

Excited Singlet States of Fluoranthene. I. Absorption, Linear and Magnetic Circular Dichroism, and Polarized Fluorescence Excitation of the Fluorofluoranthenes

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Abstract: A combination of four spectroscopic methods is used to establish firmly the existence of at least eight, and probably nine, independent electronic transitions in fluoranthene in the 200–450-nm region, their polarization directions, and signs of the *B* terms in the MCD spectra. Fluoro substitution has noticeable effect on the polarization of only two of the observed transitions. Inadequacy of one-parameter methods for evaluation of linear dichroic spectra in stretched polymers is stressed. Semiempirical π -electron calculations at several levels are compared, including an 84-term configuration interaction calculation with all those doubly excited configurations which are likely to be important in the ground state and/or low-lying excited states. The calculated number, polarizations, and relative energies and intensities of transitions in the 200–450-nm region of fluoranthene agree quite well with experiment. The spectrum can be simply related to that of acenaphthylene. The calculated signs of the *B* terms of the lowest three transitions in fluoranthene are also in agreement with experiment and insight into their origin in terms of the MO's involved is obtained. Approximate values of magnetic dipole transition moments between several excited states are obtained and their sense relative to those of electric dipole transition moments is determined. A simple parallel between the MCD spectra of fluoranthene and acenaphthylene is derived. The calculation of the effects of fluoro substitution on energies, intensities, and polarizations, using a simple, purely conjugative model, is less satisfactory.

Fluoranthene (I) is one of the most easily available nonalternant hydrocarbons and as such has been the subject of considerable interest. Its electronic absorption spectrum appears deceptively simple and until a short time ago was commonly interpreted in terms of only three² or four^{3a} electronic transitions between 200 and 450 nm. However, recent evidence shows that the bands believed to belong to the first two transitions really represent four independent partially overlapping transitions.^{4–9} This had been first suggested by Pariser–Parr–Pople (PPP) type calculations.¹⁰ The number and identity of higher energy transitions remain incompletely understood although some progress has been made.^{4,5,7,8} Other possible problems remain: Mestechkin, *et al.*,¹¹ question the existence of the weak band assigned as the first transition, while Berlman¹² has suggested that the first excited state is nonplanar. Fluoranthene also is one of the few molecules for which possible existence of double fluorescence has been discussed seriously.^{3b}

The present paper represents an attempt to improve the understanding of the number and nature of the low-lying excited singlet states of fluoranthene I, and their relation to the states of acenaphthylene II, by a comparative study of I and all five of its monofluoro derivatives (labeled 1-F-I to 8-F-I). The fluoro substitution causes only minor changes in the appearance of the spectra and leaves vibrational fine structure almost unchanged, while it shifts band origins by small amounts. It is thus suitable for recognition of inde-

pendent electronic transitions in a well-known manner.^{7,13} The picture resulting from absorption spectroscopy is confirmed and complemented by an investigation of MCD spectra and polarization directions, using both linear dichroism and polarized fluorescence (no anomalous emission

has been found). These results establish firmly the existence of at least eight and probably nine independent electronic transitions in I in the 200–450-nm region and their polarizations. Information about magnetic dipole transition moments between low-lying excited states is obtained from MCD spectra. The spectral properties, including MCD of the first three bands, are in satisfactory agreement with calculations.

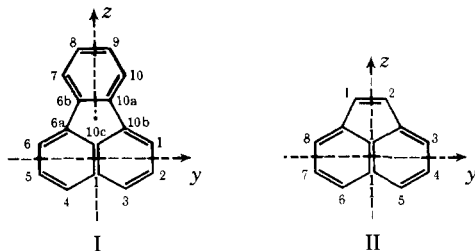
This work also initiates a systematic exploration of the effect of substituents on the excited states of fluoranthene to be followed up by an investigation of aminofluoranthenes. The availability of five different substitution positions and at least eight different excited states in I, as well as its nonalternant nature, makes it ideal for an application of quantum mechanical theories of substituent effects.

Finally, the present paper represents part of an investigation of the effect of the fluoro substituent on the electronic spectra of conjugated hydrocarbons. Although it is one of the simplest substituents, surprisingly little is known about its effects. Band shifts are known to be small, but little seems to be known about the effect on polarization directions and on intensities.

Experimental Section

Materials. Fluoranthene (I) (Aldrich, zone refined, Gold Label) was used without further purification. 3-F-I (K&K) was sublimed and chromatographed on alumina: mp 100.5–101.5° (lit.¹⁴ 98–98.5°). The preparation and purification of the other fluorofluoranthenes have been described elsewhere.¹⁵ 3-Methylpentane (3-MP, Phillips Petroleum Co.) was refluxed with sodium, distilled, and passed over a Al₂O₃–AgNO₃ column. All other solvents were spectral grade quality.

Spectroscopy. Absorption spectra in rigid glass (3-MP, 77°K) were taken in 2-mm Suprasil cells immersed in a quartz Dewar with Suprasil windows, filled with filtered liquid nitrogen, using a Cary 17 spectrophotometer. Room-temperature linear dichroism in stretched polyethylene sheets (SM Uvetenfolie, Svenska Metallverken) was obtained as an average of three measurements using procedures and instrumentation described elsewhere.¹⁶ Low-temperature linear dichroism was measured using a different batch of polyethylene, which gave a similar degree of orientation (Kordite, Mobile Chemical Corp.). The orientation improves noticeably upon cooling. The stretched sheet was immersed in a quartz Dewar with Suprasil windows filled with liquid nitrogen. The Glan prism



pendent electronic transitions in a well-known manner.^{7,13} The picture resulting from absorption spectroscopy is confirmed and complemented by an investigation of MCD spectra and polarization directions, using both linear dichroism and polarized fluorescence (no anomalous emission

rather than the sample was rotated. The polarization plane was at 45° from the vertical, ensuring approximately the same light flux for both polarizations. The Cary 17 was interfaced to a PDP-11-20 computer, permitting easy evaluation of data. A detailed description of the low-temperature equipment will appear elsewhere.¹⁷

Polarized emission was measured on samples immersed in liquid nitrogen in the Dewar used for absorption measurements, using a 25° angle between exciting and emitted beams and well-known formulas¹⁸ for evaluation of results. The instrument consisted of a 1 kW xenon arc, water filter, light chopper, two Schoeffel 250-mm scanning monochromators, a polarization scrambler, two Polacoat polarizing sheets, Centronics Q4283R photomultiplier with a Keithley 244 high voltage power supply, a PAR Model 184 preamplifier, PAR 124 lock-in amplifier, Houston Instruments 2000 series *x-y* recorder, and appropriate lenses and mirrors in the optical path. The results are averages of several measurements. A typical bandwidth was 2 nm. The emission was monitored at the wave number of its 0-0 peak: 24,700 cm⁻¹ (I), 25,000 cm⁻¹ (1-F-I and 7-F-I), 24,400 cm⁻¹ (2-F-I), 24,450 cm⁻¹ (3-F-I and 8-F-I). Scattered light prevented measurement of the excitation spectrum in the immediate vicinity of the 0-0 peak of the longest wavelength transition. No evidence was found of the previously claimed^{3b} anomalous double fluorescence and such observations were apparently due to impurities.

The instruments used for MCD spectra (cyclohexane) has been described elsewhere.^{19a}

Method of Calculation

Calculations were done in the semiempirical π -electron SCF-CI PPP approximation. Nonneighbor resonance integrals and penetration integrals were not included. The one-center parameter values were: $I_C = 11.42$ eV, $\gamma_C = 10.84$ eV, $I_F = 16.0$ eV. The numerical results quoted were obtained using $\gamma_F = 24.0$ eV but essentially the same values result using any γ_F of approximately that size (*cf.* ref 19b). Small changes in I_F also have very little effect. Two-center electron repulsion integrals were obtained from the formulas of Mataga-Nishimoto²⁰ (calculations A, B, and C) or Ohno-Klopman²¹ (calculations D and E). The resonance integrals β_{CC} and β_{CF} were either all equal to -2.318 eV (calculations A, C, D, and E) or β_{CC} 's were obtained in an iterative manner from the calculated ground state bond orders using the formulas $\beta_{\mu\nu} = -2.318 \exp[0.335(p_{\mu\nu} - \frac{2}{3})]$ and $r_{\mu\nu} = 1.517 - 0.18p_{\mu\nu}$ and adapting the values of resonance integrals and nearest neighbor electron repulsion integrals to bond lengths derived from calculated bond orders until self-consistency was reached (calculation B). The geometry assumed in the calculations (initial geometry for iterations in calculation B) consisted of three regular hexagons and all bond lengths equal to 1.40 Å. The same $r-p$ relation was used for calculation of bond lengths in all instances.

Oscillator strengths (f) were obtained using both dipole length and dipole velocity formulas. The Linderberg relation²² was used for matrix elements of the linear momentum operator. The B terms in MCD spectra were calculated in a manner described in greater detail elsewhere²³ by direct substitution into the usual perturbation formula,²⁴ summing over all excited states $|I\rangle$ obtained in the calculation and invoking the usual approximations of the simple PPP model. For transition from ground state $|G\rangle$ to excited state $|F\rangle$

$$B(G \rightarrow F) = \text{Im} \left\{ \sum_{I, I \neq G} \frac{\langle I | \mu | G \rangle \langle G | m | F \rangle \times \langle F | m | I \rangle}{(W_I - W_G)} + \sum_{I, I \neq F} \frac{\langle F | \mu | I \rangle \langle G | m | F \rangle \times \langle I | m | G \rangle}{(W_I - W_F)} \right\} \quad (1)$$

where W_I is energy of state $|I\rangle$, and m is the electric and μ is the magnetic dipole moment operator.

In calculations of type A only those singly excited configurations which have diagonal elements of the Hamiltonian less than 8 eV above that of the ground configuration were used (about 30 configurations). In calculations of type B, C, and D, all 64 singly excited configurations were used. Calculations of type E used the SECI-1 method and computer program described elsewhere.²⁵ Briefly, all singly excited configurations which have a diagonal matrix element of the Hamiltonian less than 10 eV above that of the ground configuration were first identified. Labeling MO's from the most bonding to the least bonding, all doubly excited configurations which can be obtained by excitation from molecular orbitals 3 through 8 (the highest six occupied) to orbitals 9 through 14 (the lowest six empty) were then scanned, and those which had large matrix elements with either the ground configuration and/or at least one of the selected singly excited configurations were kept, as well as all those which only differed from these in spin but not orbital assignment, if they were linearly independent. An off-diagonal matrix element was considered large if it exceeded 0.1 after division by the difference of the corresponding diagonal elements. All doubly excited configurations which had a diagonal matrix element of the Hamiltonian less than 8 eV above that of the ground configuration were also kept. In this manner, 84 spin-projected singlet configurations were selected, one of which was the ground configuration, and 32 were singly excited. Of all the selected doubly excited configurations, only one involved excitation from orbital 3 and only one involved excitation into orbital 14. This indicates that inclusion of excitations from orbitals 1 and 2 and into orbitals 15 and 16 in our scanning procedure would have made little if any difference in the results.

