

hfs of the four (basal) fluorines being 143 G whereas the coupling to the fifth (apical) fluorine is undetectable. In comparison, the valence-bond description of SF₅ involves an sp³d² octahedral configuration with the unpaired electron occupying one of the six equivalent hybrid orbitals. However, this model provides no obvious explanation of the small coupling to the fluorine ligand situated trans to the orbital of the unpaired electron.³¹ Thus it seems that MO treatments involving

multicenter bonding provide a better understanding of ligand hyperfine interactions in the esr of hypervalent (electron rich) phosphorus and sulfur radicals.

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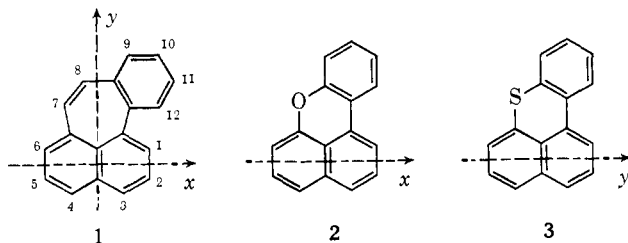
Excited States of Benzo[4,5]cyclohepta[1,2,3-*de*]naphthalene and Its Heterocyclic Analogs. Polarization Directions and Magnetic Circular Dichroism

J. F. Muller,^{1a} D. Cagniant,*^{1a} O. Chalvet,^{1b} D. Lavalette,^{1c}
J. Kolc,^{1d} and J. Michl*^{1d,e}

Contribution from the Laboratoire de Chimie Organique, Faculté des Sciences, Université de Metz, Metz, France, the Centre de Mécanique Ondulatoire Appliquée, Paris, France, the Institut du Radium, Paris, France, and the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received November 8, 1973

Abstract: The combination of low-temperature absorption, polarized emission, and linear dichroism in stretched polyethylene and room-temperature magnetic circular dichroism has been used to obtain information about excited states of **1**. Assignments and comparison with related hydrocarbons and the heterocyclic analogs **2** and **3** are based on semiempirical π -electron calculations (PPP). The polarization directions of several lowest electronic transitions in **1**, which can in principle lie anywhere in the molecular plane, have been determined by a method which should be applicable to other molecules of low symmetry and are in good agreement with calculations. Signs of B terms in the MCD spectrum agree well with calculated signs for at least the lowest four transitions. In view of the low symmetry of **1**, this study represents one of the most stringent tests of the PPP model for hydrocarbons performed to date.

We have recently described² the synthesis of the nonalternant hydrocarbon benzo[4,5]cyclohepta[1,2,3-*de*]naphthalene (**1**) (benzo[*a*]pleiadiene) and now wish to report its spectral properties and compare them with those of related hydrocarbons and of the known isoconjugate analogs, benzo[*k*]xanthene³ (**2**) and benzo[*k*]thioxanthene (**3**) (in the form of its 6-methyl derivative⁴). The electronic absorption spectra of



1–3 are complex but bear a certain mutual resemblance (Figure 1). In each, three distinct absorption regions are immediately apparent: (I) 23,800–29,400 cm⁻¹ (log $\epsilon \cong 4$), (II) 31,200–35,700 cm⁻¹ (log $\epsilon \cong 3.8$), (III) near

(1) (a) Université de Metz; (b) Centre de Mécanique Ondulatoire Appliquée; (c) Institut du Radium; (d) University of Utah; (e) A. P. Sloan Fellow, 1971–1973.

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42,000 cm⁻¹ (log $\epsilon \cong 4.6$, with a shoulder at lower wave numbers). Our discussion of the similarity between the three compounds will be based on results of Pariser–Parr–Pople (PPP) type calculations.

Because of the low symmetry of **1**, its π - π^* transition moments can lie anywhere in the molecular plane. Both the experimental determination and quantum mechanical calculation of these directions represent a considerable challenge. Such measurement has only been made for very few conjugated hydrocarbons of C_s symmetry and then usually only for the lowest energy transition. The calculation is likely to be sensitive to the quality of the approximate wave functions used, whereas in the case of more highly symmetrical hydrocarbons it only depends on their symmetry. For molecules of C_s symmetry, little is known about the ability of the common π -electron methods to reproduce transition moment directions. This is not surprising considering the lack of experimental data with which comparison could be made.

We shall use a combination of the stretched sheet and polarized emission methods to determine the experimental polarization directions and the PPP method with a varying extent of configuration interaction for the calculated directions. Problems with parameters ought to be minimized in the case of hydrocarbons (such as **1**).

Finally, we report a calculation of the signs of bands in the MCD spectrum, again using the PPP method. The calculated B terms are obtained from the same wave functions which determine polarization directions, and the fine agreement found for the lowest few transitions increases the degree of confidence one can place in the PPP model.

Experimental Section

Materials. The sample² of **1** was purified by repeated chromatography on a thin layer of silica followed by recrystallization. This removed traces of strongly fluorescent 7,8-dihydrobenzo[4,5]-cyclohepta[1,2,3-*de*]naphthalene which otherwise interfered in emission measurements. The samples of **2** and **3** were obtained as described elsewhere.³⁻⁵ The solvents were spectrograde quality.

