The MCD spectra are affected by substitution in the region above 40 000 cm^{-1} and we attribute this to the presence of several overlapping transitions under the strong absorption peak of **1** at 44 000 cm^{-1}, whose ordering, intensities, and mutual interactions are sensitive to substitution.

Transition 5. With the exception of **3-F-1**, the MCD spectra reported here clearly show the presence of at least one new transition near the one previously labeled 5 (44 000 cm^{-1}). We label the new transition 5 and identify it with the weak *y*-polarized transition calculated[3] at 42 000 cm^{-1} using extensive CI. The intense transition, previously labeled 5, is relabeled as 6. The spectra of **1,2-C_2O_3-1** and **1,2-CN-1** also show clearly the recently discovered[3] transition 7 (labeled 6 in ref 3).

Conclusions

The mirror-image MCD properties of the L and M bands of **1** and **2** as well as their absolute MCD signs can be understood in terms of the simple theory of parts 1–3,[2] although the relation of **1** and **2** to perimeter states is clearly only distant. The agreement, in return, suggests that the correlation of the L and M states of **1** and **2** with those of their respective perimeters, however remote, and the assignment of L_1 and L_2 character to these states are reasonable.

The first four signs in the MCD spectrum of **1** are remarkably insensitive to the effects of the very same substituents which affect severely the signs observed for structurally related soft chromophores such as naphthalene, and this demonstrates the value of the hard–soft distinction. The existence of such imperturbable "structural signatures" in MCD spectra may be of interest for structural work.

Finally, as many times before, MCD measurements have revealed the presence of a new excited state.

References and Notes

(1) Part 15: D. Otteson, C. Jutz, and J. Michl, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) J. Michl, *J. Am. Chem. Soc.*, companion papers in this issue (parts 1–3).
(3) E. W. Thulstrup and J. Michl, *J. Am. Chem. Soc.*, **98**, 4533–4540 (1976).
(4) J. Kolc and J. Michl, *J. Am. Chem. Soc.*, **98**, 4540–4549 (1976).
(5) J. Michl and J. F. Muller, *J. Am. Chem. Soc.*, **98**, 4550–4553 (1976).
(6) G. P. Dalgaard and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 17).
(7) M. A. Souto, D. Otteson, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 18).
(8) E. Heilbronner, J. P. Weber, J. Michl, and R. Zahradník, *Theor. Chim. Acta*, **6**, 141–158 (1966).
(9) J. Michl, *J. Am. Chem. Soc.*, **98**, 4546–4549 (1976).
(10) J. Michl, *J. Chem. Phys.*, **61**, 4270–4273 (1974).
(11) M. J. S. Dewar and J. Michl, *Tetrahedron*, **26**, 375–384 (1970).
(12) D. A. Herold, M.A. Thesis, University of North Carolina at Chapel Hill, 1972.
(13) A. Castellan and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 4).
(14) M. R. Whipple, M. Vašák, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 8).

Magnetic Circular Dichroism of Cyclic π-Electron Systems. 17.[1,2] Derivatives of Fluoranthene

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Abstract. Magnetic circular dichroism of the negative-hard chromophore fluoranthene is analyzed in terms of the simple theory of parts 1–3 and related to the properties of the perimeter. MCD spectra of the five aminofluoranthenes, the 1-, 3-, and 7-fluoranthenecarboxylic acids, and 3-azafluoranthene are reported and interpreted. The MCD signs of low-energy transitions are the same as in the parent hydrocarbon, as expected for derivatives of a hard chromophore and in striking contrast to those of the isomeric soft chromophore pyrene. An exception is found in a few instances for the sign of the third transition, whose B term is calculated to result from the balancing of two large and opposing contributions. For the same reason, simple PPP calculations which predict the signs of other low-energy transitions correctly are only partially successful for this "soft" transition.

Introduction

As discussed in some detail in part 16,[1] the qualitative model of parts 1–3[5–7] leads one to expect that peri-condensed hydrocarbons with a $(4N + 3)$-atom perimeter and one inside carbon will be negative-hard MCD chromophores. As long as transitions related to the L_1 and L_2 states of the perimeter can be identified, the contribution of their mutual magnetic mixing to the *B* term of the lower of these two states should then be negative and that to the upper of the two states should be positive. Fluoranthene (**1**) is a good example of this type of a peri-condensed hydrocarbon and we presently report an investigation of the effect of strongly interacting substituents on its MCD spectrum. In part 16,[1] we have reported an investigation of substituent effects on the MCD spectrum of another hydrocarbon which the simple theory predicts to be hard, acenaphthylene; in preceding papers of this series we have reported complementary studies of substituent effects on chromophores which the theory predicts to be soft.

