Magnetic Circular Dichroism of Cyclic π-Electron Systems. 16.[1] Derivatives of Acenaphthylene

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Abstract. Magnetic circular dichroism of the two main low-energy transitions of the hard chromophores acenaphthylene and pleiadiene (cyclohepta[*de*]naphthalene) is analyzed in terms of the simple theory of parts 1–3 and the absolute signs and mirror-image relation between the two hydrocarbons are derived from properties of their respective $(4N + 2)$-electron [11]annulenylium cation and [13]annulenide anion perimeters without any computations. The argument is generalized to conclude that uncharged peri-condensed hydrocarbons with one internal carbon will be positive-hard MCD chromophores if they have a $(4N + 1)$-atom perimeter and negative-hard chromophores if they have a $(4N + 3)$-atom perimeter. MCD spectra of five substituted derivatives of acenaphthylene are reported. In contrast to the dramatic effect of similar substituents on the MCD spectra of structurally closely related soft chromophores such as naphthalene, there is essentially no effect on this negative-hard chromophore regardless of the nature and location of the substituent, demonstrating the value of the soft–hard classification. A new excited state is found in substituted acenaphthylenes and, by extrapolation, should occur near 42 000 cm⁻¹ in the parent.

Introduction

The present series of papers starts with a description of a simple model permitting prediction of MCD signs of L and B bands of cyclic π-electron systems formally related to $(4N + 2)$-electron annulenes from an analysis of the properties of the perimeter (parts 1–3[2]). Subsequently, the consequences of the model are compared with experimental data for a variety of kata- and peri-condensed hydrocarbons with a $(4N + 2)$-electron [4N + 2]annulene perimeter, their substituted derivatives, and heterocyclic analogues (parts 4–15). In the present paper, we consider the case of uncharged hydrocarbons of the peri-condensed type, which have a $(4N + 1)$-atom or a $(4N + 3)$-atom perimeter and one inside carbon atom. They can be formally derived from a negatively (positively) charged $(4N + 2)$-electron [4N + 1]annulene ([4N + 3]annulene) perimeter by union with a methyl cation (anion). We shall now show that they are hard chromophores, those with a $(4N + 1)$-atom perimeter generally positive-hard (ΔHOMO > ΔLUMO) and those with a $(4N + 3)$-atom perimeter generally negative-hard (ΔHOMO < ΔLUMO), in agreement with existing observations on acenaphthylene[3] (**1**), pleiadiene[4] (**2**), and related hydrocarbons.[5] The definition of the symbols used here is given in parts 1–3:[2] ΔHOMO = $|E(a) - E(s)|$, and ΔLUMO = $|E(-a) - E(-s)|$, where **a**, **s**, **−a**, and **−s** refer to the frontier orbitals of the parent annulene. The present paper also presents and examines experimental data for derivatives of **1**, a representative negative-hard chromophore of this type; and in parts 17[6] and 18[7] we similarly investigate other negative-hard chromophores of this class, with emphasis on investigation of their expected "hardness".

Six excited singlet states of **1** have been characterized (see ref 3 for a recent summary). Transition K near 21 000 cm⁻¹ is weak and *y* polarized, transition L near 30 000 cm⁻¹ is strong and *z* polarized, transition M near 31 000 cm⁻¹ is strong and *y* polarized, transition 4 near 36 000 cm⁻¹ is of medium intensity and *z* polarized, transition 5 near 43 000 cm⁻¹ is very intense and *y* polarized, and transition 6 near 50 000 cm⁻¹ is of medium intensity and *z* polarized. π-Electron calculations with extensive configuration interaction using doubly excited configurations account well for these transitions and predict the presence of another *y*-polarized transition near 42 000 cm⁻¹ and two additional *z*-polarized transitions near 44 000 and 45 000 cm⁻¹, for which there has so far been no evidence. No previous attempt to relate the states of **1** to the states of its [11]annulene perimeter has been reported (cf. ref 8). It has been noted that the L state corresponds to a strongly perturbed

L_a state of naphthalene, and the M state originates half in a perturbed L_b and half in a perturbed B_b state of naphthalene.[9]