Instruments. Room-temperature absorption spectra were measured on a Beckman DB instrument and low-temperature absorption spectra on a Cary 17 instrument using a quartz dewar with Suprasil II windows and a flat quartz sample cell immersed in liquid nitrogen. Emission spectra were measured on a Jobin Yvon spectrofluorometer in EPA solvent (ether-isopentane-ethanol, 5:5:2) and in 3-methylpentane glass at 77°K, using a 1 kW Xe arc, two Schoeffel GM-250 monochromators, two Polacoat polarizing sheets, an S-20 response photomultiplier, and a PAR 124 lock-in amplifier. The emission spectrum was independent of excitation wavelength and did not change in the course of an experiment. The excitation spectrum was independent of monitoring wavelength and followed the details of the absorption spectrum. The sample was contained in a flat quartz tube immersed in liquid nitrogen in a quartz dewar vessel with Suprasil II windows. Front surface excitation was used; the angle between the axes of exciting and collecting optics was 30°. The results were evaluated using well-known formulas.⁶ Low-temperature polarized spectra in stretched polyethylene were measured as described in detail elsewhere.⁷ The stepwise reduction procedure⁸ was used in the determination of the reduction factors b , which characterize the degree of dichroism exhibited by the individual transitions. Within experimental error, all peaks of any given transition had the same b values. This procedure avoids problems due to band overlap and is much preferable to recording the more usual simple dichroic ratio. The evaluation is done by computer plotting the curves $E_{\parallel}(\lambda) - kE_{\perp}(\lambda)$ until a value k is found for a given transition at which its spectral features just disappear, and then $b = k$.

MCD spectra were measured on a Cary 60 instrument equipped with a superconducting magnet.⁹

Calculations

Geometry. The hydrocarbon **1** may be slightly non-planar. The bond between atoms 7 and 8 is essentially a double bond as indicated both by the chemical shift of protons H_7 and H_8 (δ 6.45, compare the aromatic protons in two multiplets centered at δ 7.2 (6 H) and δ 7.5 (4 H)) and by its high reactivity toward osmium tetroxide.² Models indicate that tension in the seven-membered ring is relieved by a slight twist of the naphthalene moiety and displacement of the 7-8 bond above the molecular plane. Similarly, models indicate that **3** probably is not completely planar due to the length of the C-S bond.

Method. Since slight differences in geometry and bond lengths are known^{10,11} to affect results of cal-

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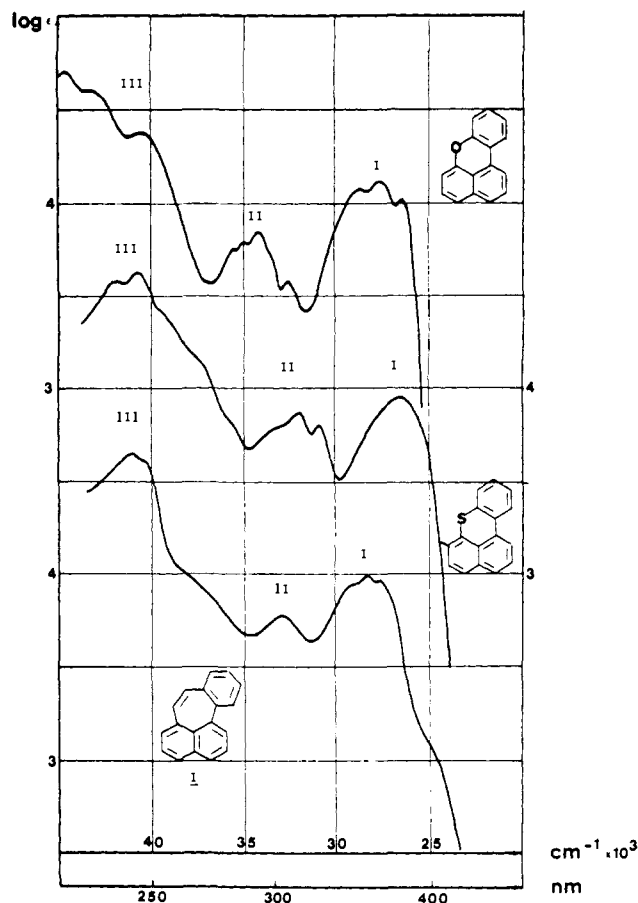


Figure 1. Room-temperature absorption spectrum of benzo[4,5]-cyclohepta[1,2,3-*de*]naphthalene (**1**) and its analogs **2** and **3** in 95% aqueous ethanol.

culations of electronic spectra of large conjugated molecules only insignificantly, and since experimental geometries are not known, we have assumed planar geometries in all calculations (C-C and C-O, 1.40 Å; C-S, 1.74 Å, regular polygons as far as possible). In some of the calculations (type A), the effect of non-planarity in **1** was simulated by reducing the values of resonance integrals β for bonds 6a-7 and 8-8a from -2.39 to -2.0 eV, corresponding to an angle of about 30° estimated from models ($\beta_{CC} = \beta^0 \cos \theta$). In others (type B) the molecule was assumed planar but the bond lengths and β 's were determined from bond orders in an iterative manner using the formula of ref 11, while in still others (types C and D) all β 's were set equal. All of these calculations gave very similar results. The method of calculation was the ordinary version of the PPP procedure, with the following values of one-center integrals W and γ and resonance integrals β . Calculation A: $W_O = -35.50$ eV, $W_C = -11.22$ eV, $W_S = -20.00$ eV, $\gamma_O = 21.55$ eV, $\gamma_C = 10.53$ eV, $\gamma_S = 10.84$ eV, $\beta_{CO} = -2.10$ eV, $\beta_{CC} = -2.39$ eV, $\beta_{CS} = -1.63$ eV. Calculation B: $\beta_{ij} = -2.318 \exp[0.335 \cdot (p_{ij} - 2/3)]$ eV. Calculations C and D: $\beta_{CC} = -2.318$ eV, $W_C = -11.42$ eV. The sulfur parameters were proposed by Fabian, Mehlhorn, and Zahradník.^{12,13} They chose reduced values of W_S and γ_S in order to

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Table I. Calculated Spectra of 1-3^a