Low-lying singlet excited states of **1** have been recently reviewed[4] and their relation to the spectra of the five aminofluoranthenes[3] and of 3-azafluoranthene[8] are fairly well understood.

The lowest transition in **1** (K) is weak, *y* polarized, and lies near 25 000 cm^{-1}. It is followed by a medium-strong *z*-polarized transition (L) near 28 000 cm^{-1}, a somewhat weaker *y*-polarized transition (M) near 31 000 cm^{-1}, a very strong *z*-polarized transition (4) near 35 000 cm^{-1} for which we propose[9] the label N, a medium-intensity *z*-polarized transition (5) near 38 000 cm^{-1}, another medium-intensity but *y*-polarized transition (6) near 38 000 cm^{-1}, a strong *y*-polarized

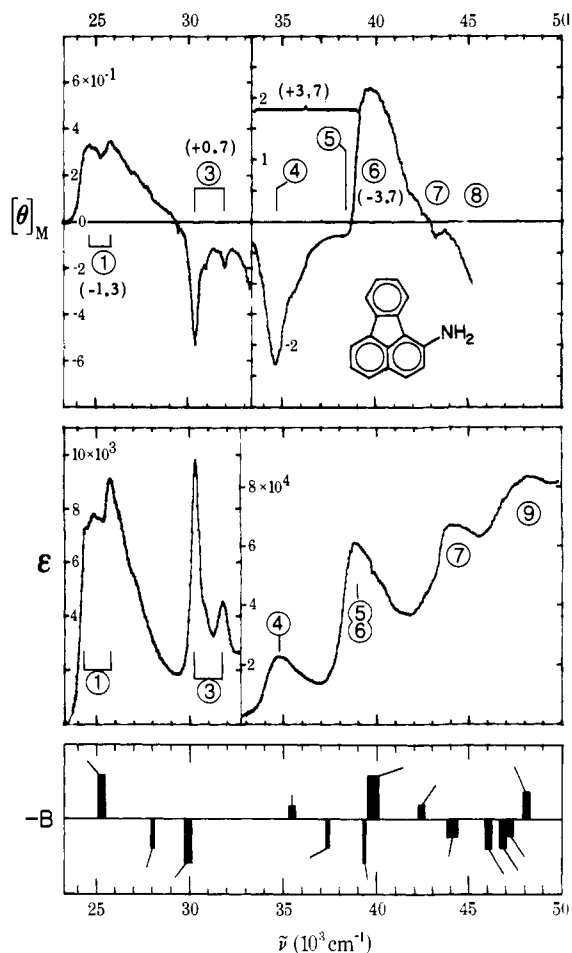**Figure 1.** 1-Aminofluoranthene: top, MCD spectrum (B terms in parentheses, units of $10^{-3}\beta_e$ D^2/cm^{-1}); center, absorption spectrum (cyclohexane); bottom, calculated values of $-B$ in units of $10^{-3}\beta_e$ D^2/cm^{-1} ($|B|$ <1, short lines; $1 < |B| < 5$, medium lines; $|B| > 5$, long lines). Calculated oscillator strengths f (dipole length) are shown: thin lines, $f < 0.1$; medium lines, $0.1 < f < 0.5$; thick lines, $f > 0.5$). Calculated polarization directions are shown as thin lines oriented relative to the formula shown.

Figure 2. 2-Aminofluoranthene. See caption to Figure 1.