Results

Low-temperature absorption spectra and polarized fluorescence excitation spectra in 3-MP glass as well as room-temperature linear dichroic absorption spectra in stretched polyethylene and magnetic circular dichroic absorption spectra in cyclohexane solution were measured for fluoranthene and each of its five monofluoro derivatives. The appearance of the spectra is quite similar for all six molecules and they are not all shown here. A representative illustration is provided in Figure 1, using data for 2-F-I. Figure 2 gives a condensed survey of the wave numbers of peaks in the low-temperature absorption spectra of the six compounds in 3-MP glass, as well as their polarization directions (approximate directions in the substituted compounds) and signs in MCD spectra. Details of the region of transitions 5 and 6 in 1-F-I and 8-F-I and the position of the origin of transition 8 in I were obtained from low-temperature stretched sheet spectra, since they were not sufficiently clear in room-temperature spectra. Polarized fluorescence excitation and linear dichroic absorption in stretched polyethylene always gave compatible results. Figure 3 shows the dichroic curves and derived absorption curves A_z and A_y of fluoranthene at 77°K, obtained in stretched polyethylene. The A_y curve is already multiplied²⁶ by $n_0 = (2 + d_{\parallel}^{\circ}) / (2d_{\perp}^{\circ} + 1)$ so that it is on the same scale as A_z . The sharp wiggles in the A_y curve near 28,000 and 35,000 cm⁻¹, where strong peaks occur in the A_z curve, are artifacts due to very slight differences in the positions of peaks in the two recorded dichroic spectra E_{\parallel} and E_{\perp} . Figure 4 gives the calculated changes in bond lengths upon excitation into the two lowest excited states. These were obtained from bond orders (elements of first-order density matrix) from calculation E, using idealized regular geometry, which is not particularly biased toward any one of the states. The pattern of bond lengths calculated for the ground state agrees with ex-

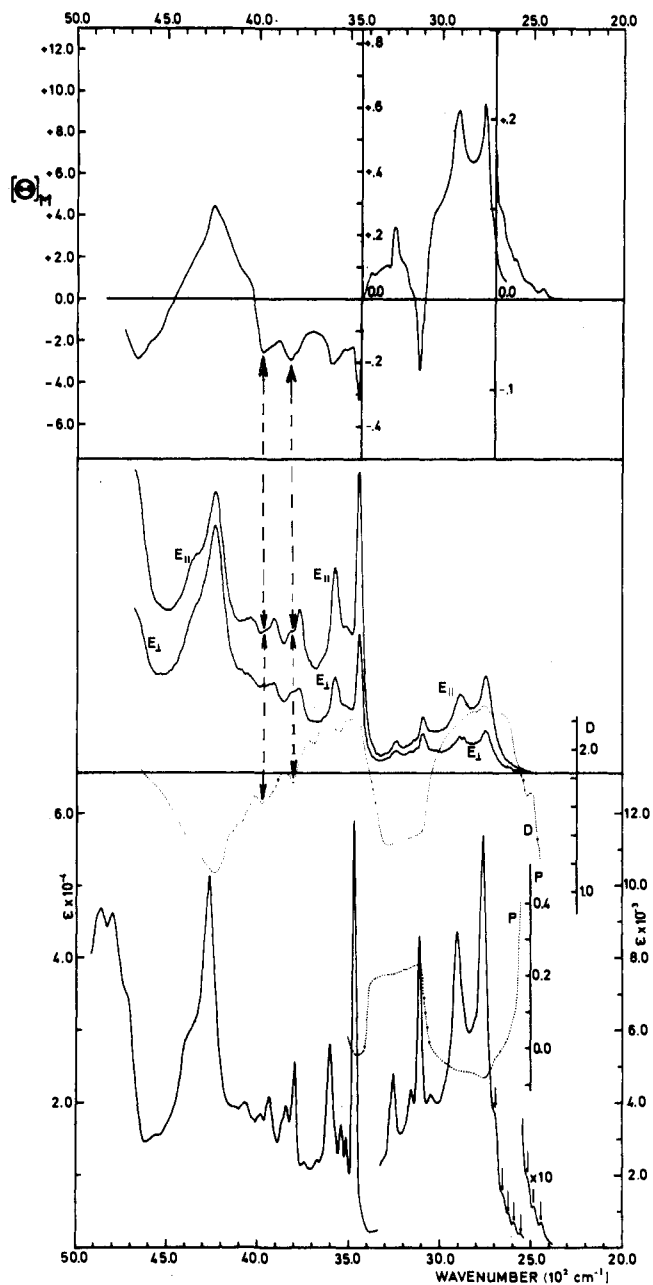


Figure 1. Spectra of 2-fluorofluoranthene. From bottom to top: absorption in 3-MP at 77°K (solid line); P , polarized fluorescence excitation in 3-MP at 77°K (dotted line); E_{\parallel} and E_{\perp} , parallel and perpendicular linear dichroic absorption in stretched polyethylene at room temperature (solid lines); D , dichroic ratio derived from E_{\parallel} and E_{\perp} and from spectra at higher concentrations (dotted line); magnetic circular dichroic absorption in cyclohexane at room temperature (top spectrum). Scales: absorption, indicated on the sides (left, valid above 33,000 cm^{-1} ; right, valid below 33,000 cm^{-1}); P and D , indicated as inserts on the right; E_{\parallel} and E_{\perp} , arbitrary; MCD, indicated on the sides similarly as for absorption.

periment,²⁷ and we believe that the pattern and relative magnitudes of changes upon excitation shown in Figure 4 are reliable. It was not considered worthwhile to perform separate calculations at the theoretical equilibrium geometries of each of the states, although this would be more correct in principle. We have done this only for the ground state (calculation B) and Figure 4 shows that the results are in slightly better agreement with experimental ground state equilibrium bond lengths but the pattern remains unchanged. Figure 5 is based on calculations of type C and relates the excited states of fluoranthene to those of acenaph-

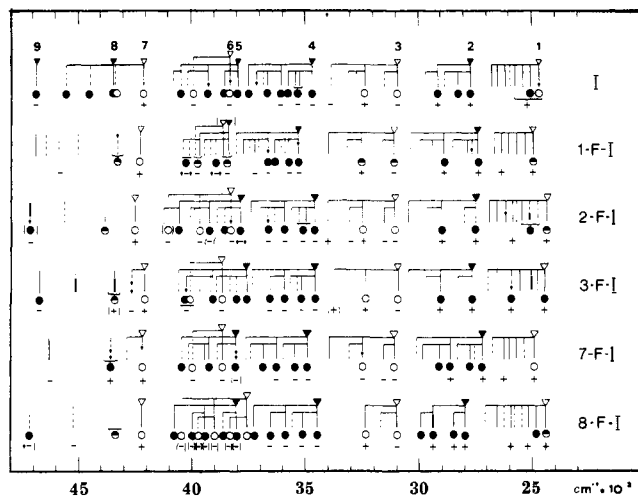


Figure 2. Effect of fluoro substitution on the absorption spectrum of fluoranthene. Energies of peaks (full lines) and shoulders (dashed lines), their polarizations (full circles, z -polarized; empty circles, y -polarized; half-full circles, intermediate; tentative assignments in parentheses), and signs in MCD spectra (plus or minus, weak peaks or shoulders in parentheses) are indicated. Assignment to independent electronic transitions 1–9, their purely electronic polarizations (z -polarized, full triangle; y -polarized, empty triangle), and tentative analysis of their vibrational structure are indicated. For experimental details see text.

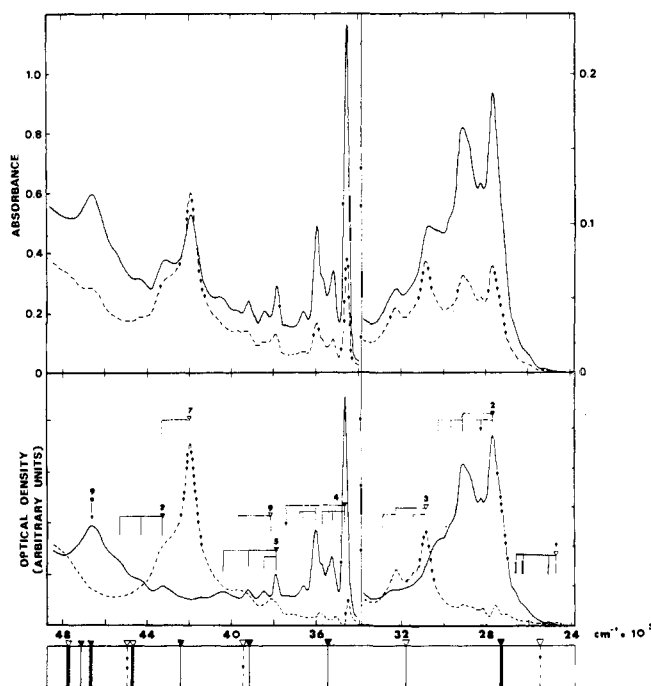


Figure 3. Polarized absorption of fluoranthene at 77°K. Upper part: linear dichroic absorption in stretched polyethylene (E_{\parallel} , full line; E_{\perp} , broken line). Lower part: reduced polarized absorption curves (A_z , full line; A_y , broken line). Separation into independent electronic transitions and tentative vibrational analysis for transitions 2–8 are indicated. At the bottom, calculated transition energies, intensities (broken line, $f < 0.02$; thin line, $f = 0.02-0.2$; thick line, $f > 0.2$), and polarizations (full triangles, z ; empty triangles, y). Calculation method E (all transitions shifted 0.29 eV to lower energies; see text).

thylene. Figure 6 uses the results of calculations of type C to provide insight into the origin of some of the B terms in the MCD spectrum.

Table I gives detailed information on substituent effects on energies, linear dichroism, polarized excitation, and MCD characteristics of the 0–0 components of the individ-

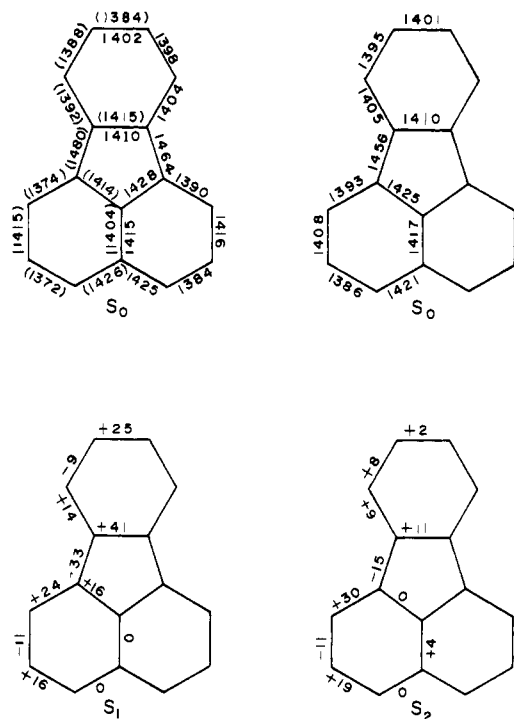


Figure 4. Bond lengths in fluoranthene. Top: values for ground state (S_0) calculated by methods B (left) and E (right) and those measured (in parentheses). Bottom: changes expected upon excitation into the first (S_1) and second (S_2) excited singlet (method E). Units 10^{-3} Å.

ual electronic transitions. In Table II, data derived from experiments are compared with calculated values for the fluoro-fluoranthenes (method A) using a simple purely conjugative model for the substituent as in ref 28. In Table III, results for fluoranthene itself calculated using methods B, C, D, and E are compared to show the effect of the increase in the size of configuration interaction and of the choice of the two-center repulsion integrals. Table IV summarizes results of MCD calculations.

Discussion

A. Electronic Transitions. Identification, Energy, Intensity, and B Terms. Figures 1–3 provide eloquent testimony in favor of the validity of the proposed^{4,5,7,8} interpretation of the spectrum of fluoranthene and the closely related fluoro-fluoranthenes in terms of at least eight separate electronic transitions, as summarized in Tables I–III. The wave numbers of the vibrations required by the tentative vibrational analysis suggested in Figure 2 for transitions 2–8 appear entirely reasonable. A detailed vibrational analysis would be of particular interest for the first excited state whose pattern appears to be a fairly close mirror image of that of the fluorescence. However, the resolution of the dichroic spectra in this region of weak absorption is particularly poor and insufficient for unambiguous assignment, and none is attempted for this state in Figures 2 and 3. Even for the other transitions, the proposed vibrational analysis remains only tentative due to the low resolution available. Fortunately, this lack of detailed understanding does not detract from the value of the approach for recognition of individual electronic transitions. The shapes of the bands are affected very little by fluoro substitution and the following intensity comparisons are all based on intensities of peaks assigned to 0–0 transitions.