	Transition no.										
	1	2	3	4	5	6	7	8	9	10	11
	1, A										
$\bar{\nu}$	26.3	29.0	33.3	36.7	38.2	40	42.8	43.5	44.6		
f_r	0.06	0.48	0.03	0.23	0.07	0.22	0.41	0.17	0.85		
θ_r	37	81	-12	81	31	70	42	-15	37		
	1, D										
$\bar{\nu}$	24.7	29.4	35.2	36.4	39.2	41.1	42.5	44.7	45.3	47.9	48.9
f_r	0.08	0.31	0.02	0.12	0.003	0.26	0.01	0.13	0.04	0.19	1.01
f_p	0.07	0.18	0.01	0.06	0.002	0.16	0.008	0.10	0.03	0.12	0.55
θ_r	46	82	-5	75	46	62	98	63	-25	52	18
θ_p	52	79	1	73	73	59	122	63	-22	57	20
	2, A										
$\bar{\nu}$		30.5	33.5	36.4	38.1	41.9	43.0	45.0	49.3		
f_r		0.55	0.03	0.01	0.03	0.10	0.03	1.48	0.65		
θ_r		85	-40	79	64	51	70	1	80		
	3, A										
$\bar{\nu}$		26.9	31.8	33.4	36.0	38.6	41.5	43.1	45.6		
f_r		0.43	0.05	0.06	0.10	0.31	0.10	0.94	0.69		
θ_r		85	-52	16	81	43	39	4	90		

^a Wave number $\bar{\nu}$ in thousands of cm^{-1} , oscillator strength f and polarization angle θ obtained from dipole length (r) and dipole velocity (p) formulas. The angle θ is measured counterclockwise from the positive direction of the x axis in formulas 1-3. The method of calculation is indicated (A, D).

fit uv spectra. Sulfur d orbitals were ignored. Two-center electron repulsion integrals were obtained from the expression of Mataga and Nishimoto¹⁴ in calculations with a relatively limited extent of configuration interaction (A, B, C) and the Ohno-Klopman expression¹⁵ in the extensive CI calculation (D). Calculations of type A use 16 singly excited configurations, obtained using the highest four occupied and lowest four empty orbitals, and eight doubly excited configurations with at most two singly occupied orbitals, obtained using the highest two occupied and lowest two empty orbitals. Calculations of types B and C use all singly excited configurations with diagonal elements of the Hamiltonian less than 8 eV above that of the ground configuration (35 and 36 configurations, respectively). Calculation D uses 21 singly and 57 doubly excited configurations selected using the SECI-1 procedure described elsewhere.^{16a} These are all singly and doubly excited configurations which can be obtained by exciting from the highest five occupied into the lowest five empty orbitals which satisfy at least one of the following two criteria: (i) their diagonal element of the Hamiltonian is less than 8 eV above that of the ground configuration; (ii) the configuration is doubly excited and has a large off-diagonal matrix element of the Hamiltonian either with the ground configuration or with one of the selected singly excited configurations. An off-diagonal matrix element is considered large if, after division by the difference of the corresponding two diagonal elements, it exceeds 0.05.

A few additional SECI-1 calculations were done with slightly modified cut-off points, including scans of all doubly excited configurations which can be obtained by exciting from the highest six occupied into the lowest

six empty orbitals, but the results were virtually identical.

The calculation of B terms in MCD spectra is described in detail in ref 16b. For transition from ground state $|G\rangle$ to excited state $|F\rangle$

$$B(G \rightarrow F) = \text{Im} \left[\sum_{I, I \neq G} \langle I | \mathbf{u} | G \rangle \langle G | \mathbf{m} | F \rangle \times \langle F | \mathbf{m} | I \rangle / (W_I - W_G) + \sum_{I, I \neq F} \langle F | \mathbf{u} | I \rangle \langle G | \mathbf{m} | F \rangle \times \langle I | \mathbf{m} | G \rangle / (W_I - W_F) \right]$$

where W_I is the energy of state $|I\rangle$ and \mathbf{m} is the electric and \mathbf{u} the magnetic dipole moment operator.

Results and Discussion

Benzo[4,5]cyclohepta[1,2,3-de]naphthalene (1). (a) **Identification of Transitions.** The essentially localized double bond character of the C_7-C_8 bond revealed by experiments² is in line with the calculated values of the bond order which can be used as a measure of delocalization¹⁷ (0.89 from calculations A and C and 0.85 from B and D).

The general features of the calculated spectrum in the low-energy region (Table I) are remarkably independent of the details of the method and extent of CI. However, numerical values of transition energies depend somewhat on such details. In particular, the large CI calculation (method D) gives excitation energies which are too high. This can be traced to a depression of the ground state energy, which is not compensated by an analogous decrease in the energies of excited states, as is understandable, since CI is still rather limited. It might perhaps be corrected by an adjustment of parameters, but this was not considered worthwhile.

The calculated spectrum starts with two transitions at the edge of the visible region, separated by 3000-4000 cm^{-1} . The one at high energy is quite strong and the other is weak. The former can be identified with the strong absorption region near 27,500 cm^{-1} in the

