

- panion paper in this issue (part 13).
 (14) W. Gerhartz and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 14).
 (15) E. Bergmann and M. Orchin, *J. Am. Chem. Soc.*, **71**, 1917–1918 (1949); A. Sieglitz, H. Tröster, and P. Böhme, *Chem. Ber.*, **95**, 3013–3029

- (1962).
 (16) A. Streitwieser, Jr., and S. Suzuki, *Tetrahedron*, **16**, 153–168 (1961).
 (17) M. J. S. Dewar and J. Michl, *Tetrahedron*, **26**, 375–384 (1970).
 (18) A. Castellan and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 4).

Magnetic Circular Dichroism of Cyclic π -Electron Systems. 18.¹ Benzofluoranthenes

Mark A. Souto, Dale Otteson, and Josef Michl*

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received November 28, 1977

Abstract: The magnetic circular dichroic spectra of benzo[*b*]-, benzo[*j*]-, and benzo[*k*]fluoranthenes are reported and analyzed, and the low-energy region is found to be in good agreement with the simple theory of parts 1–3 and with standard PPP calculations. Predictions are made for benzo[*a*]fluoranthene. The results further substantiate the claim that fluoranthene can be viewed as a negative-hard MCD chromophore with one soft transition. Previously reported anomalies in the relation of orbital energies to excitation energies in the family of fluoranthene-like hydrocarbons are rationalized.

Introduction

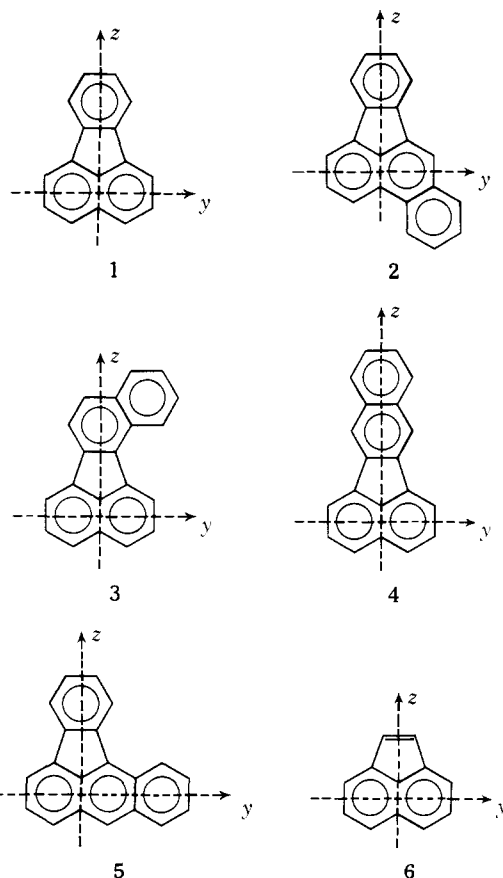
Low-lying excited singlet states of fluoranthene (**1**) are understood in fair detail.^{1–3} In the present study, we explore their response to benzo annelation leading to benzo[*b*]fluoranthene (**2**), benzo[*j*]fluoranthene (**3**), and benzo[*k*]fluoranthene (**4**) and make some predictions for benzo[*a*]fluoranthene (**5**). Our results on the less directly related benzo[*ghi*]fluoranthene are being published separately.^{4,5}

Ordinary absorption curves of **2–4** have been reported and some band assignments proposed.⁶ The spectral shapes are compatible with results of Hückel^{7,8} and Pariser–Parr–Pople^{9–11} (PPP) type calculations. Detailed comparison could not be performed for lack of more detailed experimental information, except for the case of **4**, where measured polarization directions were found to agree with those calculated.¹¹ Some interesting systematic discrepancies in the Hückel correlation were noted⁸ and a simple explanation for these will be proposed presently.

In measuring magnetic circular dichroism (MCD) of **2–4**, we have two objectives: first, to provide a safer assignment and better characterization of individual electronic transitions in the spectra of these simple representatives of the family⁸ of fluoranthene-like hydrocarbons, hopefully securing a firmer basis for the recently proposed¹² correlation of low-lying excited states in this large group of nonalternants with those of acenaphthylene (**6**) and naphthalene; second, to correlate the excited states of **2–5** with the states of their [19]annulene perimeter and to contribute to the testing of the predictive power of the simple theory described in detail in parts 1–3 of this series of papers¹³ and, in particular, of the concept of “hard” MCD chromophores.

Experimental Section and Calculations

The samples were gifts from Professor M. W. Windsor (Washington State University, Pullman, Wash.), Professor M. Zander (Rütgerswerke AG, Castrop-Rauxel, Germany), and Dr. E. Koch (Technische Universität, Braunschweig, West Germany) and were used as received. Their UV absorption spectra (Cary 17 spectrophotometer) agreed with those published.⁶ Experimental procedures for recording and evaluating the spectra and details of the PPP calculations performed are described in part 4.¹⁴ In the case of **4**, decomposition of overlapping MCD bands needed for evaluation of their *B* terms was aided by comparison with published polarized spectra;¹¹ in other cases it was guessed.