As is seen from Figures 1 and 2 and discussed in more detail below, the MCD curves help efficiently to distinguish the regions of the separate electronic transitions. A positive MCD peak implies a negative B term since $B =$

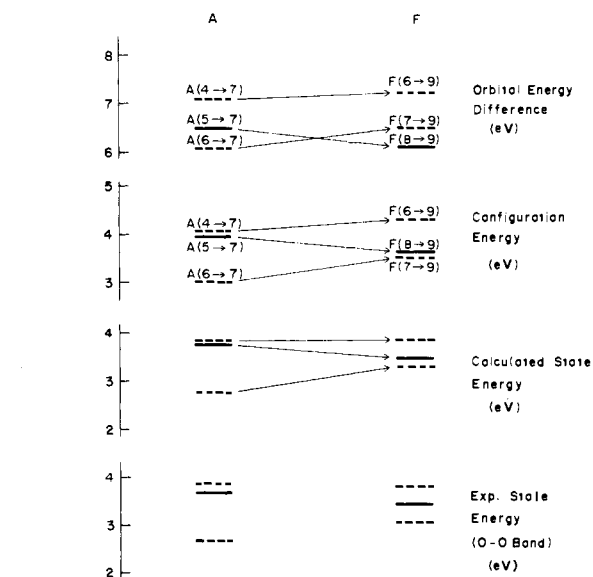
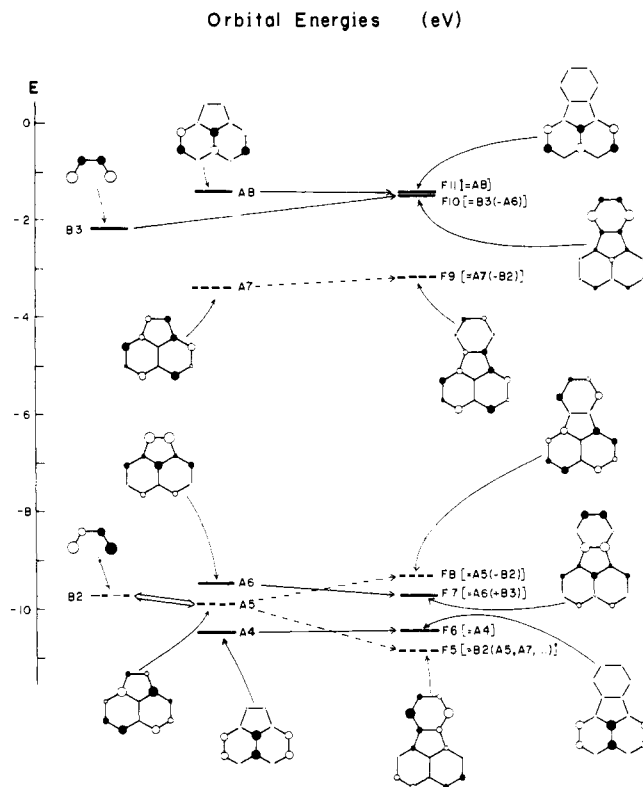


Figure 5. Relationship between fluoranthene and acenaphthylene. Size of MO coefficients is proportional to the diameter of circles shown; sign differences are indicated by shading. Solid (broken) lines indicate levels symmetric (antisymmetric) with respect to mirroring in the xz plane of formula 1. Calculation by method C.

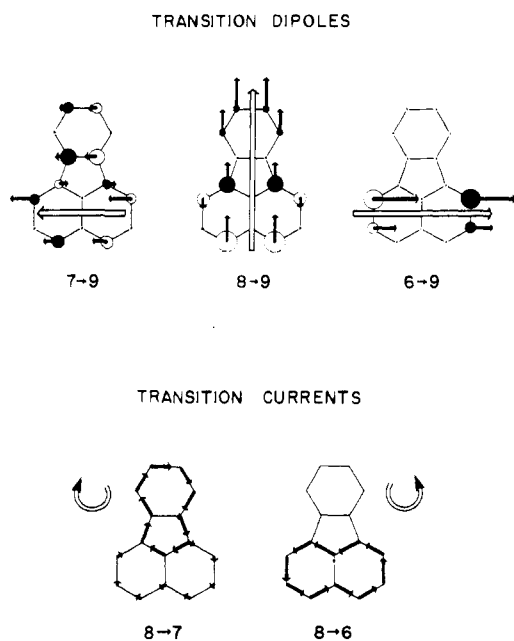
$-(33.53\nu_0)^{-1} \int [\theta]_M d\nu$, where ν_0 is the wave number of the center of the band and $[\theta]_M$ is molar ellipticity per unit field.^{24b} In the following, we shall discuss the individual electronic transitions simultaneously for fluoranthene and its fluoro derivatives (Tables I–III, Figures 1–4).

Transition 1. The authenticity of the first transition in I was questioned by Mestechkin, *et al.*,¹¹ since their calculations did not account for it. Most other calculations predict its existence.^{7,8,10,29–32} The Russian authors¹¹ also argued that the transition cannot be seen in the stretched sheet

Table I. Spectroscopy of Fluorofluoranthenes. Experimental Results

		Transition								
		1	2	3	4	5	6	7	8	9
I	E^a	24.75	27.75	30.95	34.70	38.00	38.35	42.15	43.45	45-48
	MCD ^b	+	+	-	-	-	-	+	-	-
	$1/b_j^c$	1.0-1.2	0.45	1.25	0.4	0.4	1.0-1.25	1.25	0.4	0.4
	φ_j^d	75 ± 15	10 ± 10	85 ± 5	10 ± 10	10 ± 10	75 ± 15	85 ± 5	10 ± 10	10 ± 10
	P_j^e	>0.15	-0.14	0.11	-0.05	-	-	-	-	-
	α_j^f	<45	64	47	58	-	-	-	-	-
1-F-I	E	25.00	27.45	31.10	35.30	38.40	38.60	42.30	-	45-47
	MCD	+	+	-	-	(-)	(-)	+	-	-
	$1/b_j$	0.4-0.8	0.45	0.8	0.45	-	-	1.1	-	-
	$ \varphi_j $	30 ± 30	15 ± 15	60 ± 10	15 ± 15	-	-	75 ± 75	-	-
	P_j	0.40	0.10	0.18	0.22	-	-	-	-	-
	$ \alpha_j $	0	50	42	39	-	-	-	-	-
2-F-I	E	24.40	27.55	31.10	34.60	37.90	38.35	42.55	-	45-47
	MCD	+	+	-	-	-	-	+	-	-
	$1/b_j$	0.4-1.0	0.4	0.75	0.45	0.45	0.8-1.1	1.1	-	-
	$ \varphi_j $	40 ± 40	10 ± 10	54 ± 10	15 ± 15	15 ± 15	75 ± 15	80 ± 10	-	-
	P_j	0.45	-0.07	0.22	-0.02	-	-	-	-	-
	$ \alpha_j $	0	60	38	56	-	-	-	-	-
3-F-I	E	24.50	27.70	30.95	34.60	37.60	38.70	42.15	-	45-48
	MCD	+	+	-	-	-	-	+	-	-
	$1/b_j$	0.4-0.6	0.4	1.0	0.4	0.45	0.6-1.25	1.25	-	0.40
	$ \varphi_j $	20 ± 20	10 ± 10	63 ± 10	10 ± 10	15 ± 15	65 ± 25	85 ± 5	-	10 ± 10
	P_j	0.42	0.22	0.12	0.19	-	-	-	-	-
	$ \alpha_j $	0	38	48	42	-	-	-	-	-
7-F-I	E	24.95	27.25	31.10	34.95	38.10	38.70	42.20	-	44-47
	MCD	+	+	-	-	-	-	+	-	-
	$1/b_j$	0.7-1.2	0.45	1.1	0.45	0.4-0.5	0.7-1.2	1.1	-	-
	$ \varphi_j $	65 ± 20	15 ± 15	75 ± 15	15 ± 15	20 ± 20	65 ± 25	75 ± 15	-	-
	P_j	0.45	0.21	0.12	0.19	-	-	-	-	-
	$ \alpha_j $	0	40	48	42	-	-	-	-	-
8-F-I	E	24.45	28.00	31.00	34.50	38.10	37.90	42.25	-	45-48
	MCD	+	+	-	-	(-)	(-)	+	-	-
	$1/b_j$	0.4-0.8	≥ 0.4	1.0	≤ 0.4	0.4	1.25	1.25	-	≤ 0.4
	$ \varphi_j $	30 ± 30	15 ± 15	63 ± 10	10 ± 10	15 ± 15	80 ± 10	85 ± 5	-	10 ± 10
	P_j	0.48	0.19	0.06	0.18	-	-	-	-	-
	$ \alpha_j $	0	42	52	43	-	-	-	-	-

^a Wave number of 0-0 transition in 3-MP at 77°K in units of 1000 cm⁻¹. ^b Sign of the 0-0 transition in MCD spectrum in cyclohexane at room temperature. ^c See ref 26 for examples of determination of b_j from dichroic spectra by the stepwise reduction method. ^d Deviation of the transition moment direction of the 0-0 component from the effective orientation axis in degrees, calculated from the b_j values as described in ref 26. ^e Degree of polarization of fluorescence monitored at its 0-0 peak (3-MP, 77°K). See text. ^f Angle between the transition moment directions of the individual transitions and that of the 0-0 peak of the first transition in degrees. Obtained from the degree of polarization P by straightforward application of standard formula (no corrections: see text).

Figure 6. Derivation of the sign of B terms by inspection. See text.

spectra of Thulstrup and Eggers.⁵ However, the latter authors pointed out⁵ that this is simply due to its low extinc-

tion coefficient, and its observation in stretched sheet spectra has been reported elsewhere.⁸ It is also seen in Figure 3, albeit very weakly. Part of the controversy may be simply due to a misunderstanding since the Russian authors quote some⁷ (but not all^{6,8}) of the experimental work in which the existence of the transition had been established. Any doubt that might be left is completely dispelled by the present results.

It has recently been postulated¹² that unlike the planar²⁷ ground state the first excited state of I is nonplanar. This was inferred from the observed shape of the fluorescence spectrum ("large Stokes shift"), observed lack of structure in fluorescence as opposed to absorption, and absence of concentration quenching and/or excimer formation. None of our data demand such a hypothesis, although we cannot disprove it conclusively. We observe comparable structuring in both fluorescence and the first absorption band and indeed they are fairly close mirror images of each other (*cf.* ref 7). Further, we assign the "Franck-Condon forbidden" shape of absorption and emission to two factors. First, to a change in bond lengths, which calculations suggest must be considerable, particularly for bonds 6a-6b and 6b-10a (Figure 4). Later analysis will relate this directly to a similar shape of the lowest energy band in acenaphthylene. Second, the linear dichroic spectra show that many of the vibronic components of the first transition are long-axis polarized and clearly contribute to the overall intensity by

Table II. Spectral Data for Fluorofluoranthenes

Transition	1		2		3		4		5		6		7	
	Exptl ^a	Calcd ^b	Exptl ^a	Calcd ^b	Exptl ^a	Calcd ^b	Exptl ^a	Calcd ^b	Exptl ^a	Calcd ^b	Exptl ^a	Calcd ^b	Exptl ^a	Calcd ^b
I	$E_{R,T}^c$	24.7	27.7	30.9	34.7	37.9	38.1	42.0						
	E^d	24.75	27.75	30.95	34.70	37.90	38.00	42.15						
	ϵ^e	100	11,800	5300	80,000	(12,800)	(5400)	55,000						
	f^f	0.012 ^g	0.014	0.17	0.52	0.05	0.08	0.55	0.22	(0.14)	0.01	(0.08)	0.05	0.44
	ϕ^h	90	90	0	0	90	90	0	0	0	90	90	90	90
	$[\theta]_M^i$	+0.06	>0	+0.59	>0	-0.36	<0	-3.77				-1.5		+2.7
1-F-1	ΔE^j	260	500	-330	-100	140	-400	540	100	+400	-300	+300	-300	160
	ϵ/ϵ_{Fl}^k	1.81	2.0	0.59	0.9	1.05	1.5	0.93	1.1	(0.55)	8	(0.75)	1.3	0.92
	ϕ^h	+25 ± 10	-60	-25 ± 10	-5	+67 ± 10	+75	-15 ± 10	+5	+35		-70		75 ± 15
2-F-1	ΔE^j	-330	-200	-200	-100	130	-300	-140	-200	-110	100	0	-100	410
	ϵ/ϵ_{Fl}^k	0.6	1.1	0.94	1.0	1.07	1.3	0.72	0.8	(1.37)	2.0	(1.72)	0.5	0.80
	ϕ^h	(-35 ± 10)	-35	±10 ± 10	+5	-54 ± 10	-85	+15 ± 15	0	15 ± 15	-60	75 ± 15	+30	80 ± 10
3-F-1	ΔE^j	-260	100	-40	-100	0	100	-130	-100	-400	-400	350	-600	-20
	ϵ/ϵ_{Fl}^k	1.67	9	0.52	0.9	0.39	0.6	0.61	1.0	(0.49)	2.1	(0.73)	6	0.59
	ϕ^h	+20 ± 10	-20	-10 ± 10	0	+63 ± 10	+80	-10 ± 10	0	15 ± 15	+65	65 ± 25	+35	85 ± 5
7-F-1	ΔE^j	240	-200	-510	-700	130	-100	220	-300	+120	-100	+350	200	50
	ϵ/ϵ_{Fl}^k	1.45	5	0.91	1.0	0.92	0.9	0.36	0.7	(1.35)	2.5	(2.00)	0.9	0.85
	ϕ^h	-60 ± 10	-25	-15 ± 15	+5	+75 ± 15	+90	-15 ± 15	0	20 ± 20	+30	65 ± 25	+65	75 ± 15
8-F-1	ΔE^j	-280	-500	230	100	40	0	-240	-300	+100	-300	-700	-100	110
	ϵ/ϵ_{Fl}^k	1.80	3.1	0.82	0.9	0.88	0.9	1.44	1.3	(0.68)	12	(0.76)	0.5	1.35
	ϕ^h	{ -15 ± 15 +55 ± 15	40	+15 ± 15	0	-63 ± 10	-80	+10 ± 10	-5	15 ± 15	-55	80 ± 10	-20	85 ± 5