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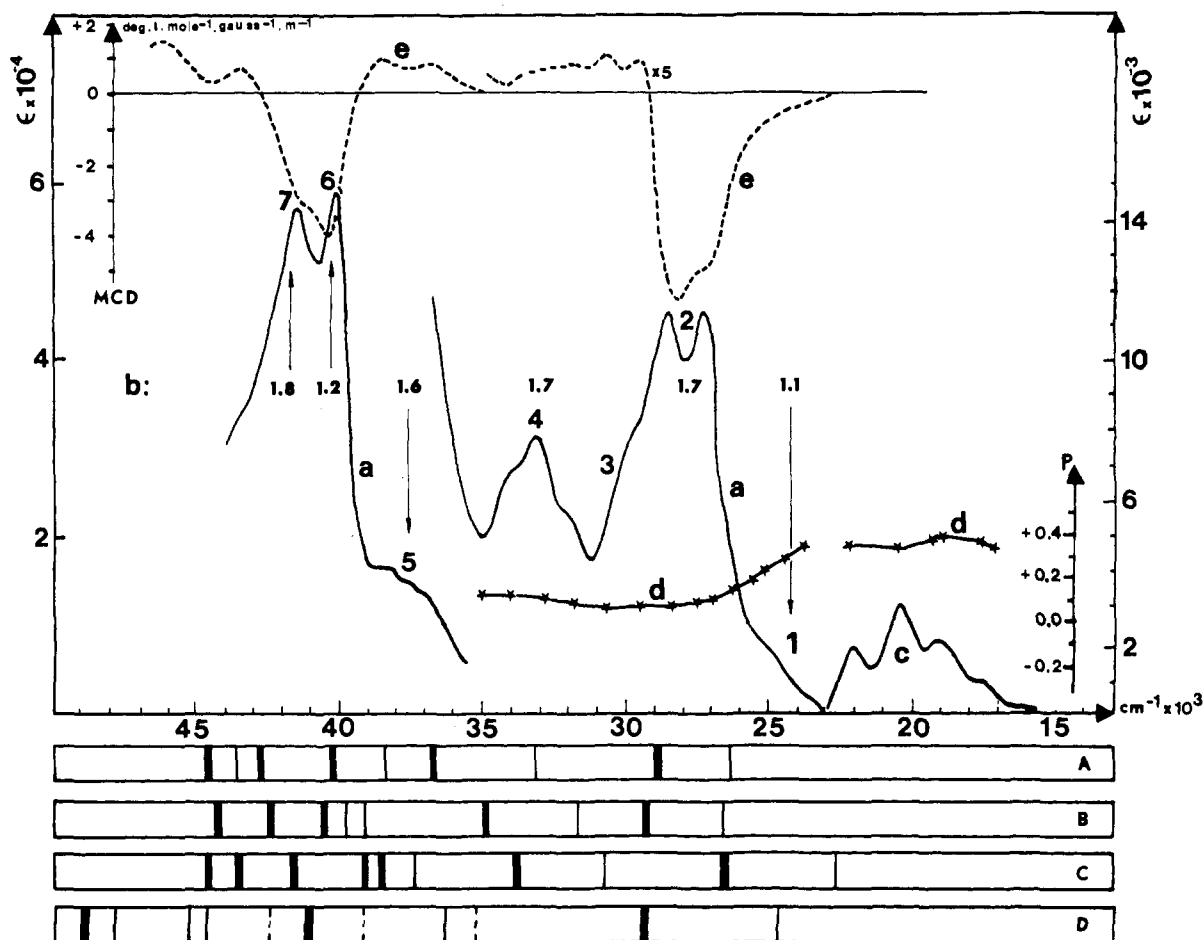


Figure 2. Spectra of benzo[4,5]cyclohepta[1,2,3-*de*]naphthalene. (a) Absorption in 3-methylpentane (3-MP, left scale of ϵ applies to the curve on the left, right scale to the curve on the right) (77°K). (b) Reduction factors for individual bands obtained from linear dichroic absorption in stretched polyethylene (see Experimental Section) (77°K). (c) Fluorescence in 3-MP (relative emission intensity, uncorrected) (77°K). (d) Polarized excitation (monitored at 450 nm) and emission (excited at 426 nm) in 3-MP (degree of polarization P , scale on the right) (77°K). (e) Magnetic circular dichroism absorption in cyclohexane (scale for molar ellipticity per unit field strength shown on the left) (room temperature). Assignment of transitions 1–7, see text. Transition energies calculated by methods A–D are shown at the bottom (thick lines, oscillator strength f above 0.2; solid thin lines, $f = 0.02$ –0.2; dashed lines, f below 0.02).

experimental spectrum previously labeled I, but the assignment of the latter presents a more delicate problem. If it indeed has an experimental counterpart, it could be the weak shoulder at 24,500–25,000 cm^{-1} , most of the band being hidden under the strong band I.

At 77°K the spectrum is better resolved (Figure 2) and agrees well with such a hypothesis. The shoulder has discernible vibrational structure (S_1 , 0–0 at 23,500 cm^{-1} , 0–1 at 25,000 cm^{-1} , $\nu_1 = 1500 \pm 100 \text{ cm}^{-1}$), separate from that of the first strong band (S_2 , 0–0 at 27,000 cm^{-1} , 0–1 at 28,400 cm^{-1} , $\nu_2 = 1400 \pm 50 \text{ cm}^{-1}$). Both bands are shifted 500–800 cm^{-1} to the red with respect to the room-temperature spectra. The large difference in intensity between S_1 and S_2 is now also clearer and makes it likely that they are two separate transitions.

Further evidence is obtained from the emission spectrum (Figure 2). The fluorescence is displaced by almost 1000 cm^{-1} to higher wave numbers on going from room temperature to 77°K. It shows a vibrational progression in $1450 \pm 50 \text{ cm}^{-1}$, in good correspondence to the value 1500 cm^{-1} separating the two weak absorption shoulders suspected to form a part of S_1 . At least five members of the progression are seen indicating that the molecule undergoes a con-

siderable change in geometry on excitation. Indeed, the calculated (method D) bond order of the C_7 – C_8 bond changes from 0.851 to 0.582 upon the $S_0 \rightarrow S_1$ excitation so that it is likely that the length of the bond increases considerably. Thus, a progression in about 1500 cm^{-1} appears entirely reasonable. The overall absorption curve in the 23,000–31,000- cm^{-1} region is far from being a mirror image of the emission. On the other hand, the fluorescence could be a fairly good mirror image of the first absorption band if the detectable part of the latter only comprises the two weak shoulders and the rest is hidden under the strong second transition. The postulate of two separate transitions S_1 and S_2 in the absorption region I shown in Figure 1 thus gains further credibility.