transition (7) near 42 000 cm^{-1}, and a medium-intensity z-polarized transition (8) near 44 000 cm^{-1}. Some of the undoubtedly numerous higher transitions have also been characterized. Similarly as in other compounds of the acenaphthylene family,[10] transition L correlates with the L_1 transition of the perimeter, and transition M correlates with its L_2 transition, as is clearly seen from the orbital correlation diagram in Figure 6 of part 16.[1] The signs of the B terms for **1** have already been reported;[4,11] for the first four transitions they agree with those of acenaphthylene[12] (−,−,+,+ in order of increasing energy), and the signs of the bands L (−) and M (+) are those expected[1] from their mutual magnetic mixing for a ($4N + 3$)-atom perimeter case. Also, the MCD spectra of the five fluorofluoranthenes have been measured[4] and found to be almost indistinguishable from that of the parent **1**, in striking contrast to the MCD spectra of the fluoro derivatives of soft chromophores such as the isomer, pyrene.[13] Like acenaphthylene,[1] and unlike another nonalternant hydrocarbon studied in this series, azulene,[14] **1** should be a very hard chromophore and magnetic mixing of states (in the sum-over-states language) should be difficult to affect not only by weakly interacting substituents such as the fluoro substituent mentioned above but even by strongly interacting ones. However, the MCD signs of all low-energy bands should not be equally "hard", i.e., resistant to change upon substitution. In particular, the sign of the third transition (M), which is believed to result from near cancellation of two opposing contributions, due to
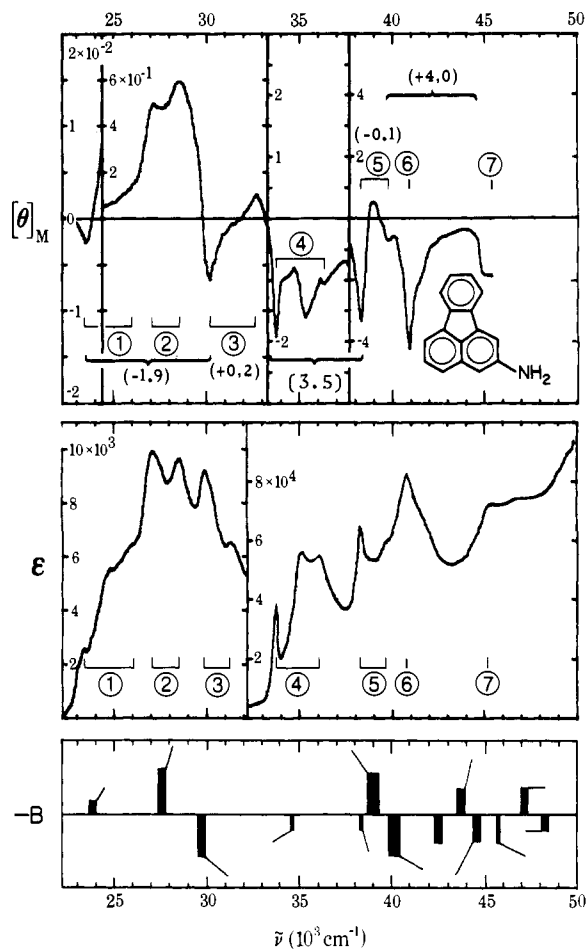
L–M and M–N mixing, ought to be "softer": the signs of the two contributions do not change easily upon substitution but their relative size may. Thus, it is of interest to examine the MCD spectra of derivatives of **1**, and in the present study, we report the effects of the more strongly interacting amino, carboxy, and aza substituents. In most instances, all MCD signs of low-lying transitions are still the same as in parent **1**. However, in 3-, 7-, and 8-amino derivatives, the MCD sign of the M transition is reversed to positive, demonstrating its "softer" nature.

In the following, we shall refer to the derivatives of **1** by abbreviations of the type X-NH$_2$-**1**, where X indicates the position of substitution.
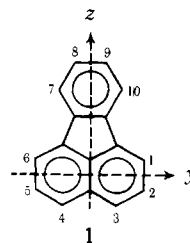
Experimental Section and Calculations

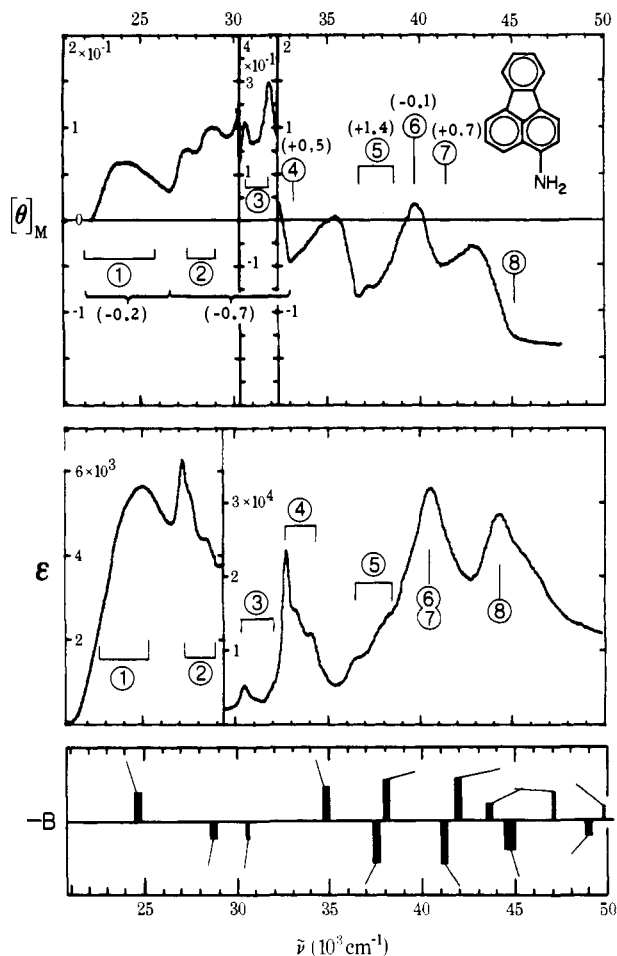**Figure 3.** 3-Aminofluoranthene. See caption to Figure 1.