Results

Spectral Interpretations. Parent Systems. Before discussing the assignment of transitions in the spectra of **2–4**, we shall summarize the available information on singlet–singlet transitions in the parent species **6**^{15,16} and **1**.^{1–3} In both **1** and **6**, as well as other related hydrocarbons, three low-energy transitions can be discerned.¹² The first of these, transition K, is weak, Franck–Condon forbidden, *y* polarized in formulas **1** and **6**, and weakly positive in the MCD spectrum. The next one, labeled L, is strong, Franck–Condon allowed, *z* polarized, and strongly positive in MCD. The third, M, is strong, Franck–

Condon allowed, y polarized, and negative in MCD. In the sum-over-states language, the MCD B terms are expressed as follows:^{5,17}

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

$$B_{I, G}^F = \text{Im} \{ \langle I | \hat{M} \mu | G \rangle \cdot \langle G | \hat{M} | F \rangle \times \langle F | \hat{M} | I \rangle / (W_I - W_G) \}$$

$$B_{I, F}^G = \text{Im} \{ \langle F | \hat{M} | I \rangle \cdot \langle G | \hat{M} | F \rangle \times \langle I | \hat{M} | G \rangle / (W_I - W_F) \}$$

$$B_{F, G}^F + B_{G, F}^F = \text{Im} \{ \langle F | \hat{M} | G \rangle \cdot \langle G | \hat{M} | F \rangle \times (\langle F | \hat{M} | G \rangle - \langle G | \hat{M} | G \rangle) / (W_F - W_G) \}$$

\hat{M} and $\hat{\mu}$ are the magnetic and electric dipole moment operator, respectively, W_A is energy of state A, and the summations run over all electronic states except as indicated. In the cases discussed presently, the contributions $B_{I, F}^G$, due to the magnetic mixing of excited state I into the final state F, are calculated to dominate the B term. Clearly, $B_{A, B}^B = -B_{B, A}^A$. Also, if transitions $G \rightarrow A$ and $G \rightarrow B$ have the same polarization, $B_{A, B}^B = B_{B, A}^A = 0$.

In **6**, the mixing terms which dominate the MCD signs of bands K, L, and M are $B_{K, L}^K = -B_{L, K}^K$, which is small and positive, and $B_{M, L}^M = -B_{L, M}^M$, which is large and negative. Then, $B(K) \approx B_{L, K}^K < 0$ (small), $B(L) \approx B_{K, L}^K + B_{L, M}^M < 0$ (large), and $B(M) \approx B_{L, M}^M > 0$ (large). Mixing with higher energy states is of secondary importance, while mixing with the ground state reinforces the small negative B term of transition K. In parts 16¹⁶ and 17¹⁷ a correlation of the L and M states of **1** and **6** with the degenerate states of their respective perimeters, L_1 and L_2 , was proposed and tested against the observed MCD signs.

The K, L, and M states of **1** correlate with the K, L, and M states of **6**. There is an additional low-lying very intense transition in **1** near 33 000 cm^{-1} which also appears in the spectra of **2-4** and other fluoranthene-like hydrocarbons and deserves a label for easy reference. We shall refer to it as transition N. It is distantly related to transition 4 in **6** and corresponds to a complicated charge exchange between the benzene and naphthalene moieties in **1**.

The presence of transition 4 has little effect on the first three B terms in **6**, but the analogous transition N affects the MCD spectrum of **1** where it is much more intense, by providing an additional important term, $B_{N, N}^N > 0$. This, as well as mixing with higher energy states, makes $B(N)$ strongly positive in **1** and all of its derivatives studied so far. $B_{K, L}^K$ (small and positive) and $B_{M, L}^M$ (large and negative) are still close to what they were in **6**, so that $B(K) \approx B_{L, K}^K < 0$ (small) and $B(L) \approx B_{K, L}^K + B_{L, M}^M < 0$ (large). Now, however, $B(M) \approx B_{L, M}^M + B_{N, M}^M$ consists of two important opposing contributions. $B_{L, M}^M$ is large and positive, as in **6**, but the newly important $B_{N, M}^M$ is negative. In **1** itself and in many substituted derivatives, the former still dominates, and $B(M)$ is positive though smaller in absolute magnitude than $|B(L)|$. In some derivatives,¹ however, the latter prevails and $B(M) < 0$. Thus, transition M is "soft", i.e., its MCD sign is sensitive to perturbations.

Spectral Interpretations. The Benzo Analogues. A proposal for identification of electronic transitions in **2-4** is shown in Figures 1-3 and is based on comparison of their UV absorption and MCD curves and on analogy to **1**. The identification is believed to be quite unambiguous for the first four transitions but becomes tenuous at higher energies. It is quite likely that more transitions are actually present than are shown. A summary of our assignments is given in Table I.