^a Derived from data in Table I; see text. ^b Method A. ^c Wave number of 0-0 transition in polyethylene at room temperature, in units of 1000 cm⁻¹. ^d Wave number of 0-0 transition in 3-MP at 77°K in units of 1000 cm⁻¹, compared with calculation. ^e Molar extinction coefficient of 0-0 transition in 3-MP at 77°K. Corrected for band overlap using band shapes from Figure 3 (uncorrected values are 100; 12,700; 8900; 80,000; 18,300; 10,900; 62,400; 8100; 33,200 for transitions 1-9, respectively). ^f Oscillator strength estimated from absorption spectrum in 3-MP at 77°K using the formula $f = 4.319 \times 10^{-9} \int \epsilon \nu d\nu$ and using Figure 3 to estimate the overlap of bands, compared with calculation by dipole length method. ^g Only y-polarized intensity was counted. Additional 0.006 or more are contributed by the z-polarized part of the transition and represent intensity stolen from transition 2 (and possibly 4). ^h Transition moment direction of 0-0 transition in degrees with respect to the effective orientation axis, assumed to lie in the z direction of formula 1, with the fluoro substituent on the right-hand side (positions 1, 2, 3, 9, 10). Clockwise deviation from the z axis is considered positive. No sign is given if the sense of the deviation is not known. ⁱ Molar ellipticity per unit field strength for the 0-0 transition in units of deg l. m⁻¹ mol⁻¹ G⁻¹. Calculated sign of the MCD peak (opposite to sign of the B term) is given for the first three transitions where it is independent of the method of calculation. ^j Shift of the 0-0 transition with respect to the corresponding transition n I, 3-MP, 77°K, units cm⁻¹. Compared with calculations by method A. ^k Molar extinction coefficient of 0-0 transition in the fluoro derivative divided by that for the parent I, 3-MP, 77°K.

Table III. PPP Calculations on Fluoranthene^a

Transition	Exptl ^b			Calcn B				Calcn C				Calcn D				Calcn E			
	E	f	Pol	E	f _r	f _v	Pol	E	f _r	f _v	Pol	E	f _r	f _v	Pol	E	f _r	f _v	Pol
1	24.75	0.012	y	28.8	0.005	0.001	y	26.7	0.01	0.003	y	26.6	0.014	0.003	y	27.7	0.010	0.005	y
2	27.75	0.17	z	29.8	0.43	0.17	z	28.1	0.49	0.18	z	28.4	0.42	0.15	z	29.6	0.32	0.22	z
3	30.95	0.05	y	31.5	0.06	0.02	y	31.0	0.07	0.02	y	31.8	0.034	0.096	y	34.1	0.039	0.023	y
4	34.70	0.55	z	36.3	0.22	0.09	z	35.9	0.22	0.09	z	36.0	0.035	0.019	z	37.8	0.051	0.062	z
5	37.90	(0.14)	z	40.6	0.02	0.005	z	40.6	0.06	0.02	z	43.2	0.0004	0.00003	z	41.4	0.022	0.014	z
6	38.15	(0.08)	y	41.9	0.06	0.02	y	41.0	0.05	0.01	y	40.4	0.021	0.005	y	41.7	0.018	0.010	y
7	42.15	0.44	y	43.1	1.16	0.50	y	43.2	1.22	0.51	y	45.2	0.21	0.09	y	47.1	0.44	0.21	y
8	43.45	(0.13)	z	42.8	0.58	0.33	z	42.0	0.53	0.30	z	46.1	1.12	0.53	z	44.7	0.15	0.09	z
9				47.0	0.001	0.0	y	46.5	0.0004	0.0001	y	48.4	1.12	0.36	y	47.3	0.002	0.001	y
10	46.9	0.26	z	46.8	0.81	0.46	z	47.1	0.81	0.47	z	47.5	0.27	0.08	z	49.0	0.96	0.48	z
11				49.3	0.001	0.001	z	49.9	0.04	0.01	z	53.0			z	49.5	0.032	0.005	z
12	ca. 49	(?)	y	49.8	0.04	0.01	y	50.1	0.08	0.03	y	53.1			y	50.1	0.39	0.16	y
13				49.8	0.01	0.008	z	50.4	0.01	0.01	z	55.2			z	52.1	0.23	0.15	z
14				51.3	0.28	0.12	y	51.4	0.32	0.13	y	55.7			z	54.6	0.008	0.002	y
15				52.6	0.002	0.002	z	52.1	0.0	0.0001	z	56.5			z	55.4	0.19	0.086	z

^a Results obtained by method A are listed in Table II. E is the excitation energy; f_r and f_v are the oscillator strengths from dipole length and dipole velocity, respectively; polarization refers to the axes shown in formula 1. ^b Energies of 0-0 transitions (E), oscillator strengths (f), and polarizations.

"stealing" from the second transition (Figure 3). This contributes at least a third of the total observed oscillator strength and undoubtedly accentuates the "Franck-Condon forbidden" appearance of the absorption band. Analogous effects are found in polarization of fluorescence.⁴ Even part of the short-axis polarized absorption intensity of transition 1 may be of "borrowed" origin due to possible interaction with transition 3. Finally, it seems to us that the absence of concentration quenching of fluorescence and the lack of excimer emission in themselves do not provide sufficient evidence.

The intensity of transition 1 can increase or decrease by up to a factor of 2 upon introduction of fluorine into the molecule, depending on the position of substitution. Its MCD curve always has positive sign (weak negative B term).

Transition 2. This transition requires little comment. Its Franck-Condon allowed shape is in line with the smaller calculated change of bond lengths upon excitation compared to the first transition (Figure 4). The MCD peak of this transition is always positive and its intensity decreases upon fluoro substitution by as much as a factor of 2.

Transition 3. The intensity of this transition is relatively insensitive to fluoro substitution except in 3-F-I, where it is only 40% of the value in I. The MCD sign for the 0-0 peak is always negative, but the 0-0 + 1400 cm^{-1} peak has a negative sign only in 7-F-I and is positive in the other five compounds. This is the only transition which shows such a sensitivity to vibronic perturbations of its MCD effect. Such sign alternations are commonplace for electronically forbidden transitions, *e.g.* in benzene,^{19a} but transition 3 is quite strongly allowed ($f \approx 0.05$ in fluoranthene). A tentative explanation of the sign reversal is presented below.

Transition 4. The intensity of this transition is quite sensitive to fluoro substitution and is reduced threefold in 7-F-I. Its MCD peak is negative in all six compounds, but the minimum value of $[\theta]_M$ changes considerably with substitution.

Transitions 5 and 6. These occur in the region 38,000–41,000 cm^{-1} . There has been evidence⁵ for the presence of both z - and y -polarized intensity in this region, but without a study of substituent shifts it was impossible to tell whether the weaker y -polarized peaks represent a separate transition, as assigned in ref 5, or if they are vibronic components of transition 5 "stealing" intensity from the nearby intense y -polarized transition at 42000 cm^{-1} (labeled 7 in Figure 3). A later study of unpolarized low-temperature spectra again indicated the presence of separate transitions,⁷ but the results were not considered conclusive because of poorly resolved fine structure in the region.

Our present results permit us to trace separately the substituent shifts of the z - and y -polarized peaks in the region (Figure 2). Since the y -polarized intensity is relatively weak and in some of the compounds can be discerned in the stretched sheet spectra only with difficulty, it is very fortunate that the two sets of peaks usually differ considerably in their MCD intensities in just the opposite way than they do in absorption intensities. They both give negative MCD peaks, but those of the y -polarized transition are stronger than those of the z -polarized transition, except in 8-F-I in which both are weak and hard to analyze. The differences in MCD and absorption intensities give rise to different peak positions in the MCD and absorption spectra. In the region of overlapping transitions in Figure 1 this is indicated by arrows which also point out the presence of y -polarized peaks in the dichroic spectra E_{\parallel} and E_{\perp} and the dips which their presence causes in the dichroic ratio D .

In view of the different responses of the positions of z -polarized (weak MCD) and y -polarized (strong MCD) sets

of peaks to substitution, and since their origins can even change their order (8-F-I), we conclude that they belong to two different electronic transitions, as shown in Figure 2. The assignment of the origin of transition 6 in fluoranthene differs from the previous tentative assignment.⁷ In 1-F-I the two transitions overlap so closely that we have not been able to determine which one originates at lower energies and the assignment shown in Figure 2 is very tentative, based on similarities to the fine structure in the other five compounds.

The intensities of these two transitions are difficult to estimate due to large band overlap, and the values listed in Table II are our best guesses.

Transition 7. This strong y -polarized transition is always positive in the MCD curve. Its intensity generally decreases slightly upon substitution.

Transition 8. The main peak of transition 7 is always followed by a shoulder which appears to be of mixed polarization. In this region, the MCD curve does not follow the shape of the absorption curve. In the fluorofluoranthenes (Figure 1), it is not completely clear whether this shoulder is due to one or two overlapping vibronic peaks, although the latter appears more likely. However, in fluoranthene itself symmetry permits unequivocal reduction and at low temperature the resolution in the resulting dichroic spectra is sufficient to clearly indicate the presence of two overlapping peaks of opposite polarization. We assign the stronger y -polarized one as part of transition 7 and the weak z -polarized one as one of the vibronic components of transition 8, possibly its origin (Figure 3; the origin might also be hidden at smaller wave numbers). Two other components of this transition are seen in Figure 3. Since we cannot safely trace the substituent effects on the peaks assigned to transition 8, we cannot exclude the possibility that they only represent intensity stolen by transition 7 from the one we label 9, so that the assignment is only tentative.

Transition 9 and Higher Transitions. It is safe to say that our experimental curves show at least one additional observed transition at higher energies. This is seen in the low-temperature spectrum in Figure 3 at 46,500 cm^{-1} . It is also present in some of the stretched sheet spectra of the fluoro derivatives, is clearly z -polarized in I, and we shall refer to it as transition 9. However, there are indications that more than one transition may be present in this region. Several apparently unrelated shoulders appear in the low-temperature spectra in 3-MP. Also, the shapes of MCD curves can no longer be related to the absorption curves, thereby indicating the presence of weaker transitions with strong MCD effects. Finally, the stretched sheet spectrum in Figure 3 indicates the presence of a y -polarized band near 49,000 cm^{-1} . However, in this spectral region the base line rises fast and we cannot assign peaks with confidence. The transition is labeled with a question mark in Table III.