Figure 4. 7-Aminofluoranthene. See caption to Figure 1.

Results

The experimental results are shown in Figures 1–9 and are to be compared with the spectra of **1** itself[11] and of its five fluoro derivatives.[4] Low-temperature absorption spectra of the five aminofluoranthenes have already been published and the assignments of individual electronic transitions as well as correspondence to transitions in the parent (**1**) have been discussed.[3] They were based both on the previous experimental results and on the MCD curves reported presently. The first two transitions in the amines correspond to the first two transitions of **1**, mixed heavily by the effect of the substituent, so that the L character is shared by both. Roughly speaking, in 2-NH$_2$-**1** and 8-NH$_2$-**1**, the order of the two transitions is the same as in **1** (the weak transition is lower in energy), and in the 1-, 3-, and 7-isomers it is reversed (the stronger transition is lower in energy). As a result, in 1-NH$_2$-**1** and 7-NH$_2$-**1** the weak transition, corresponding roughly to the lowest transition of **1**, is covered up and impossible to discern. In 3-NH$_2$-**1**, both transitions are sufficiently strong to be seen clearly. The third and fourth transitions of the amines are in clear-cut correspondence with the third and fourth transitions of **1**, but a similar correlation of higher excited states is difficult.

The introduction of aza and carboxy substituents causes a much smaller perturbation of the spectrum of **1** in the low-energy region and the order of states remains the same as in the parent. Assignment of transitions shown in the figures is based on the close similarity between the spectra and on experimental polarization directions.[3,8]

Discussion

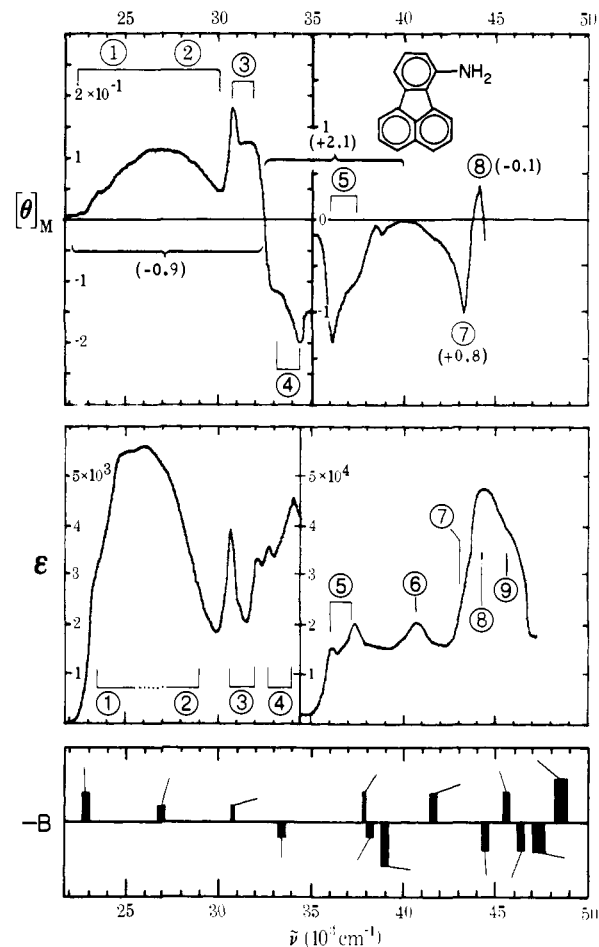**MCD Signs.** Simple arguments embodied in Figure 6 of part 16[1] as well as inspection of Hückel or PPP orbital energies

show that **1** should be a negative-hard chromophore, i.e., B(L) < 0 and B(M) > 0, and this is in agreement with existing data.[4,11] The same result was obtained from a numerical PPP calculation[4], which also gave B(K) < 0 as observed but failed to predict correctly the signs of B terms of higher transitions. The calculations also indicated that the positive contribution to B(M) due to L–M mixing is partially balanced by a negative contribution from M–N mixing.