In benzo[*k*]fluoranthene (**4**, Figure 1), in which polarization directions are known,¹¹ assignment of the observed excited states is straightforward. The long-axis-polarized strong first absorption band is red-shifted considerably in comparison with **1** and clearly corresponds to the L state of **1**. Underneath is presumably buried the weak K band, for which we find no

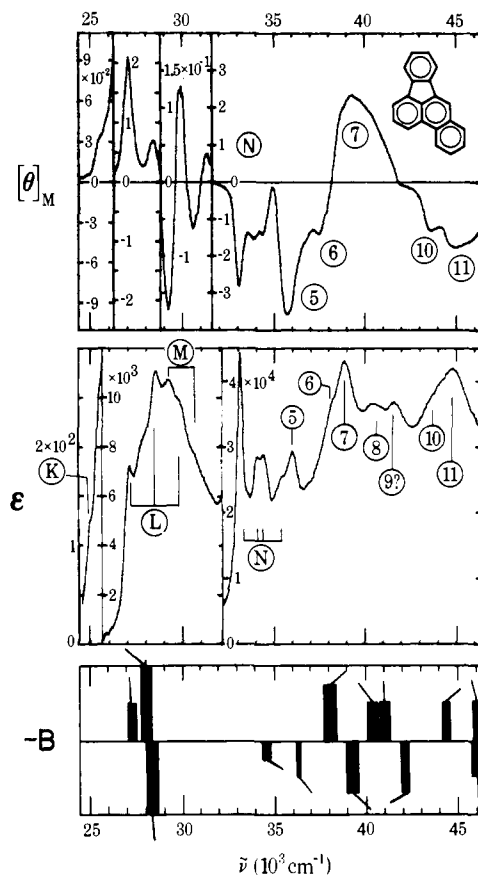


Figure 1. Benzo[*b*]fluoranthene: top, MCD spectrum (deg. L. $\text{mol}^{-1} \text{m}^{-1} \text{G}^{-1}$); center, absorption spectrum (cyclohexane); bottom, calculated values of $-B$ in units of $10^{-3} \beta_c \text{ D}^2/\text{cm}^{-1}$ ($|B| < 1$, shortest lines; $1 < |B| < 10$, medium lines; $10 < |B| < 50$, medium-long lines; $|B| > 50$, longest lines). Calculated oscillator strengths f (dipole length) are shown: thin lines, $f < 0.02$; medium lines, $0.02 < f < 0.2$; thick lines, $f > 0.2$. The shoulder at 25 000 cm^{-1} corresponds to the 0-0 peak of the first transition as verified by its coincidence with the first peak in fluorescence. Polarization directions are given as directions of flags at the end of each bar, measured from the y axis as in formula 2.

experimental evidence. The short-axis-polarized M band is at the same location as in **1** itself. It is much more obvious in the MCD than in the absorption spectrum but is also clearly present in the polarized spectra.¹¹ The very intense long-axis-polarized N band is also unmistakable. At higher energies, correlation with states of **1** is not obvious, but there is a very nice correspondence between the MCD spectrum and the published¹¹ polarized spectra.

The MCD signs of transitions L, M, and N indicate that the signs of the mixing contributions $B_{L, L}^L < 0$ and $B_{N, M}^M < 0$ are the same as in **1**. The magnetic mixing of states M and L is likely to have a somewhat weaker effect here than in **1**, since they are further apart in energy, but still makes $B(L)$ negative. Its contribution to $B(M)$ is positive but is overwhelmed by the greatly increased magnitude of $B_{N, M}^M$. Thus, $B(M) \approx B_{L, M}^M + B_{N, M}^M < 0$. The increase in magnitude of $|B_{N, M}^M|$ on going from **1** to **4** can be attributed at least in part to the greatly decreased separation of the M and N transitions and the increased oscillator strength of the latter.

In benzo[*b*]fluoranthene (**2**, Figure 2) and benzo[*j*]fluoranthene (**3**, Figure 3), polarization directions have not been measured, and correlation of the observed transitions with those of **1** is necessarily less certain. Fortunately, in both instances four transitions appear to be clearly present in the spectral region which in **1** contains transitions K through N, and band shapes and relative intensities suggest very strongly that their order is K, L, M, N, just as in **1** itself. Adopting this

		transition													
		L	K	3	M	N	6	7	8	9	10	11	12	13	
4	exptl	<i>E</i>	24.9			29.7	32.6	37.1		40.7		39.7		46.0	48.2
		<i>f</i>	0.21			0.009	0.83			0.69		0.50		>0.8	
		pol ^e	<i>z</i>			<i>y</i>	<i>z</i>	<i>z</i>		<i>z</i>		<i>y</i>			
	calcd	<i>B</i>	-0.5			-2	+6			-3		+3		-0.6	>1
		<i>E</i>	25.7	28.3	30.7	32.1	32.3	37.1	39.5	40.7	41.8	42.1	43.3	43.9	46.1
		<i>f_r</i>	0.54	0.00001	0.0020	0.18	0.75	0.26	0.00005	0.69	0.28	1.12	0.019	0.30	0.05
		<i>f_p</i>	0.23	0.00009	0.00041	0.032	0.35	0.16	0.00035	0.43	0.15	0.45	0.0083	0.19	0.013
		pol	<i>z</i>	<i>y</i>	<i>y</i>	<i>y</i>	<i>z</i>	<i>z</i>	<i>y</i>	<i>z</i>	<i>z</i>	<i>y</i>	<i>y</i>	<i>z</i>	<i>y</i>
		<i>B</i>	-1	-0.04	-0.7	-200	+200	+4	-0.1	-2	+3	-7	-3	+4	+0.1
		<i>B</i> _{1,G} ^F		<i>B</i> _{M,L} ^L = -1.8	<i>B</i> _{L,K} ^K =	<i>B</i> _{L,3} ³ = -0.8	<i>B</i> _{N,M} ^M =	<i>B</i> _{M,N} ^N							
		<i>B</i> _{1,F} ^F			-0.03		-180	=							
								+180							
				<i>B</i> _{K,G} ¹ = -0.9		<i>B</i> _{N,3} ³ = +0.4									
				<i>B</i> _{3,L} ^L = +0.8											
<i>φ</i> _{i→j}	1 → -1 (85%)	2 → -1 (72%)	4 → -1 (35%)	1 → -2 (60%)	2 → -2 (47%)	3 → -1 (27%)									