B. Electronic Transitions. Polarization Directions. **a. Fluoranthene.** Polarization directions of the strong electronic transitions⁵ as well as the weak first one⁸ have already been determined by the stretched sheet method. Since we now use a different batch of polyethylene and shall need to make direct comparisons with results for fluorofluoranthenes, we have repeated the measurements. The resulting reduction factors are $d_{\perp}^{\circ} = 0.4$ and $d_{\parallel}^{\circ} = 0.8$ at room temperature. The room-temperature reduced spectra are identical with those published earlier⁵ and are not shown. The b_j values for each individual transition were determined as usual²⁶ from the condition that the spectral features due to that transition should be absent in the curve $E_{\parallel}(\lambda) - b_j E_{\perp}(\lambda)$, where $E_{\parallel}(\lambda)$ and $E_{\perp}(\lambda)$ are the dichroic absorption curves for parallel and perpendicular orientation of the electric vector of light with respect to the film

Table IV. Magnetic Circular Dichroism of Fluoranthene^a

Transition	Exptl			Calc'n E	Calc'n D	Calc'n C	Calc'n B		
	B^b	$[\theta]_M^c$	B/D^d				$B_{i,j}^{k,f}$	$\Delta B_{i,j}^{k,f}$	
1	B^b	-0.2	B	-1.35	-1.58	-1.88	-0.47	$B_{2,1}^1 = 0.46$	-0.03
	$[\theta]_M^c$	+0.06	ΔB	+0.02	-0.07	-0.10	-0.07	$B_{4,1}^1 = +0.13$	0.00
	B/D^d	-(0.2)	B/D^e	-1.7	-1.4	-1.8	-1.25	$B_{1,G}^1 + B_{G,1} = -0.12$	0.00
2	B^b	-2.7	B	-1.31	-3.69	-6.34	-10.64	$B_{3,2}^2 = -10.4$	-0.1
	$[\theta]_M^c$	+0.59	ΔB	-0.09	+0.01	+0.09	+0.06	$B_{2,G}^2 = -0.91$	+0.01
	B/D^d	-0.22	B/D^e	-0.06	-0.12	-0.17	-0.35	$B_{6,2}^2 = +0.68$	-0.1
3	B^b	+0.6	B	+2.85	+5.09	+6.66	+9.85	$B_{1,2}^2 = +0.46$	+0.03
	$[\theta]_M^c$	-0.36	ΔB	+0.02	+0.02	-0.01	+0.005	$B_{2,3}^3 = +10.4$	+0.1
	B/D^d	+0.17	B/D^e	+1.2	+2.2	+1.3	+2.4	$B_{4,3}^3 = -1.21$	-0.02
4	B^b	+5.3	B	0.00	-0.19	+0.80	+0.87	$B_{9,3}^3 = +0.88$	+0.06
	$[\theta]_M^c$	-3.77	ΔB	+0.03	-0.01	-0.03	-0.02	$B_{2,G}^3 = -0.37$	+0.00
	B/D^d	+0.16	B/D^e	0.00	-0.09	+0.06	+0.07	$B_{3,4}^4 = +1.21$	+0.02
								$B_{6,4}^4 = -1.01$	-0.01
								$B_{8,4}^4 = +0.38$	+0.01
								$B_{12,4}^4 = +0.35$	-0.03

^a B terms in units of $10^{-3} \beta_e D^2/\text{cm}^{-1}$. Calculations used origin indicated in formula I. ΔB values give changes in calculated B terms for each 1 Å of displacement of origin in the positive direction of the z axis. Displacement along the y axis has no effect. ^b Rough estimates obtained by visually correcting for mutual overlap of transitions using curve shapes from Figure 3 and then using the equation^{24b} $B = -(33.53\nu_0)^{-1} \int [\theta]_M d\nu$ where ν_0 is the wave number of the estimated center of the band. ^c In units $\text{deg l. mol}^{-1} \text{m}^{-1} \text{G}^{-1}$, for 0-0 peaks of the transitions. ^d In units $10^{-3} \beta_e/\text{cm}^{-1}$. D values in D^2 are related to f values in Table II by $D = 2126300f/\nu_0$. ^e In units of $10^{-3} \beta_e/\text{cm}^{-1}$. D was obtained as $|\langle a|\mathbf{m}|b \rangle|^2 (D^2)$. ^f Important contributions to B . See text for definition of $B_{i,j}^{k,f}$. $\Delta B_{i,j}^{k,f}$ is the change in $B_{i,j}^{k,f}$ when the origin is displaced by 1 Å in the positive sense of the z axis.

stretching direction, respectively. The values of b_j and the derived transition moment directions ϕ are given in the first two rows in Table I to indicate the margin of error. The angles ϕ are defined as angles between j th transition moment direction and effective orientation axis, taken to be the z axis in formula I. Theoretically, of course, in I all angles ϕ should be 0 or 90°. In less symmetrical molecules, ϕ can have any value between -90 and +90° (positive sign means that the transition moment direction is displaced clockwise from the effective orientation axis).

In Figure 3 we present the reduced spectra obtained from measurements at 77°K, which show more detail than the previously published⁵ room-temperature spectra. The low-temperature work was done in still another batch of polyethylene (see Experimental Section) and the required reduction factors were $d_{\perp}^{\circ} = 0.34$ and $d_{\parallel}^{\circ} = 0.73$.

A different reduction of the room-temperature dichroic spectra has been proposed,³³ using only one adjustable parameter (equivalent to our d_{\perp}°) and deriving the other (equivalent to our d_{\parallel}°) from the assumption of uniform distribution of the angle γ , which describes the position of molecules with respect to rotation about their own long axis.²⁶ The resulting reduced curves were claimed to be identical with those of ref 5. Closer inspection shows, however, that the published³³ A_z spectrum contains contributions from the A_y part, in particular from transitions 3 and 7. It would then be necessary to claim mixed polarization even for what appear to be 0-0 components of these y -polarized transitions. The same situation occurred in other attempts to use only one adjustable reduction factor³⁴ as has already been pointed out.¹⁶ Since there is no physical basis for the assumption of uniform γ distribution for molecules other than rod shaped,³⁵ which fluoranthene definitely is not, it seems to us more reasonable to allow two adjustable parameters in the evaluation method and make the same assumption for z -polarized transitions which is already being made for y -polarized ones, namely that strong 0-0 components are purely polarized. This is supported by our results on azulene¹⁷ where direct comparison with reduced spectra obtained from mixed crystal studies is possible. Further support comes from work on planar molecules in which the y and z axes are equivalent, such as triphenylene, which orient quite well, solely on the basis of nonuniform γ distribution. We do not claim that the assumption of uniform γ dis-

tribution should never be used, only that it should not be made automatically. For approximately rod-shaped molecules, it appears to be quite valid, as has been shown for anthracene,^{26,36} 2,3-dimethylantracene,³⁶ acridine,²⁶ and even benzo[*k*]fluoranthene.³⁷

Meaningful polarized fluorescence excitation spectra of fluoranthene are hard to obtain because of the weakness of the first transition and the degree of vibronic mixing with the oppositely polarized second transition both in absorption and in fluorescence. This has already been noted earlier.⁴ We have tried to select only the very weak 0-0 component of fluorescence for detection but ran into instrumental limitations. Although the degrees of polarization we have measured presently (Table I) are considerably better than those published earlier⁴ and are fully compatible with the stretched sheet results, the angles α_j between the moment direction of the first and j th transitions which one would derive by straightforward application of the formula $\cos^2 \alpha_j = (P_j + 1)/(3 - P_j)$ are only about 45° instead of 0° and about 60° instead of 90°. In addition to the problem of separating the 0-0 component of fluorescence for observation, the measured values of P are also affected by overlap of the individual transitions. In particular, transition 3 is strongly affected by the tail of transition 2. The superiority of the stretched sheet method is clearly apparent. The only reason for including the calculated angles α in Table I is to give a feeling for the possible errors on by far the worst case examined. Note that in the convention adopted here α_j is a positive angle irrespectively of whether the j th moment direction is displaced clockwise or counterclockwise from the moment direction of the first transition. Polarization measurements do not distinguish between the two possibilities. On the other hand, we consider the angles ϕ_j to have a sign, although the stretched sheet method does not permit its determination, since the relative signs can be sometimes determined if the two methods are combined.

b. Fluorofluoranthenes. In principle, the low symmetry of these molecules permits polarization directions of π - π^* transitions to lie anywhere in the molecular plane. Since these directions are unknown, the values of orientation factors cannot be determined from the spectra although their limits can, by assuming that the transition with the highest b_j value lies in the orientation axis ($d_{\perp}^{\circ} = 1/b_j$) and that with the lowest b_j value lies perpendicular to it²⁶ ($d_{\parallel}^{\circ} =$

b_j). The values of $1/b_j$ were determined for band origins as assigned in Figure 2 using the standard procedure of stepwise reduction²⁶ and are given in Table I.

The absolute values of the angles ϕ_j of deviation from the orientation axis were evaluated using the formula²⁶

$$\tan^2 \phi_j = \frac{[(1/d_{\perp}^{\circ}) - b_j][2 + d_{\parallel}^{\circ}]/[b_j - d_{\parallel}^{\circ}][2 + (1/d_{\perp}^{\circ})]}$$

The required values of d_{\perp}° and d_{\parallel}° were obtained in two ways. In the first of these, it was assumed that the orientation and position of the orientation axis in a fluoro and amino derivative substituted in the same position are the same, since both have nearly identical shape, and that one out of all observed transitions in the two molecules is polarized in the orientation axis and one perpendicular to it, corresponding to minimum and maximum values for b_j , respectively. The second way of evaluation assumed simply that all fluorofluoranthenes have the same orientation factors as fluoranthene itself, as is indicated upon inspection of Table I. The results of the two evaluations of $|\phi_j|$ were the same within estimated limits of error and are given in Table I. In all five fluoro derivatives, polarizations of all transitions except 1 and 3 (and possibly 8) are within experimental error of those found in fluoranthene, *i.e.*, 0 or 90°. Transition 3, polarized at $\phi = 90^{\circ}$ in I itself, deviates measurably from this direction in 1, 2, 3, and 8-F-I, but not in 7-F-I. However, the deviation is always less than 45°. The values for transitions 5 and 6 are less accurate than most others, because of their complicated mutual overlap (*cf.* Figure 2). The accuracy of the determination is particularly poor for the first transition because of its low intensity, but in most fluoro derivatives it appears that ϕ_1 is distinctly different from 90° found in I.

Fortunately, measurements of polarized fluorescence excitation spectra (Table I) permitted a certain improvement in the accuracy of the results for the first transition. At the same time, relative signs of some of the deviation angles ϕ_j , in particular ϕ_3 vs. ϕ_1 , could be determined. Polarized fluorescence excitation is measured somewhat more reliably for the fluorofluoranthenes than for the parent hydrocarbon I. This is apparently due to the generally increased intensity of the first transition and a smaller relative importance of vibronic mixing. The results for the first transition approach in all cases the expected limiting value of 0.5 (Table I) and we believe that most of the remaining error is due to experimental depolarization and mutual overlapping of transitions. Although the derived absolute values of angles α_j between the direction of the first transition moment and that of the j th transition moment still cannot be taken at their face value, they are undoubtedly subject to much smaller error than was the case for I itself.

The way in which the values of $|\phi_j|$ were combined with those of $|\alpha_j|$ in order to narrow down the possible limits for polarization direction of the first transition, to check overall compatibility, and to determine the relative signs of the ϕ 's will now be discussed briefly on the example of 2-F-I. For this compound b_j 's can be determined from stretched sheet spectra for eight transitions. From the b_j values approximate $|\phi_j|$'s can be found within $\pm 15^{\circ}$ or less, except for the first transition where a determination from the stretched sheet spectra is only possible within $\pm 40^{\circ}$. From the polarized fluorescence the degree of polarization P is well established for 4 transitions (Figure 1). From their definition, the correct values of α_j must satisfy $\phi_j - \phi_1 = \pm \alpha_j$, so that $|\phi_1| = |\phi_j \pm \alpha_j|$. Now, $|\phi_j|$ and α_j are known for $j = 1$ through 4 (Table I) so that the following four equations can be written for $|\phi_1|$, with error margins indicated considering only the uncertainty in the experimental values of ϕ_j but not α_j : $|\phi_1| = 40 \pm 40^{\circ}$ ($j = 1$); $|\phi_1| \approx 50 \pm 10$ or $70 \pm 10^{\circ}$

($j = 2$); $|\phi_1| = 16 \pm 10$ or $92 \pm 10^{\circ}$ ($j = 3$); $|\phi_1| = 41 \pm 15$ or $71 \pm 15^{\circ}$ ($j = 4$). To satisfy all equations simultaneously, the value $|\phi_1| = ca. 75^{\circ}$ appears best, but because of the expected considerable uncertainty in the α_j 's, which expands the margin of acceptable deviation, it is not possible to safely exclude a solution $|\phi_1| = ca. 35^{\circ}$. Using either value for $|\phi_1|$, a set of relative signs for ϕ_1 through ϕ_4 can be determined from α_j for these transitions. The absolute sign of ϕ_3 is then chosen to agree with the calculations. Since the calculated value of ϕ_3 in 7-F-I is 90° , in this one case the sign of ϕ_1 is chosen to agree with that calculated. This procedure leads to a unique determination of ϕ_1 and of the signs for ϕ_2 through ϕ_4 for 1-, 3-, and 7-F-I. In the other cases there are two possible solutions for ϕ_1 , and both are given in Table II. The two are equally likely in the case of 8-F-I, but for 2-F-I one solution appears less likely and is placed within parentheses in Table II. However, the uncertainties do not affect the determination of the relative signs of the ϕ_j 's.