Substituent Effects on MCD Signs. The spectra shown in Figures 1–9 provide eloquent support for the concept of hard MCD chromophores. In 2-NH$_2$-**1** and 3-NH$_2$-**1**, the very weak onset of the first MCD band has a sign opposite to the bulk of the band. To measure the onset, very high concentrations were required and the weak effect might be an experimental artifact. More likely, they are a reflection of a positive contribution to B(K) from mixing with some distant excited state. In no other transitions are there any indications of strong involvement of vibronic interactions. With four exceptions, the sign pattern for the first five B terms in **1** (observed signs, $-,-,+,+,+$ in order of increasing energy) is preserved in the derivatives, regardless of the position of the substituent and its $+E$ or $-E$ nature, and in striking contrast to the case of the isomeric soft chromophore pyrene.[13] In 1-NH$_2$-**1** and 7-NH$_2$-**1**, the sign of the B term of the weak second transition cannot be determined since the transition is too weak in MCD. In 3-NH$_2$-**1**, the lowest two transitions correspond more or less equally to the first two transitions in **1**. Their MCD signs should then be determined by mixing with the third transition and be positive as in **1**, and positive peaks are observed. The four instances in which the persistent sign pattern of **1** is perturbed are the signs of B(M) in 3-NH$_2$-**1**, 7-NH$_2$-**1**, 8-NH$_2$-**1**, and 7-COOH-**1**, which are negative while they are positive in **1** itself,[4] in its five
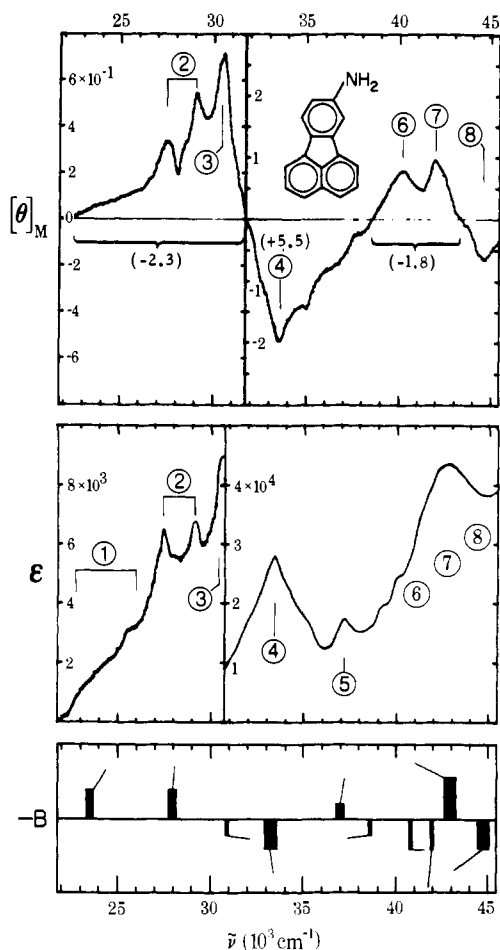
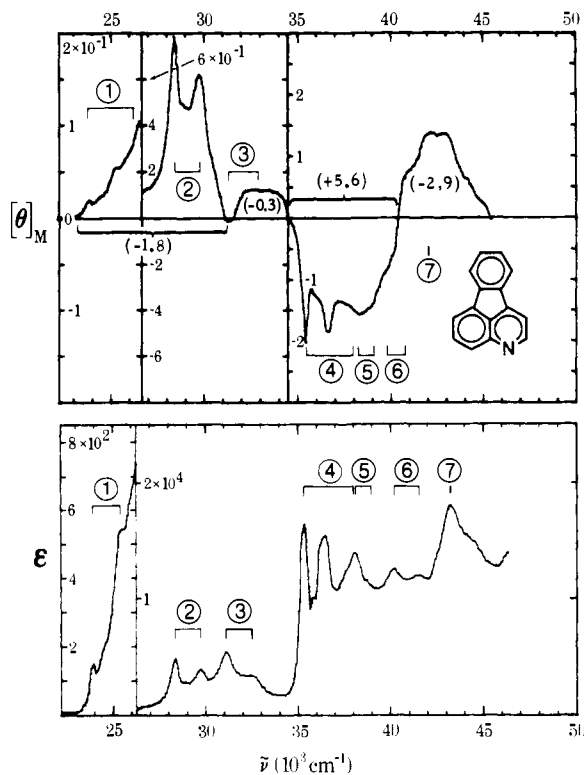**Figure 5.** 8-Aminofluoranthene. See caption to Figure 1.