Magnetic circular dichroism of **1** has already been investigated.[3] The signs of the *B* terms of its transitions in order of increasing energy are as follows: K, −; L, −; M, +; 4, +; 5, −; 6, +; The mirror-image relation of the MCD signs of the corresponding bands of **1** and **2** (K, L, and M) was rationalized by showing that **1** and **2** were approximately paired in the sense of alternant-pairing symmetry[9] and by using a general theorem[10] for such paired systems. The absolute MCD signs of the lowest three transitions can be derived by inspection of the form of the Hückel orbitals of these hydrocarbons.[9] Presently, we shall provide an alternative view of the origin of the mirror-image relationship and of the absolute signs, on the basis of the model of parts 1–3.[2]

In the following, we shall refer to the derivatives of **1** by symbols such as 1,2-CN-**1** for 1,2-dicyanoacenaphthylene, 1,2-C₂O₃-**1** for 1,2-acenaphthylenedicarboxylic anhydride, etc.

1   **2**
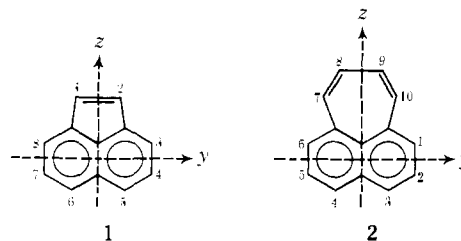
Experimental Section

The samples were prepared by published methods (F=**1**'s,[11] 1,2-CN-**1**,[12] 1,2-C₂O₃-**1**[12]) and purified by gradient sublimation. Measurements were performed as in part 4[13] (acetonitrile was the solvent for 1,2-CN-**1** and 1,2-C₂O₃-**1**).

Results

The experimental results are shown in Figures 1–5 and are to be compared with the spectra of **1** itself and of 1,2-Br-**1** shown in ref 3. Identification of the previously known transitions 1–5 is clear-cut; the previously identified transition 6 is just outside the range reported here. A new transition is now identified near 42 000 cm⁻¹ and is labeled 5, while the old intense transition 5 is assigned number 6.

Discussion

Relation of States of 1 and 2 to Perimeter States and MCD Signs. Before we can use the simple theory of parts 1–3[2] to
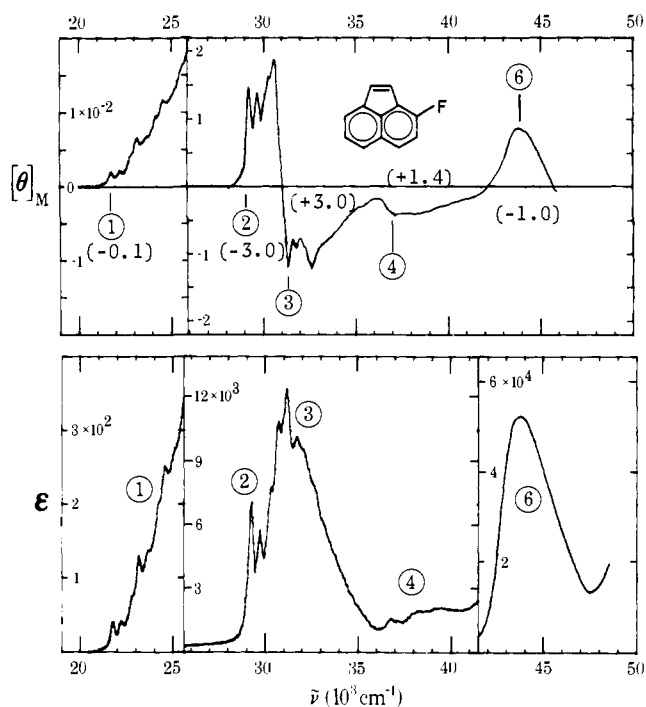

Figure 1. 3-Fluoroacenaphthylene spectra: top, MCD (*B* terms given in units of $10^{-3}\beta_e$ D^2/cm^{-1}); bottom, absorption.