To summarize, the data in Table II show that fluoro substitution generally has very little effect on polarization directions. Only the very weak transition 1, and one of the medium intensity transitions, 3, are affected to a significant degree.

C. Comparison with Theory. a. Fluoranthene. Effect of Extensive Configuration Interaction. Results of the various calculations using only singly excited configurations and standard parameter values are very similar (Tables II and III) and are in good agreement with experiment for at least the first four transitions. This was already known from previous work as pointed out in the introduction. Our purpose in performing a larger scale SECI-1 calculation was not to improve the already quite impressive numerical agreement of the calculated energies of the main low-lying transitions with experimental values, but to see whether the number of excited states in the 200–450-nm region, their order, composition of their wave functions in terms of configurations, intensity of transitions into them, and the sign and origin dependence of the B terms of these transitions are affected when several dozen of the most strongly interacting doubly excited configurations are introduced. Such changes are well known to occur in certain other molecules.³⁸ Also, we were interested in finding out whether inclusion of a relatively large number of doubly excited configurations in a molecule of this size will not result in too many transitions being predicted for this region.

These various effects should be largely independent of the particular values of semiempirical parameters used (except for the effect of the shape of $\gamma = \gamma(r)$) and we have therefore kept the parameter values which had been known to reproduce experimental results in calculations using a small extent of CI. As a result the energies obtained in the SECI-1 calculations (set E) agree less well with experiment. In particular, since many doubly but no triply excited configurations are included, the 0.29-eV lowering of the ground state energy is out of proportion to the lowering suffered by the singly excited states.³⁹ To facilitate comparison with experiment in Figure 3, we have subtracted 0.29 eV from all calculated excitation energies. However, this has not been done in Table III. While the absolute values of SECI-1 excitation energies can normally be expected to be worse than SCI in the absence of parameter readjustment, their order is probably closer to that which would be obtained by exact solution of the PPP model (full CI). At least, this has been shown to be the case for smaller molecules.²⁵ Also the values of oscillator strength evaluated using the dipole length and dipole velocity formulas are somewhat closer together and presumably more reliable.

In the case of fluoranthene, going from SCI to SECI-1

has no fundamental effect for low-lying states. No new low-lying states are introduced and admixture of doubly excited character into existing states is moderate. The lowest eight excited states can be traced directly from one calculation to the other since their wave functions remain almost unchanged. The close-lying transitions 5 and 6 change their order. The reason for this is decrease in the energy of the sixth SCI excited state due to admixture at about 20% of the doubly excited 8,8 \rightarrow 9,9 configuration to become the fifth SECI-1 excited state. Also transitions 7 and 8 change their order. The order of the even higher transitions becomes quite scrambled, the tracing becomes hard, and the effect of going to SECI-1 is clearly quite profound. Intensities calculated from dipole length and dipole velocity formulas agree a little more closely in the SECI-1 calculation, but their order of magnitude remains unchanged for the first six transitions. For higher transitions, changes in calculated intensity are considerable. The agreement of SECI-1 with experimental order of states, as judged by energies, polarizations, and intensities, is excellent up to surprisingly high energies (Figure 3, Table III). If one assumes that the weak calculated transitions 9 and 11 are hidden under other absorption, the only flaws in the calculated results are the somewhat too high absolute values of energies and the reversed order of transitions 7 and 8. The absolute values of the calculated oscillator strengths are rather inaccurate, but the relative values are reasonable and agreement with experiment is improved for transitions 7 and higher. The relative intensity of transition 2 remains much too high.

Table III also shows the effect of the alternation of bond lengths (B vs. C), which is only minor. The difference between the two commonly used approximations for two-center integrals is displayed in columns C and D. The most striking effect is on calculated oscillator strengths. In particular, the relative intensity of transition 4 is described much better when Mataga integrals are used, although it still remains too small. This can be traced to considerable changes in the weights of various configurations in the fairly complicated wave function of the fourth excited state. We shall note below that this same sensitivity to details of calculation makes it very hard to predict the *B* term of this transition.

b. Fluoranthene. Relation to Spectrum of Acenaphthylene.

Although it is certainly gratifying to find satisfactory agreement between experimental and calculated spectral properties, it seems to us equally important to relate the main features of the observed spectra to those of similar compounds. In particular, it appears interesting to find out whether the spectrum of fluoranthene (I) can be simply derived from the spectrum of its parent nonalternant hydrocarbon, acenaphthylene (II). Such a relation is not readily apparent upon cursory glance at the ordinary absorption curves⁴ and, as far as we are aware, has never been discussed in the literature.

Nevertheless, inspection of the reduced spectra suggests the existence of a definite relationship. The weak Franck-Condon forbidden band of II which is responsible for its yellow color (0-0 band at 21,500 cm^{-1}) bears resemblance to the weak Franck-Condon forbidden band due to transition 1 in the A_y spectrum of I (Figure 3), while the intensity and shape of the two strong uv bands of II of opposite polarizations at 29,500 and 31,000 cm^{-1} are reminiscent of the bands in I due to transitions 2 and 3. On the other hand, the very strong *z*-polarized transition 4 of I appears to have no counterpart in the spectrum of II.

In the following we show that the PPP model confirms the suspected existence of such relations and offers a simple explanation of the striking blue shift of the weak first transition as one goes from II to the larger conjugated system of

I. The method used goes back to Dewar⁴⁰ and to Sandorfy's⁴¹ "HMO resemblance scheme" and to a previous analysis of the MO's and states of I in terms of MO's and states of naphthalene and benzene, which failed to yield simple spectral correlations.⁴

The discussion takes advantage of the fact that in both hydrocarbons configuration interaction plays only a secondary role in the description of the lowest three excited states. These correspond approximately to electron jumps from the highest, second highest, and third highest occupied MO into the lowest empty MO. Figure 5 shows how MO's of II combine with those of butadiene to yield the MO's of I. Only the frontier MO's are indicated. The shape and energies of the MO's were obtained from an SCF-PPP calculation (method C) but the interactions can be easily understood on a purely qualitative basis. First, the acenaphthylene MO's A4 and A8 are not expected to interact with the butadiene MO's since their expansion coefficients at the crucial atoms 1 and 2 of II are extremely small. They become fluoranthene orbitals F6 and F11, respectively. Second, the other two orbitals symmetrical with respect to mirroring in the *xz* plane, A6 in II and B3 in butadiene, interact relatively weakly since they are far from each other in energy. Their bonding combination, in which A6 predominates, gives rise to the fluoranthene MO F7, while the antibonding combination, in which B3 predominates, becomes F10. Finally, of the three interacting antisymmetric orbitals A7, B2, and A5, the former is relatively far in energy from the other two and is not changed much as it becomes F9, while B2 and A5 are almost degenerate and interact strongly. They give rise to F8, in which A5 predominates but B2 is not negligible, and F5, which is a fairly complicated mixture with large weight of B2. The correspondence A4 \rightarrow F6, A5 \rightarrow F8, A6 \rightarrow F7, A7 \rightarrow F9, B3 \rightarrow F10, and A8 \rightarrow F11 is easily verified by inspection of nodal properties and coefficient size in Figure 5. The decrease in the energy of A6 as it becomes F7 and increase in the energy of A5 as it becomes F8, and the resulting crossover, are now qualitatively understood as due to the interactions B3-A6 and B2-A5. The effects of these shifts on orbital energy differences are shown in the center of Figure 5. The difference between F8 and F9 is smaller by 0.36 eV than the corresponding difference between A5 and A7, while the difference between F7 and F9 is bigger by 0.46 eV than the corresponding difference of A6 and A7. The difference of F6 and F9 is almost the same as that of A4 and A7.

To derive energies of one-electron jumps, it is necessary to subtract a two-electron term from the orbital energy difference.⁴² Its size is related to the extent to which charge distribution in the orbitals overlaps in space and thus to the shape of the MO's and this is illustrated in Figure 5. For the jumps A5 \rightarrow A7 and F8 \rightarrow F9 it is smaller than for the others, and as a result these jumps require relatively higher energy than their orbital difference would suggest. The jump F7 \rightarrow F9 actually requires less energy than F8 \rightarrow F9, although the orbital energy differences would suggest the opposite. While the relative spacing of the configuration energies A(4 \rightarrow 7), A(5 \rightarrow 7), A(6 \rightarrow 7) could not have been predicted without knowledge of the corresponding two-electron terms, the shifts of the energies in going from II to I could still be predicted from changes in orbital energies provided only that the two-electron terms remain unchanged or change but little. Figure 5 shows that this condition is fulfilled. This is reasonable considering that the two-electron terms are determined by orbital shapes and these did not change very much between II and I.

Introduction of configuration interaction (Figure 5) has only a minor effect on the relative state energies and does not change the overall picture derived from orbital correla-

tion between II and I: the lowest energy transition in II corresponds to transition 1 in I and the cause of the blue shift (calculated 0.57 eV, experimental 0.4 eV) is the interaction of orbitals B3 with A6 and B2 with A7 (incidentally, these are the interactions which, in a different geometrical approach, facilitate the Diels-Alder reaction of butadiene with acenaphthylene according to Fukui's frontier orbital theory⁴³). The next higher transition in II corresponds to transition 2 in I, and the red shift (calcd 0.27 eV, exptl 0.2 eV) is due to the interaction of orbitals B2 and A5 which is only partially canceled by the interaction of B2 and A7. The third transition in II corresponds to transition 3 in I and lies within a few hundredths of an electron volt at the same energy in both (calculated and experimental). Similarity in band shapes and intensities is directly related to the similarities in the MO's of II and I, in particular to similar nodal structure. This causes similar bond weakening or strengthening in the two compounds upon similar excitations. For instance, the Franck-Condon forbidden shape of the first transitions is no doubt related to the introduction of an important node between acenaphthylene atoms 1 and 2 upon excitation in both molecules (compare A6 vs. A7 and F7 vs. F9; cf. Figure 5).

It might be argued that comparison with experiment ought to be done for vertical rather than 0-0 transitions. This would not change the qualitative picture obtained. Moreover, strictly speaking, comparison with properties of II (and butadiene) should not be done at the equilibrium geometry carbon skeleton in these molecules but at the equilibrium geometry of the corresponding section of the fluoranthene skeleton. Our approximation of equal bond lengths and use of 0-0 transitions for identification of bands thus appears acceptable.

It is possible to carry out a similar analysis for higher excited states but problems arise, mostly due to extensive configuration interaction. It is, however, worthwhile to discuss the origin of the intense transition 4 in I which has no obvious counterpart in II (the next intense transition in I, no. 7, is vaguely related to the intense fifth transition⁴ in acenaphthylene). While we have been able to relate fluoranthene transitions 1-3 to predominantly, although not strictly, locally excited states of II using simple correspondence between MO's of the two hydrocarbons, the CI description (method C) of transition 4 in I is superposition of configurations F(5 → 9) and F(7 → 10), and each of these involves one orbital with no counterpart in II. These are orbitals F5 and F10, corresponding approximately to B2 and B3, respectively. The two configurations correspond to electron jumps from an acenaphthylene MO to a butadiene MO (7 → 10) or *vice versa* (5 → 9) and thus clearly have no counterpart in II alone. The configurations could be called charge-transfer configurations, and transition 4 in I could perhaps be called a charge-transfer transition, but the term is misleading since the two principal contributing configurations transfer charge in opposite directions and the net transfer is negligible. Calculated (SECI-1) excited states dipole moments indicate that if any of the states has an increased dipole moment it is the lowest excited state (π -electron contribution is $2.2D$ vs. $0.6D$ in the ground state). The CI description of state 4 is even more complicated when Ohno-Klopman integrals are used (method D), but configurations F(5 → 9) and F(7 → 10) remain important and the picture of the transition does not change drastically. The sensitivity of the wave function of this state to the details of the calculation is probably related to the relatively poor calculated values of observables such as $\langle G | \mathbf{m} | 4 \rangle$ and $\langle 3 | \boldsymbol{\mu} | 4 \rangle$ (see below).