		transition													
		K	L	M	N	5	6	7	8	9	10	11	12	13	
5	calcd	<i>E</i>	22.1	24.7	28.2	32.5	34.9	36.9	37.4	38.2	39.0	41.3	43.8	44.3	44.6
		<i>f_r</i>	0.33	0.21	0.080	0.012	0.068	0.077	0.82	0.55	0.30	0.91	0.027	0.45	0.069
		<i>f_p</i>	0.066	0.055	0.031	0.002	0.018	0.043	0.42	0.24	0.19	0.42	0.014	0.26	0.037
		<i>α_r</i>	105	86	4	121	76	37	169	160	143	35	146	79	75
		<i>α_p</i>	114	92	3	169	84	37	164	158	142	38	150	84	72
		<i>B</i>	-5	-3	+6	+0.3	+2	-9	+7	-3	+7	-8	+3	+3	+0.7
		<i>B</i> _{1,G} ^F		<i>B</i> _{G,K} ^K	<i>B</i> _{G,L} ^L +	<i>B</i> _{K,M} ^M =	<i>B</i> _{7,N} ^N =								
		<i>B</i> _{1,F} ^F		<i>B</i> _{K,G} ^K	<i>B</i> _{L,G} ^L	+3.4	+0.47								
				= -1.4	= -1.0										
				<i>B</i> _{M,K} ^K = -3.4	<i>B</i> _{M,L} ^L = -2.9	<i>B</i> _{1,M} ^M =	<i>B</i> _{8,N} ^N =								
						+2.9	-0.38								
				<i>B</i> _{L,K} ^K = -1.1	<i>B</i> _{K,L} ^L = +1.1		<i>B</i> _{M,N} ^N =								
							+0.26								
	<i>φ</i> _{i→j}	1 → -1 (77%)	2 → -1 (69%)	3 → -1 (54%)	4 → -1 (70%)										

^a Experimental energies of 0-0 transitions *E* were estimated from MCD and UV spectra (25 °C), *f* is experimental oscillator strength and *B* is the measured *B* term in units of $10^{-3}\beta_e D^2/\text{cm}^{-1}$. Calculated oscillator strengths *f_r* and *f_p* and polarization directions *α_r* and *α_p* in degrees from the *y* axis shown in formulas 1-5 were calculated from dipole length (*r*) and dipole velocity (*p*) formulas. The *B* terms ($10^{-3}\beta_e D^2/\text{cm}^{-1}$) were calculated with the origin approximately in the center of the molecule and depended very little on its exact location within the molecule. Weights of dominant configurations *φ*_{i→j} in percent and magnitudes of the most important contributions *B*_{1,G}^F and *B*_{1,F}^F to the *B* term *B*(*F*) are given. ^b Data taken from ref 2. ^c Calculation c from ref 2. ^d 0-0 energy as verified by fluorescence emission and fluorescence excitation spectra in 3-methylpentane at 77 K. ^e Polarization directions from ref 11.