Figure 7. Fluoranthene-1-carboxylic acid: top, MCD spectrum (B terms in parentheses, units of $10^{-3}\beta_e$ D^2/cm^{-1}); bottom, absorption spectrum (ethanol).

fluoro derivatives,[4] and in the other five derivatives investigated here. Such potential softness of the third transition can be anticipated as described above and was actually first noted[4] upon inspection of the vibronic pattern in the MCD curves of **1** and its fluoro derivatives. Some of the factors which affect

Figure 6. 3-Azafluoranthene: top, MCD spectrum (B terms in parentheses, units of $10^{-3}\beta_e$ D^2/cm^{-1}); bottom, absorption spectrum (cyclohexane).
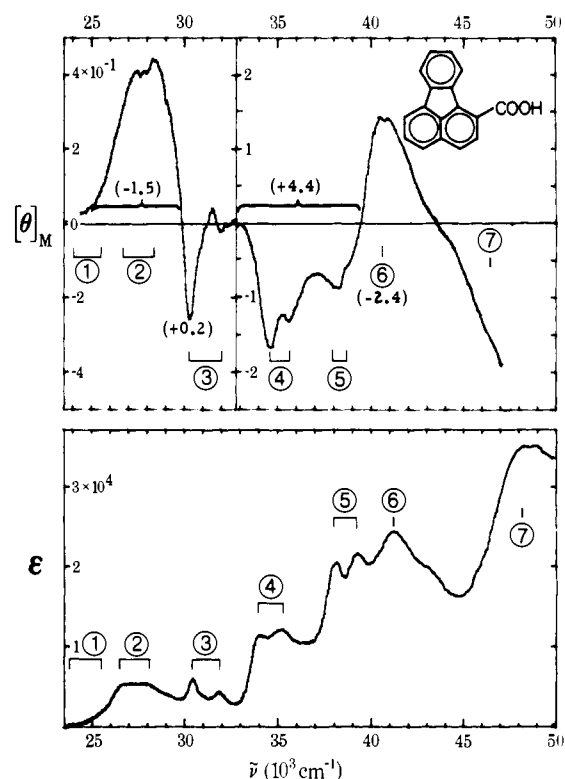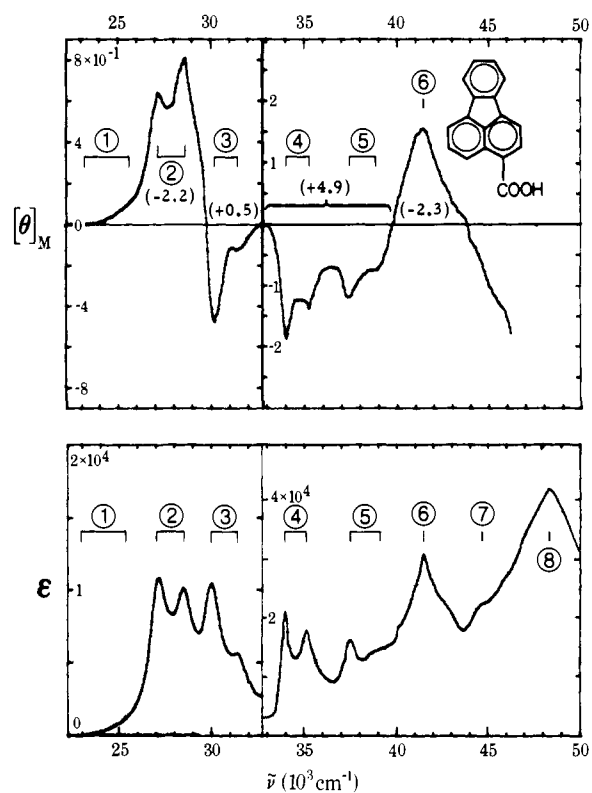

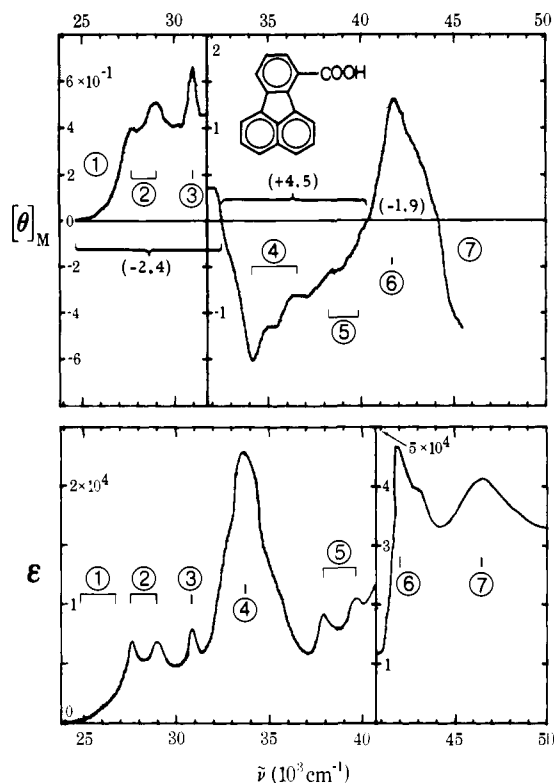**Figure 8.** Fluoranthene-3-carboxylic acid. See caption to Figure 7.