Figure 3. 5-Fluoroacenaphthylene. See caption to Figure 1.

understand the MCD signs of **1** and **2**, we need to relate their states to the L and B states of a (4*N* + 2)-electron perimeter, even if only distantly. This can be achieved, at least for the L and M states, by formally constructing **1** from a [11]annulenyl cation and a methyl anion and **2** from a [13]annulenyl anion and a methyl cation. The perturbation of the annulene states by such a union is large, but inspection of the nodal properties of the Hückel MO's of **1** and **2** shows that they correspond to those of the respective annulenes and this is all that is important for the sense of the electric and magnetic dipole moments by which the signs of contributions to *B* terms are determined.

A diagram exhibiting the correlation at the Hückel MO level is shown in Figure 6, and its fundamental features apply
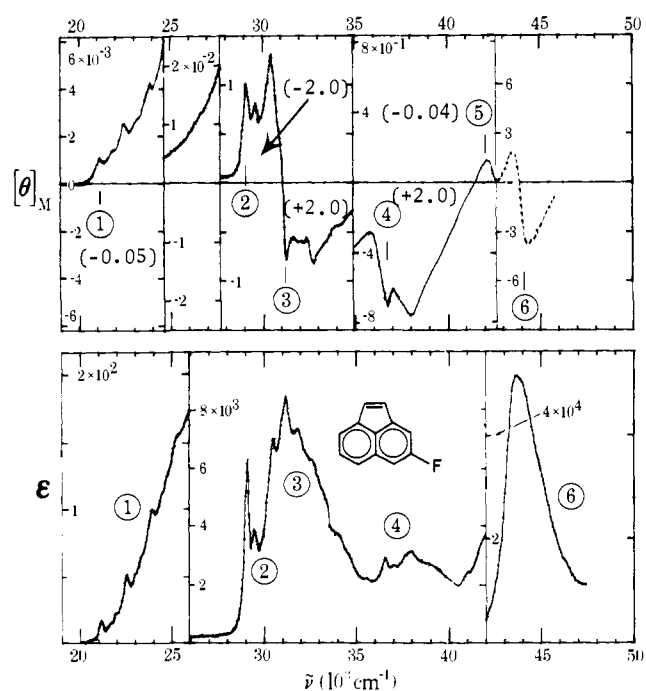
equally well to other peri-condensed hydrocarbons with (4*N* + 1)-atom or (4*N* + 3)-atom perimeters and one internal carbon. Also, starting with a benzannulene will typically make little difference. Clearly, the methyl atomic orbital (*φ*) will insert itself between the bonding **s**, **a** and antibonding **−s**, **−a** pairs of annulene orbitals. It has no first-order effect on orbitals **a** and **−a** which have the wrong symmetry, and, roughly speaking, it will "push away" orbitals **s** and **−s** to lower and higher energies, respectively, by mixing with them strongly. Thus, it will produce a new orbital between the **a** and **−a** orbitals in the annulene. In the (4*N* + 3)-atom cation, **−s** is near *φ* in energy, and the out-of-phase combination of **−s** with *φ* will be shifted far up in energy from **−a**. In the (4*N* + 1)-atom anion, **s** is near *φ* in energy, and the in-phase combination of

Figure 2. 4-Fluoroacenaphthylene. See caption to Figure 1.