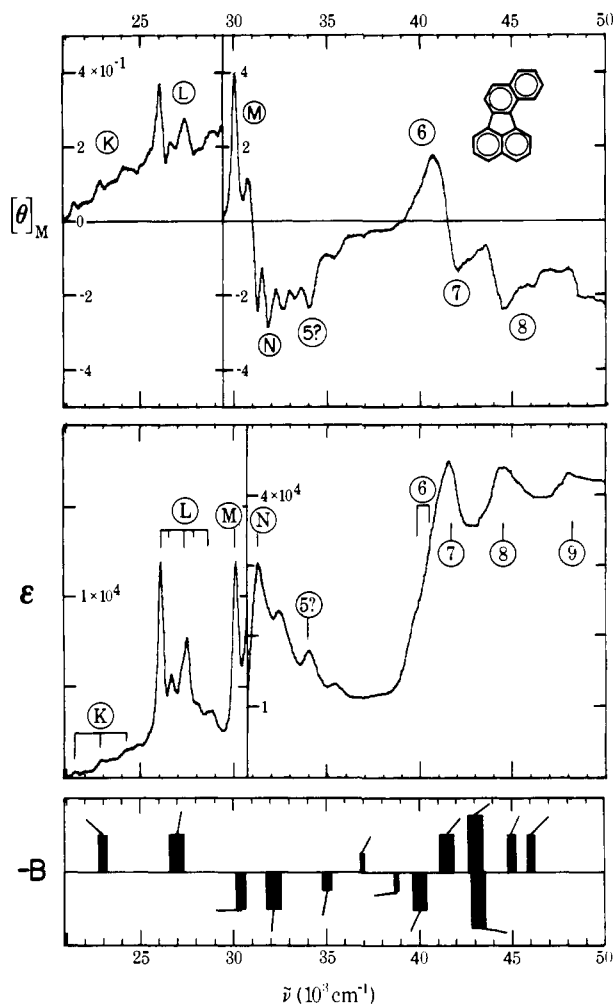


Figure 2. Benzo[*j*]fluoranthene: top, MCD spectrum; center, absorption spectrum (cyclohexane); bottom, calculated values of $-B$ in units of $10^{-3}\beta_e D^2/\text{cm}^{-1}$ ($|B| < 0.5$, short lines; $0.5 < |B| < 5$, medium lines; $|B| > 5$, long lines). Calculated oscillator strengths and polarization directions are shown (see caption to Figure 1).

assignment, the MCD signs again show that the signs of magnetic mixing contributions $B_{i,F}^F$ are still the same as in **1**, $B_{L,K}^L < 0$, $B_{M,L}^L < 0$, and $B_{N,M}^M < 0$. In **2**, their relative magnitudes are as in **1**, so that the signs of $B(L)$ and $B(M)$ are dominated by $B_{L,M}^M$: $B(K)$, $B(L) < 0$ and $B(M)$, $B(N) > 0$, exactly as in **1**. The opposing contributions of $B_{L,M}^M$ and $B_{N,M}^M$ to $B(M)$, however, are even more nearly balanced than in **1**. In **3**, the balance is reversed: $B(M) \approx B_{L,M}^M + B_{N,M}^M < 0$. In this respect, **3** is similar to **4** and the reason can again be seen at least in part in the considerably decreased separation of the M and N bands and increased separation of the L and M bands. The negative signs of $B(K)$ and $B(L)$ remain the same as in **1**, indicating again that $B_{L,K}^L < 0$ (small) and $B_{M,L}^L < 0$ (large).

To summarize, we feel that labels in Figures 1-3 and Table I contain a reasonable identification of electronic states which correlate with the K, L, M, and N states of **1**. In addition, we propose that the signs of contributions $B_{i,F}^F$ of mutual magnetic mixing of these four states keep their signs on going from **1** to **2**, **3**, or **4**, in agreement with the concept of a "hard" chromophore.¹³ The MCD signs of transitions K, L, and N, which are dominated by a single contribution or several contributions of like signs, remain the same for all four hydrocarbons and are likely to remain the same even in other members of the fluoranthene family of hydrocarbons (transition K is not observed in **4**). On the other hand, the MCD sign of transition M, de-

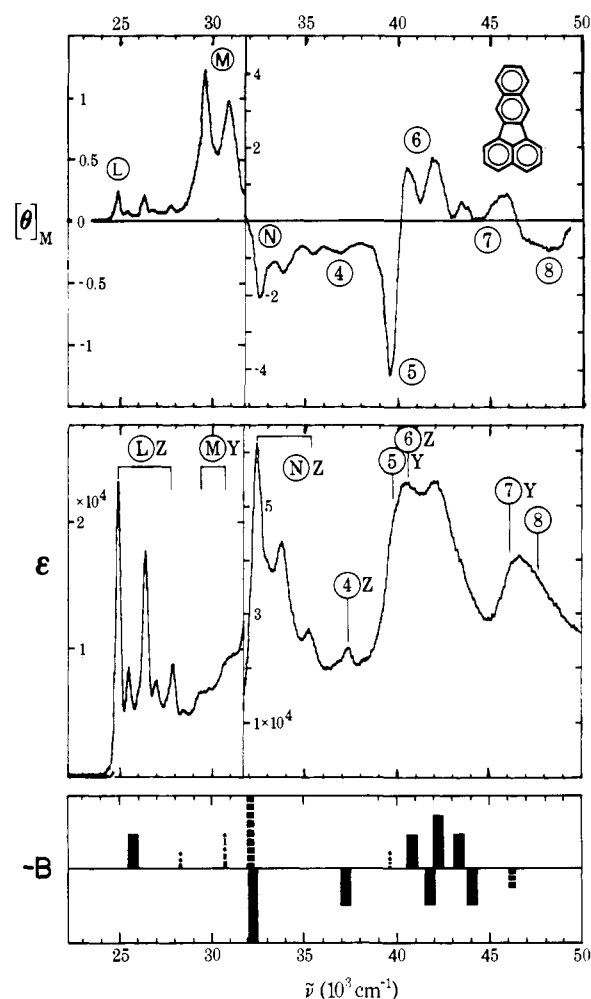


Figure 3. Benzo[*k*]fluoranthene: top, MCD spectrum; center, absorption spectrum (cyclohexane); bottom, calculated values of $-B$ in units of $10^{-3}\beta_e D^2/\text{cm}^{-1}$ ($|B| < 0.5$, shortest lines; $0.5 < |B| < 5$, medium-short lines; $5 < |B| < 50$, medium-long lines; $|B| > 50$, longest lines). Solid (dashed) lines are z (y) polarized in formula **4**. Calculated oscillator strengths are shown (see caption to Figure 1).

termined by two opposing contributions of comparable magnitude, represents a "soft spot" on the otherwise "hard" sign sequence and is easily affected by factors such as relative energy separation of transitions L and M on the one hand and M and N on the other. The "softness" of transition M has already been noted in an investigation¹ of substituent effects on **1**.

