent for lower excited states F, and proceed to use this decomposition of the B terms as a convenient way of discussing their origin in a simple manner. Both SCI and SECI-1 calculations suggest that the small positive term of transition K is mostly due to a positive contribution $B_{\mathrm{L,K}}{}^{\mathrm{K}}$ from magnetic mixing of the first (K) with the second (L) excited state, and partly also to a positive contribution ($B_{K,G}{}^{K} + B_{G,K}{}^{K}$) from mixing of the ground with the first excited (K) state. The much stronger positive term of transition L is due to a large positive contribution $B_{M,L}{}^{L}$ from mixing of the second (L) with the third (M) excited state, which overshadows all others, such as the small negative contribution $B_{K,L}{}^{L}$ due to mixing with the first excited state (K), and the equally small positive contribution ($B_{L,G}{}^{L} + B_{G,L}{}^{L}$). The same magnetic mixing of the second (L) with the third (M) excited state also dominates the B term of transition M, and this is then approximately equal in size, but of positive sign ($B_{L,M}{}^{M} = -B_{M,L}{}^{L}$). The absolute signs of the mixing terms are readily rationalized by inspection of the nodal properties of the orbitals involved in the transitions.[11] The situation is different for the fourth transition. Its small negative B term is calculated to originate in small contributions from six other excited states, many of these quite high in energy. All six contributions are negative, so that there is no doubt about the sign of their sum.

This type of discussion is not possible for higher excited states, since assignment of the calculated to the observed transitions is not clear-cut. However, from the experimental MCD spectrum of I (Figure 2), and the very similar spectrum of 8,9-Cl_2-I (not shown, signs given in Figure 3), it appears that the MCD signs of transitions 5 and 6 of I (minus and plus, respectively) are determined by their mutual mixing. These almost degenerate transitions are identified unambiguously by their polarizations (5, y and 6, z), and under the effect of 8,9-dichloro substitution they change their order (6 below 5, Figure 3). Simultaneously, they change their MCD signs (6 negative, 5 positive), so that the MCD peak at lower energy is still negative and the one at higher energy positive, as they were in I itself. This reversal of sign is expected for the contribution to the B terms of transitions 5 and 6, which is due to their mutual mixing, as the presence of $W_I - W_F$ in the denominator in the formula for $B_{I,F}{}^{F}$ shows clearly. Contributions to B terms which do not correspond to magnetic mixing of states which switch their order are not likely to change much upon 8,9-dichloro substitution in I, as indicated by the great similarity of the two MCD spectra.

The sense of the direction of the magnetic transition moments in space with respect to that of two electric dipole transition moments is given by the signs of the B terms. It is readily seen that the results for I are just the opposite of those found for III.[12] In the following paper,[7] we shall see that the similarities and differences between I and III are easily understood in simple MO terms.

4. The Stretched Sheet Method. After III, I is another case of an almost circular molecule for which the stretched sheet method yielded correct absolute polarization directions by assigning the orientation axis simply on the basis of molecular shape, i.e., long axis as z and short axis as y in formula I. This claim is supported by the fact that 8,9-Cl_2-I, which is more elongated in the z direction, shows similar but stronger dichroism, and its correctness is established by agreement with single-crystal data[10] on the first transition in II. Thus it appears that the method generally permits absolute polarization assignments, at least for symmetrical planar molecules of low polarity in nonpolar polymers such as polyethylene. It should nevertheless be pointed out that in the presence of heteroatoms, molecular shape is not the only factor determining the orientation distribution, although it still appears to be the dominant one.[15,20]

The photochemical conversion of IV to 8,9-Cl_2-I in stretched polyethylene is interesting in that it converts strongly bent molecules originally oriented with the long axis of the naphthalene ring system (y in formula IV) along the stretching direction into planar molecules whose preferred orientation aligns the short in-plane axis of the naphthalene ring system (z in formula I) along the stretching direction. All of the change in molecular shape, but only a part of the change in orientation, occurs at 77 K during the photochemical process. It then appears that the solute molecules are quite firmly entangled in the polymer chains and are free to equilibrate their orientation only after the increased temperature makes the latter mobile. Local heating during the photochemical process is apparently insufficient for this purpose. Possibly, molecules of different shapes prefer different sites in the polymer and translational diffusion is involved in the equilibration process. These aspects of the present work are now being investigated further.

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