Figure 9. Fluoranthene-7-carboxylic acid. See caption to Figure 7.

the relative magnitude of the two contributions to $B(M)$, due to L–M and M–N mixing, are obvious from inspection of the formula for $B_{I,F}^F$[5]

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

and they are mostly reflected in other observable properties. E.g., the relative importance of the M–N mixing will increase if the energy separation of transitions M and N decreases or if the intensity of transition N increases. The relative importance of the M–N mixing decreases if the directions of the M and N transition moments turn such that they are no longer mutually perpendicular as they were in **1** itself, and this is reflected in observed[3] polarization directions. On the other hand, a change in the magnitude of the magnetic dipole transition moment between M and N would escape detection in other available results.

Because of the large number of factors which affect the balance of the two contributions, it is not possible to state unequivocally what makes four of the derivatives different from all the others. One contributing factor clearly is the circumstance that just in these four derivatives the M–N energy separation equals 1900–2200 cm^{-1}, while in the others it equals 3800 cm^{-1} or more. On the other hand, the L–M energy separation changes little from one molecule to another. In 7-NH$_2$-**1** and 8-NH$_2$-**1**, transition moment directions[3] are at angles more favorable for M–N mixing than for L–M mixing; in 3-NH$_2$-**1**, both are unfavorable since most of the low-energy transitions of this molecule appear to be polarized very close to the direction of its long axis (this accounts for the relatively small magnitude of all of its B terms at low energies).

Comparison with Calculations. The adequacy of the picture just given on the basis of purely qualitative considerations can be checked against PPP calculations of the standard type, which have not been optimized for MCD in any way and contain only the nearest-neighbor interactions, as discussed in more detail in part 4.[18] These were performed only for the amino derivatives, for which the situation is less than straightforward, and the results are included in Figures 1–5.

It has already been shown that the energies, intensities, and polarizations calculated at the present level of approximation are in quite good agreement with experiment for the lowest few transitions and in only mediocre agreement for higher energy transitions.[3] The calculated MCD signs are correct for the first three transitions in parent **1**, while the description of the fourth (N) and higher transitions is deficient (the oscillator strength of transition N as well as the extent of M–N mixing are grossly underestimated). Because of the difficulty with this mixing, which is one of the two closely balancing factors determining the MCD sign of the relatively "soft" third (M) transition, one can understand why the wrong sign is obtained for it in 3-NH$_2$-**1** and 8-NH$_2$-**1**. Also the calculated sign of the second transition in 3-NH$_2$-**1** is incorrect. This is probably related to the circumstance[3] that the transitions near it in energy have almost the same polarizations so that they provide relatively small contributions to B(L), quite sensitive to small absolute errors in calculated polarizations, and those contributions cancel approximately against those provided by more favorably polarized high-energy transitions, whose properties are probably calculated quite poorly.

In all other instances, the calculated and observed MCD signs agree for the lowest three transitions, as in parent **1**. For the higher transitions, the agreement, if any, is probably purely fortuitous.

Conclusions

The MCD signs of the two of the low-energy transitions in **1** which are simply related to perimeter states are as expected from the arguments given in part 16[1] for a peri-condensed hydrocarbon with a $(4N + 3)$-atom perimeter and one inside carbon. The agreement lends additional weight to the proposed assignment of L$_1$ and L$_2$ character to the L and M states of **1**, respectively. The signs of other bands have not been accounted for by the simple theory and mostly not even by a full PPP calculation in the standard approximation.

As expected for a hard chromophore, the first five MCD signs in **1** are remarkably insensitive to even quite strong perturbations by +E and −E substituents which modify the shape of the absorption curve profoundly and which completely dominate the MCD signs of the isomeric soft chromophore, pyrene,[13] and this nicely demonstrates the value of the hard–soft distinction suggested by the simple theory of parts 1–3.[5-7]