Discussion

Comparison with Qualitative Theory. Similarly as **1** and **4**, benzofluoranthenes are peri-condensed hydrocarbons with a $(4N + 3)$ -annulene perimeter. As discussed in more detail in ref 16, such chromophores should tend to be negative-hard, i.e., the magnetic mixing of their L_1 and L_2 states should contribute a negative amount to the B term of the lower of these transitions and a positive amount to the B term of the higher one. Since L correlates with the L_1 state and M with the L_2 state of the perimeter,¹⁶ this agrees with the present experimental results and PPP calculations. On the other hand, peri-condensed hydrocarbons with a $[4N + 1]$ annulene perimeter, such as the benzo annelated pleiadienes whose MCD signs are discussed in ref 12, should generally tend to be positive-hard, again in agreement with observations.

Because of the only rather remote relation of other states of the benzofluoranthene to the states of the corresponding annulene, it does not appear profitable to discuss their MCD

signs in terms of the qualitative notions of parts 1–3.¹³

Comparison with PPP Calculations. The agreement for transition energies and relative intensities is quite respectable for the lowest half-dozen transitions or so which can be more or less unequivocally recognized in the spectra. At higher energies, numerous transitions overlap, and comparison of calculated with experimental spectra becomes very difficult. The MCD signs are predicted correctly for K, L, and N transitions, as well as some of the higher ones. It is likely that the signs of *B* terms calculated in the higher energy region have little meaning, because too many $\pi\pi^*$ states lie close in energy, because multiply excited configurations have not been considered, and because mixing with other types of states may become more important ($\sigma\pi^*$, etc.). The *B* term of the M transition, consisting of two opposing contributions, is particularly difficult to calculate. Our result is correct in the case of **2** and **4**, but wrong in the case of **3**.

Most numerical values of computed *B* terms are much too large, at least partly since they are based on dipole lengths which are well-known to be overestimated at the SCI (singly excited CI) level used here, occasionally since energy differences are underestimated, and perhaps also because considerable overlap of the observed MCD bands causes some of the measured *B* values to be underestimated. Origin dependence of the results is very small and causes no practical difficulty.

Table I also presents calculated results for benzo[*a*]fluoranthene, **6**, for which no MCD measurements are available at this time. The calculated transition energies and relative intensities are in reasonable agreement with the shape of the published⁶ absorption curve. The calculation suggests that the M band still keeps its individuality and corresponds closely to the M bands in **1** and **6**. However, the K and L transitions are mixed and have similar polarizations. They both derive their calculated MCD signs predominantly from magnetic mixing with the M state. The MCD predictions for the first three transitions should be quite reliable.

Anomalies in the Hückel Correlation for Fluoranthene-Like Hydrocarbons. The position of the first intense absorption band of benzenoid hydrocarbons (L_a) is known to correlate linearly with the difference of the Hückel energies of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals.^{7b,18} It was found some time ago that this is also true of the first intense band of fluoranthene-like hydrocarbons, i.e., **1–5** and various polycyclic analogues.⁷ Subsequent calculations at the Pariser–Parr–Pople level^{9–11} showed, however, that part of the agreement found at the Hückel level was fortuitous since in some of the hydrocarbons, particularly in [*j*]annelated fluoranthenes, the HOMO → LUMO transition does not correspond to the first intense absorption band but to a weak band or shoulder at lowest energies, for reasons which were not clear. With this corrected assignment of HOMO → LUMO transitions, **3** and many related fluoranthene-like hydrocarbons lay off the regression line in the Hückel plot, having anomalously low experimental excitation energies for the size of their Hückel HOMO–LUMO energy difference. It was noted that in this respect they resembled **6**, in which the HOMO → LUMO absorption band is quite weak and lies at quite anomalously low energy.⁸

A rationalization of this behavior can be based on the present results and those of ref 12. Taken together, they suggest quite convincingly that the K, L, and M transitions can be traced throughout the family of fluoranthene-like hydrocarbons and that their basic characteristics remain similar to what they are in **6**. The L transition corresponds to the “first intense absorption band” of the Hückel correlations, the K transition to the “weak band or shoulder at lower energies”. In **6**, K corresponds to a HOMO → LUMO excitation. This is also true in **3**, other [*j*]annelated fluoranthenes, and some analogues with

two five-membered rings but not in **1**, **2**, **4**, and most other fluoranthene-like hydrocarbons, since the top two occupied orbitals switch their order on going from **6** to the latter. The reason for this change in orbital ordering is obvious upon inspection of the MO's of **6** and those of the fragments which are being added, and it is also clear why the [*j*]annelated series differs from the others.^{2,12} As a result, the Hückel correlation for HOMO → LUMO transitions involves the L band for most fluoranthene-like hydrocarbons but the K band for some.