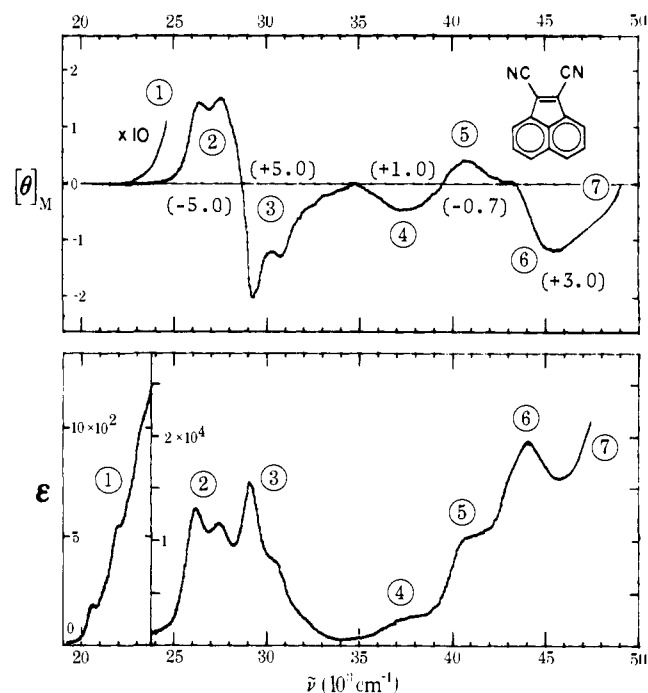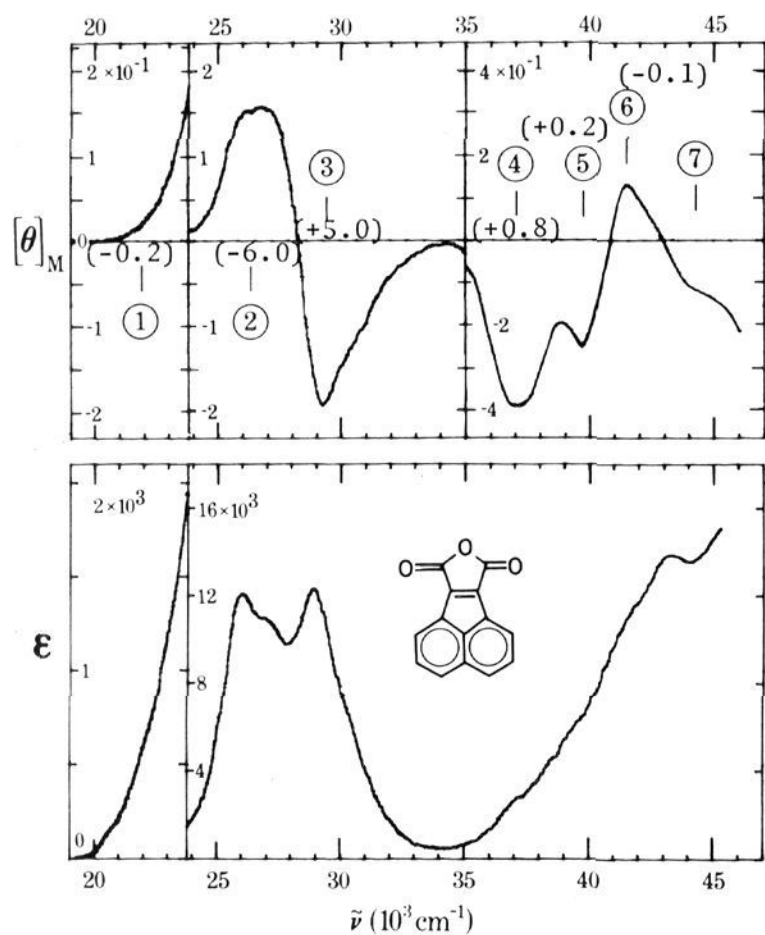**Figure 4.** 1,2-Dicyanoacenaphthylene. See caption to Figure 1.

Figure 5. 1,2-Acenaphthylene- dicarboxylic anhydride. See caption to Figure 1.

Figure 6. Hückel approximation for relative magnitudes of ΔHOMO and ΔLUMO for peri-condensed hydrocarbons with one internal atom by correlation with the MO's of their $(4N + 2)$-electron perimeter.