The separation between what appear to be the 0–0 components of the first absorption band (S_1) and the emission is very nearly equal to one quantum of the 1500- cm^{-1} vibration postulated to be responsible for the progressions in each. This suggests that the true 0–0 peaks overlap and that only the 0–1 component in either absorption or emission is seen in the spectrum. However, if such an additional 0–0 peak exists in either absorption or emission, it must be extremely weak since all our attempts at locating it failed. Also, in

EPA solvent the apparent 0-0 component of S_1 shifts by about 800 cm^{-1} to lower wave numbers upon cooling from room temperature to 77°K , while the apparent 0-0 peak of fluorescence shifts by about 1000 cm^{-1} to higher wave numbers, indicating that their low-temperature separation of about 1500 cm^{-1} is coincidental and corresponds to a genuine Stokes shift. This might be related to differences in the degree of nonplanarity of the molecule in various states.

Additional evidence for two separate transitions S_1 and S_2 is obtained from polarization studies. While the degree of polarization of fluorescence is independent of emission wavelength within experimental error (Figure 2), that of fluorescence excitation is highest at the origin of suspected S_1 and then falls off, apparently due to vibronic mixing with S_2 , and remains essentially constant near 0.1 for the higher transitions. Also the degree of linear dichroism in stretched polyethylene is distinctly different in the region of weak absorption (S_1) and the following region of strong absorption (S_2); cf. the values of b in Figure 2. Thus, there is little doubt left about the separate existence of S_1 and S_2 as predicted by the calculations.

Combination of low-temperature absorption, polarized emission, linear dichroism in stretched polyethylene as characterized by b values for individual transitions, and magnetic circular dichroism also permits assignments of higher excited states as indicated in Figure 2.

Transition into S_3 is very weak, as it is calculated to be, and not discernible in absorption, polarized fluorescence excitation, and linear dichroic spectra. However, its location is clearly indicated by the MCD curve which is negative for S_1 and S_2 , approximately following the shape of the absorption curve, and abruptly becomes positive near $29,000\text{ cm}^{-1}$, at least 2000 cm^{-1} above the 0-0 band of S_2 . This is hardly ascribable to vibronic effects within S_2 . The positive contribution of S_3 to the MCD effect must be even larger than it appears to be in Figure 2, since it is undoubtedly partially canceled by the continued negative contribution due to S_2 .

Transition into S_4 is obvious in the absorption spectrum but very poorly developed in the MCD spectrum. The polarization direction agrees with that of the transition into S_3 , judging from polarized fluorescence excitation and linear dichroism in stretched polyethylene. Both this fact and the relative intensity and location of the transition agree with calculations.

Also the transition into S_5 , which is obvious in both absorption and MCD, has a clearly similar polarization direction. Calculations predict several transitions in this region, some with the right polarization, and insufficient spectral resolution does not permit us to rule out the likely possibility that several transitions indeed contribute to what appears to be transition into S_5 . Transitions assigned as 6 and 7 appear to be due to vibrational fine structure of one and the same transition from absorption and MCD spectra alone, but the degree of linear dichroism shows that while the transition assigned to S_7 is polarized approximately in the same direction as those into S_2 and S_4 , that assigned to S_6 is polarized very differently. The very high intensity of S_7 makes a purely vibronic origin for the different polarization unlikely and we prefer to assign

S_6 and S_7 as separate transitions as indicated in Figure 2. Calculations predict several very strong transitions in this spectral region, some of them with correct polarizations. Method D is probably most reliable for these higher transitions, but meaningful comparison with the experimental data is difficult. The additional predicted transitions may exist but have not been discerned in the experimental spectra. Indeed, the shape of the MCD curve, which changes sign near $42,000\text{ cm}^{-1}$, makes this quite likely. A more specific assignment of calculated transitions to the observed transitions into S_5 , S_6 , and S_7 is suggested in the following section but must be considered tentative.

(b) Polarization Directions. The measurements using polarized light are not only useful for identification of individual electronic transitions but also permit an estimate of the absolute polarization directions, using the method of ref 8. For this purpose, one needs an estimate of the orientation factors⁸ K_1 and K_2 which characterize the orientation distribution of the long and short in-plane molecular axes in the anisotropic medium. The values of reduction factors b obtained for the individual peaks in the spectrum (Figure 2) demand that $K_1 \geq 0.47$ and $K_2 \leq 0.36$. The equality sign would hold if one of the observed transitions happened to lie exactly in the effective orientation axis (long axis) of the molecule and if another one lay exactly perpendicular to it (along the short axis).⁸ Since orientation factors for nonpolar molecules in stretched polyethylene are related to molecular shapes, a reasonable approximation can be obtained by inspection of the K values of hydrocarbons of similar shape but sufficiently high symmetry which permits unequivocal determination of their orientation factors. We have used benzo[*c*]phenanthrene and benzo[*ghi*]fluoranthene for this purpose. The former orients slightly worse ($K_1 = 0.52$, $K_2 = 0.29$) than the latter ($K_1 = 0.55$, $K_2 = 0.26$). In the same batch of polyethylene, orientation factors for fluoranthene, which one would expect to orient better than **1**, are $K_1 = 0.60$ and $K_2 = 0.27$.