In order to lie on a common Hückel regression line, a transition must be reasonably well described as a single-electron promotion between two MO's and must derive the same contribution to its energy from the two-electron term $-(J - 2K)$ as all the others do (if effects of CI are neglected, singlet excitation energy equals the orbital energy differences minus the Coulomb repulsion integral, *J*, plus twice the exchange integral, *K*). While the magnitude of *J* is dominated by the molecular size and shape and should not be significantly different for the various benzofluoranthenes, the magnitude of the exchange integral is given by the self-repulsion energy of the overlap density and this is a sensitive function of the spatial distribution of the two orbitals involved in the transition.¹⁹ In a transition of a charge-transfer type, such as the K transition in **1–6**, the two orbitals are largely located in different regions of the molecule, their overlap density is small, the exchange integral is small, and the excitation energy is relatively low considering the orbital energy difference. In a transition between two orbitals localized on the same atoms, such as the L_a transition of benzenoid hydrocarbons or the L transition in **1–6**, the exchange integral is large and the excitation energy relatively high. In the Hückel correlation for fluoranthene-like hydrocarbons,⁸ some of the transitions were of K type and some of L type, so that it is only reasonable that points for the molecules whose HOMO → LUMO transition is of K type, such as **5** and **3**, deviate in the plot in the direction of anomalously low experimental excitation energies. This rationalization has an interesting corollary: since the singlet-triplet splitting is given by $2K$, those molecules which deviate anomalously should have a smaller singlet-triplet splitting. This is known to be so in the case of **6**.¹⁵

Acknowledgment. This work was supported by U.S. Public Health Service Grant GM 21153. We are indebted to Professors M. W. Windsor and M. Zander and to Dr. E. Koch for kind gifts of samples and to Professor H. Eyring for kind permission to use his MCD instrument. Helium gas was provided by a departmental grant from the Office of Naval Research.

References and Notes

- (1) Part 17: G. P. Dalgaard and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue.
- (2) J. Kolc, E. W. Thulstrup, and J. Michl, *J. Am. Chem. Soc.*, **96**, 7188–7202 (1974).
- (3) E. W. Thulstrup, M. Nepraš, V. Dvořák, and J. Michl, *J. Mol. Spectrosc.*, **59**, 265–285 (1976).
- (4) J. Kolc and J. Michl, to be submitted for publication.
- (5) S. M. Warnick and J. Michl, *J. Am. Chem. Soc.*, **96**, 6280–6289 (1974).
- (6) R. A. Friedel, *Appl. Spectrosc.*, **11**, 13–24 (1957); E. M. Layton, Jr., *J. Mol. Spectrosc.*, **5**, 181–198 (1960); E. Clar, “Polycyclic Hydrocarbons”, Vol. 2, Academic Press, New York, N.Y., pp 312–316.
- (7) (a) A. Pullman, B. Pullman, E. D. Bergmann, G. Berthier, E. Fischer, Y. Hirshberg, and J. Pontis, *J. Chim. Phys. Phys.-Chim. Biol.*, **48**, 359–367 (1951); R. Zahradnik, J. Michl, and J. Koutecký, *J. Chem. Soc.*, 4998–4999 (1963); (b) A. Streitwieser, Jr., “Molecular Orbital Theory for Organic Chemists”, Wiley, New York, N.Y., 1961, p 217.
- (8) R. Zahradnik and J. Michl, *Collect. Czech. Chem. Commun.*, **31**, 3442–3452 (1966).
- (9) J. Koutecký, P. Hochman, and J. Michl, *J. Chem. Phys.*, **40**, 2439–2456 (1964).
- (10) M. M. Mestechkin, L. S. Gutyrya, and V. N. Poltavets, *Opt. Spektrosk.*, **30**, 547–551 (1971); J. Najbar and J. Labanowski, *Acta Phys. Pol. A*, **47**, 217–225 (1975).
- (11) J. Michl and J. H. Eggers, *Tetrahedron*, **30**, 813–817 (1974).
- (12) J. Michl and J. F. Muller, *J. Am. Chem. Soc.*, **98**, 4550–4553 (1976).
- (13) J. Michl, *J. Am. Chem. Soc.*, companion papers in this issue (parts 1–3).

- (14) A. Castellan and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 4).
 (15) E. W. Thulstrup and J. Michl, *J. Am. Chem. Soc.*, **98**, 4533-4540 (1976).
 (16) J. W. Kenney, III, D. A. Herold, J. Michl, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 16), and references therein.
 (17) P. N. Schatz and A. J. McCaffery, *Q. Rev., Chem. Soc.*, **23**, 552-584 (1969).
 (18) E. Heilbronner and J. N. Murrell, *J. Chem. Soc.*, 2611-2615 (1962); J. Koutecký, J. Paldus, and R. Zahradnik, *J. Chem. Phys.*, **36**, 3129-3134 (1962); R. Zahradnik, *Fortschr. Chem. Forsch.*, **10**, 1-58 (1968).
 (19) J. Michl and E. W. Thulstrup, *Tetrahedron*, **32**, 205-209 (1976).