It is interesting to note that it has been suggested on a purely empirical basis as early as 1950 that effects of anne-

lation and substitution are best accommodated by postulating that the "p band" of fluoranthene is "localized" in the naphthalene portion of the molecule.⁴⁴ At present we would say that the transitions 1-3 constituting what used to be called the "p band" are, roughly speaking, localized in the acenaphthylene portion while transition 4 ("β band") definitely involves the whole π -electron system of I. The statement is only approximate since even those orbitals of I which can be traced back to II are at least partially delocalized over the whole molecule.

c. Fluoranthene. MCD Spectrum. The signs of the B terms for the first three transitions are predicted correctly by all methods tested (Table IV), and a more detailed discussion seems warranted. Formula 1 shows that the B term for the F th transition is obtained as a sum of contributions B_{I,G^F} due to the mixing by magnetic field of excited states I into the ground state G plus a second sum representing mixing of the ground state G as well as excited states I other than the F th into the F th excited state (contributions B_{G,F^F} and B_{I,F^F} , respectively). Change of origin would not change the sum total if the calculation was performed in full CI basis (FCI)²³ but magnitudes of the individual contributions would change, since $\langle a | \boldsymbol{\mu} | b \rangle$ and $\langle a | \mathbf{m} | a \rangle$ are origin-dependent quantities. This shows that any attempt to analyze the magnitude of a given B value in terms of specific contributions due to mixing with other states should be taken with a grain of salt since it is tied to a particular choice of origin. However, it appears physically sensible to choose the origin somewhere inside the carbon skeleton of the molecule. If it so happens that moving the origin within this area (*ca.* $5 \times 7 \text{ \AA}$ in our case) does not affect the individual contributions significantly, a discussion of the origin of the B values in terms of such specific contributions from mixing with various other states can be useful.

Since FCI calculations on molecules of the size of I are not practicable, all of the calculated B terms shown in Table IV were obtained with severely truncated CI basis sets, and thus are origin dependent. This is rather disturbing since for any one chosen transition any desired value of B could be obtained by the suitable choice of origin. On the other hand, Table IV shows that the degree of origin dependence of the B terms is quite small, so that the results are not affected significantly by moving the origin over small distances, say *ca.* 7 \AA along the z axis inside the molecule. Because of molecular symmetry, displacement of the origin along the y axis has no effect. In the following, we shall adopt the viewpoint²³ that it is physically reasonable to choose the origin somewhere within the molecule and that each such choice gives us an approximation to the B value which would be obtained with a full origin-independent FCI calculation, and which has a good chance of providing a reasonable approximation to reality, at least for a few low-lying states, for which mixing with σ -electron states can be hopefully neglected, in view of the well-established reasonableness of the PPP model for simulation of other spectral properties.

Table IV shows that the uncertainty due to origin dependence is insignificant compared to the uncertainty originating from the truncation of the CI basis and from reasonable freedom in parameter choice. The agreement with experimental signs for the first three transitions in fluoranthene, and similar agreement found for half-a-dozen other nonalternant hydrocarbons, to be reported elsewhere,²³ however indicates that the PPP model and the approximations made in calculating the B values are not totally inappropriate.

Inspection of our numerical results for the lowest six excited states (units of $10^{-3} \beta_e D^2 / \text{cm}^{-1}$) shows that the vast majority of the terms in the two sums in eq 1 are negligibly small (10^{-2} units or less), less than a dozen are of the order

of 0.1, and less than half-a-dozen are anywhere near 1. Occasionally, one of the terms is as large as 5 and it then usually dominates over all other contributions. Table IV shows that the origin dependence of the individual contributions is also quite small and only rarely approaches 0.1 for 1-Å displacement. This is true for the terms in which $\langle a | \mu | b \rangle$ is the only origin-dependent term. The two contributions to the B term of the F th transition which are due to mutual mixing of the ground and F th excited states by the magnetic field are nonzero for y -polarized transitions and contain $\langle G | \mathbf{m} | G \rangle$ and $\langle F | \mathbf{m} | F \rangle$, respectively, and these matrix elements are very strongly origin dependent. However, the sum of the two contributions contains only the difference $\langle F | \mathbf{m} | F \rangle - \langle G | \mathbf{m} | G \rangle$, which is origin independent, and of course, $\langle F | \mu | G \rangle$, which introduces a similar weak origin dependence as is experienced by all other contributions. For both y -polarized transitions 1 and 3, the sum of these terms turns out to be very close to zero.

Because of the only weak origin dependence of the individual contributions (or a pair of contributions as discussed above), it appears meaningful to discuss their physical significance. Again, most of the uncertainty does not come from the origin dependence but from the differences between the results of the various approximations shown in Table IV. The calculated B terms are generally too large and the discrepancy diminishes with increasing extent of CI. The exaggerated values of B terms are not surprising considering that the matrix elements of the electric dipole operator which are used in their calculation also commonly lead to excessively high values of oscillator strengths. Table IV also compares the experimental and calculated values of the ratio B/D in which this particular problem is removed. Here, dipole strength D is defined as the square of the electric dipole transition moment in square debyes.

Notwithstanding the only qualitative meaning of the calculated values, some general statements about their physical origin appear safe. They have been derived from analysis of the individual contributions to each B term. These are only weakly origin dependent and the resulting picture is the same in all calculations performed (illustrated for method B in Table IV).

The negative sign of the B term of the first transition is due to magnetic mixing of the second excited state into the first one (contribution $B_{2,1}^1$). The same mixing provides a positive contribution $B_{1,2}^2$ to the B term of the second transition, but this is overridden by a much larger negative contribution $B_{3,2}^2$ due to mixing the third excited state, also aided by a smaller negative contribution $B_{1,G}^2$ due to mixing of the first excited state into the ground state. The strong mixing of the second with the third excited state provides a large positive contribution $B_{2,3}^3$ to the B term of the third transition. Other contributions to this term are much smaller and tend to cancel.

For the fourth transition, agreement with experimental sign is not always obtained and this is understandable upon inspection of the origin of contributions to its B term. No single contribution dominates. There is a positive contribution from mixing of the fourth with the third excited state, similar negative contribution from mixing with the seventh excited state, and several not much smaller contributions from even higher excited states. The value of the sum reflects a delicate balance of these contributions, and since the quality of our wave functions and energy differences for higher excited states is rather doubtful it is not surprising that the results depend on the approximation used and are unreliable. The complicated origin of the B term of the fourth transition appears to be related to its more complicated CI description in terms of MO configurations and, as already pointed out, it is quite likely that our failure to cal-

culate its B term reliably has the same physical origin as our failure to obtain a more reasonable value for its oscillator strength.

The situation is even worse for the higher excited states and it seems that the present type of calculation will only be useful for the prediction of signs of the lowest few B terms, or more specifically those B terms which are dominated by a single contribution. Of course, it has been suspected for a long time that this will be so (e.g., ref 24b), but it has not been clear just how often such a situation will arise.

It is heartening to observe that domination by a single large contribution appears to be the rule for the lowest few transitions not only in fluoranthene but also the other nonalternant hydrocarbons investigated by us so far,²³ since it indicates that interpretation of MCD spectra will be easier than suspected at first sight. One of the reasons for this situation is the relative spacing of transitions and the alternation of their polarization directions. In fluoranthene and many other hydrocarbons this is such that near each of the low-lying transitions there are one or two transitions of opposite polarization, for which the energy difference in the denominator is small and the contribution to the B term large. The next nearest neighboring transitions have unsuitable polarization directions and do not contribute, while the contributions of those even farther removed in energy suffer from much larger energy differences in the denominator. It is less clear that the contribution of one of the two neighboring transitions of suitable polarization will always dominate over the other. Three obvious reasons why this might occur are contained in the form of eq 1: first, the transition moment from the ground state into one of the neighboring transitions may be much smaller than that from the other, and this is immediately obvious from the absorption spectrum; second, the magnetic transition dipole moment between the state under investigation and one of the neighboring states may be much smaller than that for the other; third, the energy separations may be very unequal. For instance, the overwhelming size of $B_{3,2}^2$ compared with $B_{1,2}^2$ can be partly blamed on the small transition moment $\langle G | \mathbf{m} | 1 \rangle$ of the weak first transition compared to that of the much stronger third transition. In order to understand why $B_{4,3}^3$ is smaller than $B_{2,3}^3$, one notes that both the second and the fourth transitions are strong, but the energy separations differ considerably, favoring $B_{2,3}^2$.

Such fortunate circumstances as for transition 3 in I may not always obtain and we feel that it is desirable, at least for the time being, to always perform a relatively detailed analysis, preferably based on a fairly extensive calculation, say at least including all singly excited configurations, in order to identify all the largest contributions, rather than just blindly assume that only mixing due to the nearest neighbor transitions will be important.

It might be argued that our evidence for $B_{4,3}^3$ being substantially smaller than $B_{2,3}^3$ is based on calculations alone (Table IV) and is not necessarily correct. We feel that experimental data support such a claim and even provide some evidence supporting the calculated negative sign of $B_{4,3}^3$, which reduces the overall positive magnitude of the B term of the third transition. This is based first on the observation that the latter is considerably smaller than the oppositely signed B term of the second transition and second on the reversal of sign of the MCD curve for the third transition as one goes to a higher vibrational level. Since all of the third transition is y polarized, the simplest way to understand relative MCD signs and intensities of the individual vibronic levels, which involve totally symmetrical vibrations, is to assume that these are purely a result of changes in the energy difference in the denominator. Then, the effect of mixing with the second state predominates for the

0-0 peak of the third transition, which is relatively close to the strong peaks of the second transition (Figure 3). On the other hand, the 0-1 peak of the third transition is closer to the high-intensity region of the fourth transition, the effect of mixing with it is stronger, and since $B_{4,3}^3$ opposes the effect of $B_{2,3}^3$, the MCD curve reverses its sign. If $B_{4,3}^3$ were not negative, it would merely reinforce the effect of $B_{2,3}^3$, and the MCD sign reversal between the 0-0 and 0-1 peaks of the third transition would be harder to understand, considering that both are y polarized. Further, negative $B_{4,3}^3$ implies positive $B_{3,4}^4$ and the B term of the fourth transition indeed is positive. Our calculations apparently underestimate the relative magnitude of $B_{4,3}^3 = -B_{3,4}^4$ with respect to the other $B_{j,k}^i$'s and as a result the calculated B term of the third transition is too large (positive) compared with that of the second transition (negative), and the calculated B term of the fourth transition is not sufficiently large (positive) compared with the others. Clearly much of the positive B value of the fourth transition must originate from mixing with y -polarized states at higher energies, presumably with the seventh excited state (Figure 3), but this effect is apparently underestimated by the calculation. Perhaps the calculated values of both $\langle 3|\mu|4 \rangle$ and $\langle 4|\mu|7 \rangle$ are too small due to inadequate description of the complicated CI mixing involved in the states 4 and 7.