We conclude that the orientation factors for **1** are likely to lie between the limits $K_1 = 0.5$, $K_2 = 0.3$ and $K_1 = 0.55$, $K_2 = 0.26$. Combining these values with those of b given in Figure 2, using the procedure described in ref 8, and considering probable error limits in the determination of b , one is led to the following values for the angles between polarization directions of transitions in **1** and the effective orientation axis: $\varphi(S_1) = 50-60^\circ$, $\varphi(S_2) = \varphi(S_4) = 20-40^\circ$, $\varphi(S_5) = 30-40^\circ$, $\varphi(S_6) = 45-55^\circ$, and $\varphi(S_7) = 20-35^\circ$. This result can be compared with the observed degree of polarization of the emission (Figure 2), which gives a rough estimate of a $20-50^\circ$ angle between the polarization of the transition into S_1 and those into S_2 and S_4 , using the formula $\cos^2 \alpha = (3P + 1)/(3 - P)$. Thus, we conclude that the polarization directions of the transitions into S_1 , S_2 , and S_4 all deviate in the same sense from the direction of the effective orientation axis.

To proceed further, one needs to estimate the position of the effective orientation axis with respect to the molecular framework. We do not feel that this can be done with confidence for **1**, considering that it most likely deviates from planarity, other than saying that the effective orientation axis ought to lie more or less perpendicular to the smallest molecular cross section

rather than parallel to it. Instead, we shall assume that the polarization angle α of the first transition lies at 50° counterclockwise from the positive sense of the x axis in formula **1**, as suggested by calculations (Table I). Two possible sets of absolute polarization directions α are then compatible with the experimental data, since the deviation angle of the first transition from the effective orientation axis can be either positive or negative. The first solution assumes that the effective orientation axis lies at an angle of about 105° counterclockwise from the positive sense of the x axis in formula **1**. This position appears acceptable considering the shape of the molecule. Then, $\alpha(S_1) = 45\text{--}55^\circ$, $\alpha(S_2) = \alpha(S_4) = 65\text{--}85^\circ$, $\alpha(S_3) = 65\text{--}75$ or $135\text{--}145^\circ$, $\alpha(S_6) = 50\text{--}60$ or $150\text{--}160^\circ$, and $\alpha(S_7) = 70\text{--}85$ or $125\text{--}140^\circ$. The second solution requires the effective orientation axis to lie at an angle of about 175° counterclockwise from the positive sense of the x axis in formula **1** and this appears highly improbable. In this case, the angles α would be $\alpha(S_1) = 45\text{--}55^\circ$, $\alpha(S_2) = \alpha(S_4) = 15\text{--}35^\circ$, $\alpha(S_3) = 25\text{--}35$ or $135\text{--}145^\circ$, $\alpha(S_6) = 40\text{--}50^\circ$ or $120\text{--}130^\circ$, and $\alpha(S_7) = 15\text{--}30$ or $140\text{--}155^\circ$. The relative errors in all values given are believed to be realistic as indicated, but there clearly is uncertainty in the assumed polarization direction of the first transition.

Comparison with calculations (Table I) again strongly favors the first of the above solutions and, moreover, suggests a resolution of the remaining ambiguity for $\alpha(S_3)\text{--}\alpha(S_7)$. The agreement with both calculations A and D is good for the lower transitions: $\alpha(S_1)$, assumed to agree with calculation D; $\alpha(S_2)$, exptl $65\text{--}85^\circ$, calcd 80° ; $\alpha(S_3)$, too weak for experimental determination; $\alpha(S_4)$, $65\text{--}85^\circ$, calcd $73\text{--}81^\circ$.

As already mentioned, the higher transitions are more difficult to assign to the calculated results. Still, the observed polarization directions are at least compatible with calculated angles (method D): $\alpha(S_5)$, exptl $65\text{--}75^\circ$, calcd 60° (overlapping calculated transitions 6 and 8, assuming that 5 and 7 are too weak to be observed); $\alpha(S_6)$, exptl $150\text{--}160^\circ$, calcd 160° (calculated intense transition 11); $\alpha(S_7)$, exptl $70\text{--}85^\circ$, calcd 55° (calculated transition 10, almost degenerate with 11, assuming transition 9 is too weak to be observed).

Considering the crude nature of the PPP model and the difficulties posed by low molecular symmetry, the overall level of agreement represents a pleasant surprise. Since the polarization directions predicted by small CI and SECI-1 (method D) calculations differ very little, we did not consider it necessary to go to the SECI-2^{16a} level. Further confirmation of the reasonableness of the PPP wave functions comes from a consideration of the MCD spectrum.

(c) MCD Spectrum. Because of severe band overlap, only the order of magnitude can be derived for the individual B terms from the MCD spectrum of Figure 2. It is about 10^{-3} (BM D²)/cm⁻¹. However, the signs can be assigned without much difficulty: $B(S_1)$, $B(S_2)$, $B(S_6)$, and $B(S_7)$ are positive (negative MCD peak); $B(S_3)$, $B(S_4)$, and $B(S_5)$ are negative.

As discussed in more detail elsewhere,^{16b} the numerical values of B terms calculated using the PPP model are generally sensitive to details of the calculation, such as choice of parameters and extent of CI, and even depend slightly on the choice of origin unless exact solu-

tions are found (full CI). For the four lowest transitions in **1**, however, the order of magnitude and sign remains independent of such details.

We have calculated them using two different choices of semiempirical electron-repulsion integrals,^{14,15} varying the extent of CI (all singly excited configurations or SECI-1), and placing the origin anywhere inside the carbon skeleton of the molecule. The results were always the same, $B(S_1) > 0$, $B(S_2) > 0$, $B(S_3) < 0$, $B(S_4) < 0$, in perfect agreement with experiment using the band assignment outlined above. In line with the findings of ref 16b, the exact magnitude of the B terms depends on the details of the calculation. It is always near 10^{-3} (BM D²)/cm⁻¹, in agreement with experiment.