Liquid Crystals Composed of *N*-Acylamino Acids. 1. Circular Dichroism and Selective Light Transmission in Cholesteric Liquid Crystals Composed of *N*-Acylamino Acids and Organic Solvents

Kazutami Sakamoto,*^{1a} Ryonosuke Yoshida,^{1a} Masahiro Hatano,^{1b} and Taro Tachibana^{1c}

Contribution from the Central Research Laboratories, Ajinomoto Co. Inc., Suzuki-cho, Kawasaki-ku, Kawasaki, Kanagawa, 210 Japan, the Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira 2-1-1, Sendai, Miyagi, 980 Japan, and the Department of Chemistry, Ochanomizu University, Otsuka 2-1-1, Bunkyo-ku, Tokyo, 112 Japan.
 Received November 28, 1977

Abstract: Optically active *N*-acylamino acids formed a new type of lyotropic cholesteric liquid crystals when they were swelled and dispersed as a suspension in solvents such as benzene, chlorobenzene, chloroform, and *n*-hexane. An appropriate solvating ability to swell but not to dissolve any given *N*-acylamino acid may be a necessary condition for a solvent to form the liquid crystalline phase which appears as a suspension. These suspended liquid crystals showed some characteristics of lyotropic cholesteric liquid crystals: (1) circular dichroism (CD) bands with a single sign, (2) the liquid-crystal-induced CD (LCICD) bands due to achiral molecules added to these systems, and (3) a spherulite-like phase having an optically negative sign. These suspended liquid crystals showed the iridescent color typical of cholesteric liquid crystals. These colors were found to originate from the difference of the refractive indices of the solvents from those of suspended liquid crystals, the so-called "Christiansen effect", and not from the chiral structure in the liquid crystals.

We reported recently that the amorphous powdered *N*-lauroyl-L-glutamic acid (L-LGA),² which was soaked into aromatic solvents such as benzene or toluene, showed not only birefringence under a polarized microscope but also a positive circular dichroism (CD) band around 300-400 nm.³ An achiral dye such as azulene or anthracene dissolved in this system exhibited also a type of liquid-crystal-induced circular dichroism (LCICD) in the wavelength region of the absorption bands. From these phenomena, the L-LGA-aromatic solvent system was assumed to form a liquid crystal with the cholesteric helical structure.

The L-LGA-aromatic solvent systems, being a suspension of liquid crystals, exhibited an iridescent color like typical thermotropic cholesteric liquid crystals. This color varied reversibly with temperature change, and the color of the scattered light was complementary to the transmitted light through the system.

Robinson et al.⁴ found a cholesteric color for the poly- γ -ethyl-L-glutamate (PELG) solution in ethyl acetate, where the cholesteric pitch is comparable to the wavelength of the visible light. They demonstrated that the origin of this cholesteric color is the selective reflection of the circularly polarized light of one sense by the cholesteric pitch.⁵ Hatano et al. found recently a brilliant iridescent color and a CD band due to the selective reflection in the cholesteric structure for the PELG solution in vinyl acetate.⁶ Furthermore, they found that achiral dye molecules became optically active when they were dissolved into the liquid crystalline phase of poly(γ -benzyl L-glutamate) (PBLG) and that definite CD bands appeared in the wavelength region where absorption bands of the dyes exist.⁶

These results indicate some similarities on the optical properties between the lyotropic liquid crystals of polyglutamate solution and the *N*-acylglutamic acid-aromatic solvent systems such as (1) the appearance of an iridescent color, (2) the existence of the CD bands due to the cholesteric helical structures, and (3) the spectral profile of the LCICD bands of achiral molecules intercalated into the systems.

In this paper, we report the properties of the new liquid crystals composed of optically active *N*-acylamino acids and organic solvents comparing with the polyglutamate solutions on the ground of these similarities.

Experimental Section

Liquid crystalline phase was analyzed with a Nikon PH-10 polarized microscope. The wavelength-dependent spectrum of the transmitted light travelling through the L-LGA-benzene system was measured on a Hitachi 200 spectrophotometer using a 10-mm quartz cell. Refractive indices and optical dispersive powers⁷ of the mixed-solvent systems were measured with an Abbe-type refractometer at 21 °C. The CD measurements of the L-LGA-aromatic solvent systems were made on a JASCO J-20A spectropolarimeter, where the samples were inserted slowly into quartz cells having a 0.1-0.5-mm path length. Powdered *N*-acylamino acid and any given solvent were suspended in a cell, and the optical measurements were conducted with the sediment formed in the cell kept at 15-60 °C.

No appreciable change could be detected when the cell was rotated around the light beam,⁸ and so it was concluded that no linear dichroism contribution to the CD bands could be observed.

N-Acylglutamic acids used here are the same ones as in the preceding papers.⁹⁻¹⁴ Dialuminum stearate was purchased from Wako Pure Chemical Industries, Ltd., and was used without further purification. The solvents used were of spectral grade and were used