References and Notes

(1) Part 16: J. W. Kenney, III, D. A. Herold, J. Michl, and J. Michl, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) This paper is also part 3 in the series "Excited Singlet States of Fluoranthene". For part 2, see ref 3; for part 1, see ref 4.
(3) E. W. Thulstrup, M. Nepraš, V. Dvořak, and J. Michl, *J. Mol. Spectrosc.*, **59**, 265–285 (1976).
(4) J. Kolc, E. W. Thulstrup, and J. Michl, *J. Am. Chem. Soc.*, **96**, 7188–7202 (1974).
(5) J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 1).
(6) J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 2).
(7) J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 3).
(8) J. Michl, *Theor. Chim. Acta*, **15**, 315–331 (1969).
(9) M. A. Souto, D. Otteson, and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 18).
(10) J. Michl and J. F. Muller, *J. Am. Chem. Soc.*, **98**, 4550–4553 (1976).
(11) D. A. Schooley, E. Bunnenberg, and C. Djerassi, *Proc. Natl. Acad. Sci. U.S.A.*, **56**, 1377–1382 (1966).
(12) E. W. Thulstrup and J. Michl, *J. Am. Chem. Soc.*, **98**, 4533–4540 (1976).
(13) M. Vašák, M. R. Whipple, A. Berg, and J. Michl, *J. Am. Chem. Soc.*, com-

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panion paper in this issue (part 13).

(14) W. Gerhartz and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 14).

(15) E. Bergmann and M. Orchin, *J. Am. Chem. Soc.*, **71**, 1917–1918 (1949); A. Sieglitz, H. Tröster, and P. Böhme, *Chem. Ber.*, **95**, 3013–3029

(1962).

(16) A. Streitweiser, Jr., and S. Suzuki, *Tetrahedron*, **16**, 153–168 (1961).

(17) M. J. S. Dewar and J. Michl, *Tetrahedron*, **26**, 375–384 (1970).

(18) A. Castellan and J. Michl, *J. Am. Chem. Soc.*, companion paper in this issue (part 4).

Magnetic Circular Dichroism of Cyclic π-Electron Systems. 18.[1] Benzofluoranthenes

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

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

Introduction

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

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

In measuring magnetic circular dichroism (MCD) of **2–4**, we have two objectives: first, to provide a safer assignment and better characterization of individual electronic transitions in the spectra of these simple representatives of the family[8] of fluoranthene-like hydrocarbons, hopefully securing a firmer basis for the recently proposed[12] correlation of low-lying excited states in this large group of nonalternants with those of acenaphthylene (**6**) and naphthalene; second, to correlate the excited states of **2–5** with the states of their [19]annulene perimeter and to contribute to the testing of the predictive power of the simple theory described in detail in parts 1–3 of this series of papers[13] and, in particular, of the concept of "hard" MCD chromophores.

Experimental Section and Calculations

The samples were gifts from Professor M. W. Windsor (Washington State University, Pullman, Wash.), Professor M. Zander (Rütgerswerke AG, Castrop-Rauxel, Germany), and Dr. E. Koch (Technische Universität, Braunschweig, West Germany) and were used as received. Their UV absorption spectra (Cary 17 spectrophotometer) agreed with those published.[6] Experimental procedures for recording and evaluating the spectra and details of the PPP calculations performed are described in part 4.[14] In the case of **4**, decomposition of overlapping MCD bands needed for evaluation of their *B* terms was aided by comparison with published polarized spectra;[11] in other cases it was guessed.

1   2

3   4

5   6
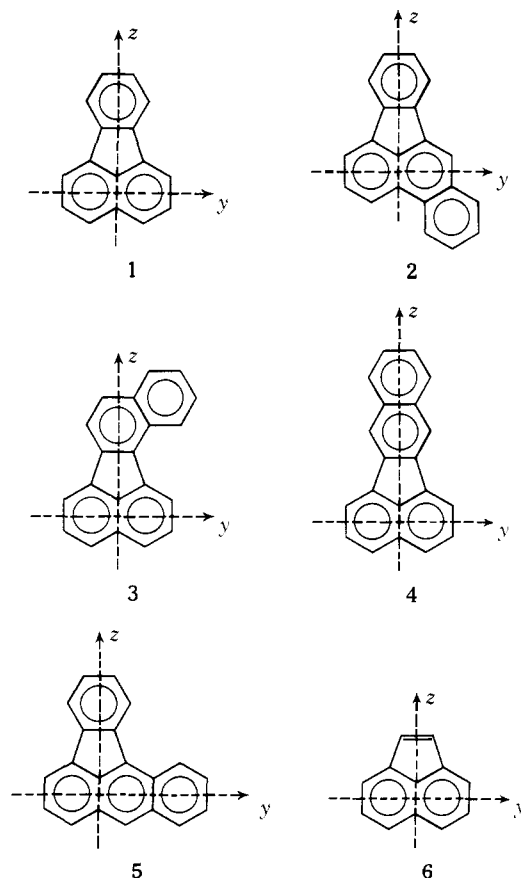
Results

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