Results for the high-energy region of the spectrum are much more equivocal. Many transitions of both signs are predicted, and the results depend on the amount of CI used in the calculation. Assuming as above that the SECI-1 results are most likely to be meaningful, and assigning again calculated transitions 5–8 to S_5 , we would predict $B(S_5) < 0$, since the sum of the calculated B terms for transitions 5–8 is clearly negative. This agrees with experiment. Some positive calculated B terms follow and the experimental curve indeed changes sign in going to S_6 and S_7 , but we do not think that the calculated B terms can be physically meaningful in this energy region and further agreement with experiment undoubtedly is due to sheer coincidence.

The excellent agreement found in the lower energy region, however, is very heartening in view of the fairly complicated nature of the formula for B , which depends sensitively on the nature of ground and excited state wave functions as well as energies,^{16b} and indicates that the PPP model performs very well. This also lends more credence to the assumption made in the preceding section, namely, that the calculated and experimental polarization direction for the first transition coincide.

Benzo[*kl*]xanthene (2) and Benzo[*kl*]thioxanthene (3). Table I shows that the calculated spectra of **2** and **3** begin with a strongly allowed transition ($f = 0.5$). This is the most striking difference between the results for **1** and its heterocyclic derivatives **2** and **3**. The difference can be understood if one refers to Figure 3 which shows the molecular orbitals of **1**, **2**, **3**, and 1-phenylnaphthalene. The energy separation between the virtual orbitals 10 and 11 in benzo[3,4]pleiadene (**1**) (0.26 eV) is much smaller than the corresponding separations in the other three compounds (1.33 eV on the average). Indeed, while the S_1 of **1** originates in a mixture of configurations $9 \rightarrow 11$ and $9 \rightarrow 10$, the S_1 of **2**, **3**, and 1-phenylnaphthalene is represented by almost pure $9 \rightarrow 10$ excitation (90%). In this respect, the heterocyclic compounds are much closer to 1-phenylnaphthalene than to **1**.

A comparison of these results with those for pleiadene¹⁸ **6**, benzopleiadene^{18b} **7** and **8**, and pleiadene^{18b-20} **5** gives an overview of the behavior of the first bands in this series of pericondensed compounds. This is shown

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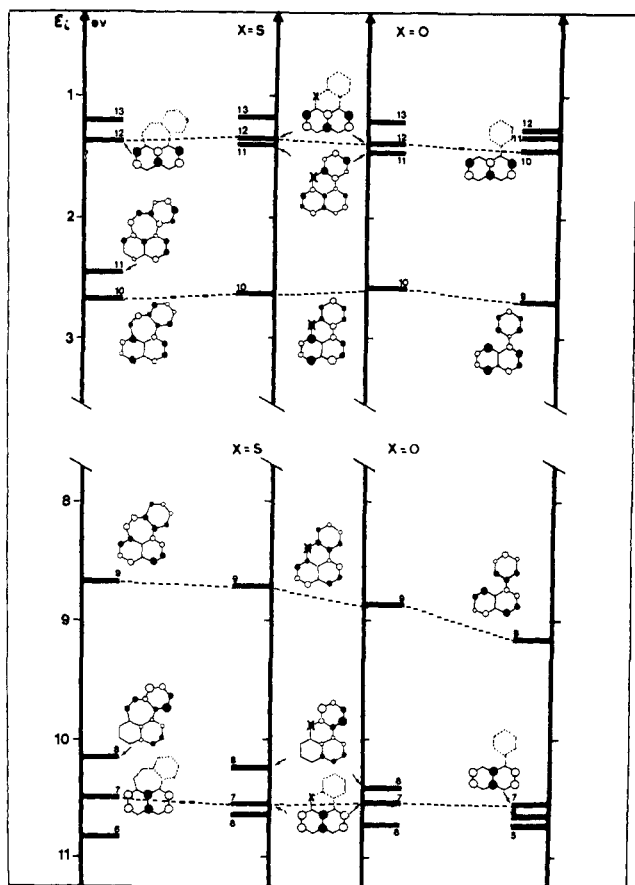


Figure 3. Schematic representation of the frontier π -electron SCF molecular orbitals of 1, 2, 3, and phenyl-naphthalene.

in Figure 4 which combines the experimental results with indicated vibrational structure above the respective calculated results. This figure suggests a classification of these pericondensed compounds in two distinct classes. The first contains the heterocycles, similar to 1-phenylnaphthalene, with the first transition strong and polarized along the naphthalene short axis (Clar's "p" type). Increased conjugative ability of the heteroatom shifts the band to lower wave numbers ($S > O$). The second class comprises the pleiadienes. Unlike the former, it is characterized by two bands in the visible ($10,000$ – $30,000$ cm^{-1}). The position of one of these (II) is almost constant near $27,000$ cm^{-1} . Its polarization along the naphthalene short axis and its oscillator strength and experimental extinction coefficient ($\log \epsilon \cong 4$) are reminiscent of the naphthalene "p" band. The other band (I) is characteristic of the pleiadienes. Its position changes from $10,000$ cm^{-1} for benzopleiadene (7) to $24,500$ cm^{-1} for benzo[3,4]-pleiadene (1). Its extinction coefficient is between 200 and 1000 and its calculated polarization is along the long axis of the naphthalene moiety except in the dissymmetrical benzo[3,4]pleiadene.