Guided by the results of calculations, we take the MCD spectrum of fluoranthene to imply the following. First, $B_{2,1}^1 = \text{Im}\{\langle 1|\mu|2 \rangle \langle G|\mathbf{m}|1 \rangle \times \langle G|\mathbf{m}|2 \rangle / (W_2 - W_1)\}$ is a negative number approximately equal to the B term of the first transition (ca. $-0.2 \times 10^{-3} \beta_e D^2/\text{cm}^{-1}$; unfortunately its magnitude is almost impossible to estimate because of vibronic interactions and strong overlap). Second, $B_{3,2}^2 = \text{Im}\{\langle 2|\mu|3 \rangle \langle G|\mathbf{m}|2 \rangle \times \langle G|\mathbf{m}|3 \rangle / (W_3 - W_2)\}$ is a negative number approximately equal to the B term of the second transition (estimated as $-2.7 \times 10^{-3} \beta_e D^2/\text{cm}^{-1}$). Third, $B_{4,3}^3 = \text{Im}\{\langle 3|\mu|4 \rangle \langle G|\mathbf{m}|3 \rangle \times \langle G|\mathbf{m}|4 \rangle / (W_4 - W_3)\}$ is a negative number whose magnitude is very roughly equal to the sum of the B terms of the second and third transitions (ca. $-2.1 \times 10^{-3} \beta_e D^2/\text{cm}^{-1}$). Estimating the centers of the four bands to lie at 27,000, 29,500, 31,000, and 35,500 cm^{-1} , respectively, we get $W_2 - W_1 = 2500 \text{ cm}^{-1}$, $W_3 - W_2 = 1500 \text{ cm}^{-1}$, and $W_4 - W_3 = 4500 \text{ cm}^{-1}$. From experimental oscillator strengths (Table II), we get $|\langle G|\mathbf{m}|1 \rangle| = 0.97 \text{ D}$ (very approximately because of extensive overlap and vibronic intensity borrowing), $|\langle G|\mathbf{m}|2 \rangle| = 3.53 \text{ D}$, $|\langle G|\mathbf{m}|3 \rangle| = 1.85 \text{ D}$, $|\langle G|\mathbf{m}|4 \rangle| = 5.74 \text{ D}$. Thus, we obtain, in units of Bohr magneton, $|\langle 1|\mu|2 \rangle| = 0.15$ (very approximately), $|\langle 2|\mu|3 \rangle| = 0.6$, and $|\langle 3|\mu|4 \rangle| = 0.9$. Because of obvious severe problems with band overlap and vibronic interactions, these numbers have only qualitative significance and the main reason for quoting them is to show that their order of magnitude is reasonable.

The calculated numbers depend somewhat on the particular approximations made. For method B, the results are $|\langle 1|\mu|2 \rangle| = 0.14$, $|\langle 2|\mu|3 \rangle| = 1.6$, $|\langle 3|\mu|4 \rangle| = 0.8$, which are in qualitative agreement with the above "experimental" values.

Since the first two transitions in fluoranthene can be quite well represented as one-electron jumps, and the third one almost as well, as already discussed above, the signs of $B_{2,1}^1$, $B_{3,2}^2$, and $B_{4,3}^3$ can be simply related to properties of the molecular orbitals involved in the transitions (no. 6-9). On the one hand, this serves as an experimental test of certain aspects of the orbitals rarely if ever tested otherwise; on the other hand, it provides the ultimate in "intuitive" understanding of the low-energy part of the MCD spectrum of fluoranthene, if the form of the MO's is taken for granted. As discussed above, if desired, the form of the MO's can be understood by reference to the MO's of butadiene and ace-

naphthylene whose shape can in turn be similarly reduced in several steps to those of ethylene and thus to the most primitive quantum mechanical notions.

The procedure used for simple visualization of the origin of the signs of $B_{I,F}^F$'s from the form of MO's involved in the one-electron jumps representing transitions $G \rightarrow I$ and $G \rightarrow F$ follows in a straightforward manner from formula 1 and is discussed in more detail elsewhere.²³ To summarize briefly, the sign of $B_{I,F}^F$ is obtained as a product of three signs. The first of these is the sign of the energy difference $E_I - E_F$ (positive if $I > F$, negative if $I < F$). The second sign is given by the relative orientation of the directions of dipole length transition moments and is positive if the head of the arrow representing the dipole length of F th transition is displaced clockwise from that representing the I th transition, and negative if the displacement is in the counterclockwise sense. The third sign is given by the direction of the magnetic field caused by the transition current between F th and I th excited states and is determined from the prevailing sense of circulation given by arrows directed along bonds, where the length and direction of each arrow are determined from MO expansion coefficients using a simple recipe described below. If the overall circulation is directed counterclockwise, the contributed sign is positive, if its sense is clockwise, the contributed sign is negative.

The second and third signs are determined unambiguously once the phases of all MO's involved are chosen. If any one of these is multiplied by -1 , neither or both signs change, so that there is no net effect, as is reasonable, since values of observables do not depend on the phase of a stationary wave function. Thus, MCD spectroscopy, like ordinary polarized spectroscopy, cannot determine the absolute sense of an electric dipole transition moment (second sign), but, unlike ordinary polarized spectroscopy, determines the relative sense of two such moments with respect to the sense of the magnetic dipole transition moment between the two excited states, and thus provides an interesting new way of checking the correctness and internal consistency of simple models of molecular structure.

As an example, we apply the procedure to the contributions to the B term of transition 2 provided by its neighbors, transitions 1 and 3. These are $B_{1,2}^2$ and $B_{3,2}^2$, and since $B_{I,J}^J = -B_{J,I}^I$, they also provide us with the signs of $B_{2,1}^1$ and $B_{2,3}^3$, which, according to the preceding discussion, determine the signs of the B terms of transitions 1 and 3. We shall represent transition 1 as a one-electron jump $7 \rightarrow 9$, transition 2 as $8 \rightarrow 9$, and transition 3 as $6 \rightarrow 9$. We shall choose the orbital phases by specifying that shaded circles indicated in Figure 5 correspond to positive sign. Then, the vectors representing the three transition dipole lengths are as shown in Figure 6. At each atomic center, transition density, given as the product of the expansion coefficients at that particular atom of the MO's involved in the one-electron jump, is indicated by a circle. Its diameter is proportional to the size of the transition density, and shading corresponds to positive sign. This picture is easily derived from the MO forms given in Figure 5. Contribution of each atomic density to the transition dipole length is obtained by multiplication by the x or y coordinate of the atom and is shown as a vector located at the corresponding atomic center, whose length is proportional to the contributed dipole length and whose sense is given by the product of the signs of the transition density and the x or y coordinate. Only contributions from either x or y are shown, since the others cancel due to molecular symmetry. The sum total of all the atomic contributions is equal to the transition dipole vector and is shown as a double arrow in the center of the molecule.

Transition currents are shown in the lower part of Figure

6. They are given for the transition between excited states 2 and 1 and 2 and 3. In the former case, the current is obtained from the coefficients of orbitals 8 and 7, in the latter of MO's 8 and 6. This follows since $\langle I \rightarrow J | \hat{A} | K \rightarrow L \rangle = \langle J | \hat{A} | L \rangle \delta_{IK} - \langle K | \hat{A} | I \rangle \delta_{JL}$. To obtain the arrows showing the transition current, for instance from excited state 2 to state 3, we calculate the quantity $\rho = C_{\alpha 8} C_{\beta 6} - C_{\alpha 6} C_{\beta 8}$ for each bond, where $C_{\mu i}$ stands for the expansion coefficient of the i th MO at the μ th atom and is taken from Figure 5, and α and β are the two termini of the bond, labeled in such a way as to make ρ positive. Then, an arrow is drawn from atom α toward atom β and its length is proportional to $C_{\alpha 8} C_{\beta 6} - C_{\alpha 6} C_{\beta 8}$. This easy and simple procedure is justified elsewhere²³ and depends on the fact that all bond lengths are equal in our model. The quantity $C_{\alpha 8} C_{\beta 6} - C_{\alpha 6} C_{\beta 8}$ for a bond reflects a fairly intricate interplay between the size of the MO coefficients and the nodal properties of both MO's involved but it can be quite straightforwardly derived by inspection of the form of MO's in Figure 5.

Once the transition dipole vectors and sense of current circulation have been derived by inspection of Figure 5 as displayed in Figure 6, it is a simple matter to determine the signs of $B_{1,2^2}$ and $B_{3,2^2}$ using the rules given above. For $B_{1,2^2}$ we get $(-)(+)(-) = (+)$, for $B_{3,2^2}$ we get $(+)(-)(+) = (-)$, in agreement with our analysis of the experimental data as well as the full numerical calculation.

Admittedly, the "prevailing" sense of current circulation is an ill-defined concept. A more quantitative definition is described elsewhere²³ but is not needed here since no question arises about the sense of the circulation (Figure 6).

An interesting possibility to relate the MCD spectra of I and II now exists since we have shown that transitions 1, 2, and 3 in I are in close relation to transitions 1, 2, and 3 in II, respectively: they correspond to one-electron jumps between orbitals of very similar shape and nodal properties in I and II. Since the orbitals do not change much between I and II, the transition dipole vectors and transition currents should also remain more or less the same. Loss of contributions from the "butadiene" part of I should be at least partially made up for by increase of the average size of MO coefficients in the "acenaphthylene" part, required by the normalization condition. The order of states also remains the same in I and II, and we would thus expect the same signs for $B_{1,2^2}$ and $B_{3,2^2}$ in the two molecules. Since the B terms of the first three transitions in I have simple origin, with very few important contributions, and since II has even fewer low-lying excited states which might contribute (transition 4 of I is missing in II), there is reasonable hope that the MCD spectrum of II is simply related to that of I. Thus, the B term of the first transition in II should be dominated by $B_{2,1^1}$, which is negative, and should be even smaller than in I because of increased energy separation of transitions 1 and 2. The B term of the second transition in II should be dominated by $B_{3,2^2}$, as in I, the more so since transition 1 is now farther in energy and transition 3 closer, and should thus be large and negative. The B term of the third transition in II should be determined by $B_{2,3^2}$, particularly since transition 4 of I has no analogy in II while transition 2 is even closer in energy. This term should therefore be large and positive. These conclusions are in agreement with our unpublished experimental as well as calculated results for II. This reinforces our belief that the parallel drawn between the excited states of I and II is reasonable.

d. Fluorofluoranthenes. The results in Table II show that the purely conjugative model used, although claimed to be successful in another instance,²⁸ is too crude for a prediction of the very small substituent effects on excitation energies. Even the signs of many substituent shifts are pre-

dicted inaccurately, and this is true even for the lowest energy transitions. The calculated angles correctly predict that polarization directions of the strong transitions do not change much from the 0 and 90° values of fluoranthene. The calculations appear to underestimate the effects of substitution on the moment direction of transition 3 and generally overestimate the effects on transition 1. Numerical agreement of the calculated and experimental polarization angles for these two transitions is very poor. A comparison of calculated oscillator strengths with observed relative size of ϵ_{\max} for corresponding transitions shows that some trends are correctly reproduced for the first four transitions, but again, the overall level of agreement is disappointing.

The most obvious and still simple potential remedy is to include the inductive effect of the fluoro substituent on the adjacent carbon atom. We plan to collect experimental data for additional fluoro-substituted hydrocarbons before proceeding to improved calculations. Also, we feel that the purely conjugative model used here is too crude to warrant extensive CI calculations on the SECI-1 level, or calculations of MCD spectra.

Summary

The present work can be summarized as follows. (1) Eight (possibly nine) separate electronic transitions in I have been located in the 200–450-nm region and characterized by their energies, intensities, polarizations, and B terms. This was achieved by the powerful combination of linear dichroic, magnetic circular dichroic, and substituent effect measurements. (2) The approximate magnitude of magnetic dipole transition moments between several pairs of excited states has been derived, as have their direction in space with respect to electric dipole transition moments from the ground state to the excited states. (3) Contrary to earlier suggestions by some other authors, pure I does not exhibit double emission, the previously detected first excited state is authentic, and its spectral properties do not require a postulate of nonplanarity. (4) One-parameter methods in the evaluation of linear dichroic spectra in stretched sheets, advocated by some authors, are inadequate for general use. (5) Semiempirical π -electron calculations for fluoranthene are in good agreement with experimental results, including the B terms for the lowest three transitions. Origin dependence of calculated B terms is annoying in principle but does not represent a practical problem since it is small and only orders of magnitude are calculated anyway. (6) CI calculations with extensive use of doubly excited configurations cause excessive depression of the ground state energy in the absence of parameter readjustment but improve agreement with experiment for the higher lying states. No low-lying states with significant doubly excited character are predicted and no new states unaccounted for by experiment are predicted up to quite high energies. (7) Low-lying excited states of I can be simply understood in terms of those of the parent hydrocarbon II and similarities in their absorption and MCD spectra are thus easily accounted for. (8) Fluoro substitution has little effect on excitation energies and polarization directions (except for the relatively weak transitions 1 and 3) but affects significantly the intensities and size of B terms of several transitions, particularly the intense transition 4. (9) The effects of fluoro substitution are in very poor agreement with calculations using a simple purely conjugative model and development of a better model is called for.

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