Using the perturbation approach LCMO²¹ one can rationalize⁵ the behavior of the highest occupied and two lowest empty molecular orbitals along this series of molecules and thus arrive back at one of the conclusions published in 1952 by Pullman and collaborators;²² the energy of the first absorption band should

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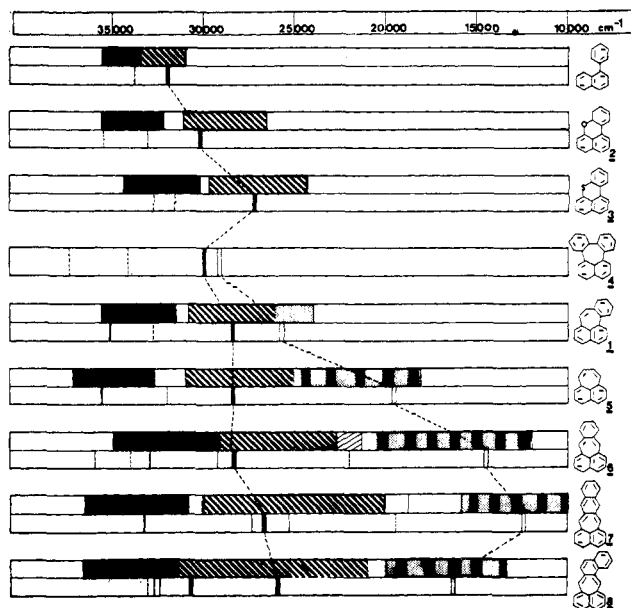


Figure 4. Correlation of experimental and calculated electronic spectra of 1-phenylnaphthalene, the pleiadienes, and their heterocyclic analogs. For each compound, the shaded areas in the upper part indicate the width of the principal absorption bands (with band maximum at center), as well as the vibrational structure. The lower parts show the calculated energies of vertical transition f (thick lines, f above 0.25; thin lines, $f = 0.04$ – 0.25 ; dashed lines, f below 0.04). The first transition of the pleiadienes is indicated by a double line.

increase in the series pleiadene (6) < pleiadene (5) < benzo[3,4]pleiadene (1) < dibenzo[1,2,3,4]pleiadene (4).

Conclusion

It has been possible to discern the lowest four singlet-singlet transitions in the absorption spectrum of 1 using a suitable combination of spectroscopic methods and to identify more tentatively three additional regions of absorption which probably correspond to several overlapping transitions each. Energies, intensities, polarization directions, and signs of B terms have been determined and found to agree well with PPP calculations. The quality of the agreement deteriorates as one proceeds from lower to higher transitions.

In order to tie down the relative polarization directions to the molecular framework and make them absolute, it was necessary to assume that the direction of one of them agrees with that calculated (the lowest energy one). As more information about solute orientation in stretched polymers becomes available, it may become possible to remove this assumption.

It is worth noting that the comparison of measured polarization directions and B terms of a low-symmetry molecule such as 1 with those calculated is one of the most stringent tests to which the wave functions of the simple PPP model have ever been subjected. The model has certainly passed with flying colors.

Finally, while 1 can be integrated logically into the series of the pleiadienes, it has a distinguishing feature; S_1 and S_2 result from a mixing of configurations due to the proximity of the two lowest empty orbitals. Calculations predict similar proximity in the so far unknown dibenzopleiadene 4. In 4, the separation between S_1 and S_2 should be even smaller (Figure 4),

the experimental bands should be completely superimposed, and the spectrum should resemble those of **2** and **3**. The principal point of resemblance between the pleiadienes **1** and **4-8** on the one hand and their heterocyclic analogs **2** and **3** on the other is the constancy of the location of the first strong band at $27,000 \pm 500 \text{ cm}^{-1}$. Since the band seems to be somewhat related to the short-axis polarized "p" band of naphthalene, this indicates that the sulfur atom in the peri position causes similar transverse conjugation as a double bond. Nevertheless, any further spectral analogy appears fortuitous or missing altogether, and this

shows the limitations of the notion of isosterism. Thus, the apparent similarity of the spectra of **1**, **2**, and **3** is much more complex than the simple concept of isosterism would lead one to believe.

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Arrival Time Distributions in High-Pressure Mass Spectrometry. IV. Origin of Linear van't Hoff Plots under Nonequilibrium Conditions in Chemical Ionization Studies of Reversible Ionic Reactions¹

G. G. Meisels,* G. J. Sroka, and R. K. Mitchum

Contribution from the Department of Chemistry, University of Houston, Houston, Texas 77004. Received August 18, 1973

Abstract: Arrival time measurements in the water system confirm earlier suggestions that, under typical operating conditions, equilibrium in proton hydration is not achieved within the average residence time of ions in chemical ionization sources. Previous evidence cited to support the establishment of equilibrium, the independence of results of water concentration, and the linearity of van't Hoff plots can be understood quantitatively on the basis of a model which recognizes the temperature dependence of ion residence times in the source and derives the apparent equilibrium constant from its operational definition using the kinetics of sequential or of opposing quasi-first-order reactions.

The study of ionic equilibria in the gas phase has received considerable attention during the past few years because of its ability to provide heats of reaction of gaseous ions,²⁻¹³ including those defining intrinsic acidities and basicities, and a better understanding of the solvation process. One system of great interest and

fundamental importance is the hydration of the proton.^{2a,3,5,6,11,12,14} Early investigations based on ion sampling from a field free source at approximately atmospheric pressure^{2,3} led to heats of hydration which were in reasonable agreement with each other, with heats of reaction measured by a collisional detachment technique,¹⁵ and with theoretical calculations based on *ab initio* considerations.¹⁶ However, in a series of extensive investigations using chemical ionization techniques and hydrocarbons as major constituents, under conditions where pressure was on the order of a few Torr and small extraction fields were present, a set of heats of reaction was derived which differed sharply from those reported earlier for the first two hydration steps.^{6,11} The discrepancy is particularly perplexing because independence of water concentration and linearity of van't Hoff plots were unquestionable, and these are frequently accepted as indicators of achievement of equilibrium.

We report here why these criteria are insufficient evidence for the attainment of equilibrium in chemical ionization sources and present a partial resolution of the discrepancies.

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