s with ϕ will be shifted far down in energy from **a**. The corresponding interaction with the more distant symmetrical orbitals, **s** of the $(4N + 3)$-atom cation and $-$**s** of the $(4N + 1)$-atom anion, is weaker, so that the **a**, **s** pair of the former and the $-$**a**, $-$**s** pair of the latter will be split less. The net result is ΔHOMO $< \Delta$LUMO for the $(4N + 3)$-atom perimeter (negative-hard) and ΔHOMO $> \Delta$LUMO for the $(4N + 1)$-atom perimeter (positive-hard). Figure 6 illustrates this point not only for **1** and **2** but also for two isomeric peri-condensed hydrocarbons formed by a union of a methyl to different positions on the perimeter. It may not always be straightforward to identify the transitions in the peri-condensed hydrocarbon which correlate with the L and B transitions of the annulene ion. In the case of **1** and **2**, the L band correlates with the L_a band of naphthalene and the M band with the L_b band of naphthalene,[9] so that they should also correlate with the (degenerate) L_1 and L_2 bands of the corresponding annulenes, respectively, and this can indeed be verified in Figure 6. The B bands should be at very high energies and it may be impossible to establish meaningful correlations for them. Since the L and M bands have been identified in a large number of peri-condensed hydrocarbons related to **1** and **2**, it appears reasonable to extend the identification L $\leftrightarrow$ L_1 and M $\leftrightarrow$ L_2 to all of them. On the other hand, there may well be others for which no such simple correlation can be established. Where it exists, the above analysis indicates that the mutual mixing of the two L states will contribute positively to the B term of the lower of them in the case of $(4N + 1)$-atom perimeter and negatively in the case of $(4N + 3)$-atom perimeter. This is in agreement with the experimental data for **1**,[3] **2**,[4] and many related polycyclic hydrocarbons.[5,7] It is also in agreement with a full PPP calculation which, moreover, yields the correct signs for the first five observed B terms. This was discussed elsewhere[3] and need not be repeated here.

In all cases, including **1** and **2**, the presence of an additional orbital inserted between **a**, **s** on the one hand and $-$**a**, $-$**s** on the other will cause the appearance of additional low-energy states. These will involve excitation into the additional orbital in $(4N + 1)$-atom perimeter systems, in which it is the lowest or second lowest empty orbital, and excitation from the additional orbital in $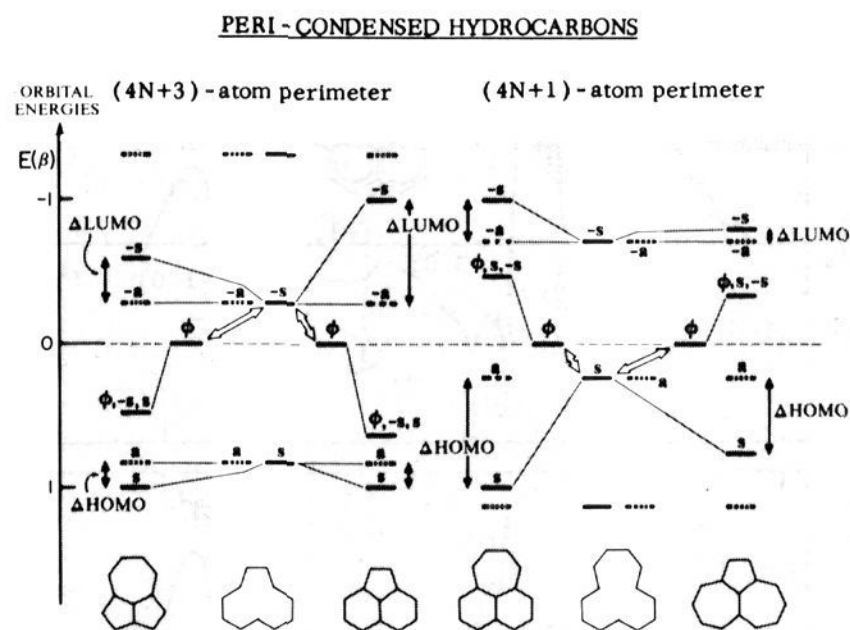(4N + 3)$-atom perimeter systems, in which it is the highest or second highest occupied orbital. The lowest energy one among such excitations (from orbital **a** in the $(4N + 1)$-atom perimeter case and into orbital $-$**a** in the $(4N + 3)$-atom perimeter case) should be responsible for the lowest excited state of the hydrocarbon, and this is true for **1**, **2**, and many related hydrocarbons, where it causes the appearance of the K band.[5,7,9] The next such excitation, from orbital **s** in the $(4N + 1)$-atom perimeter case and into orbital $-$**s** in the $(4N + 3)$-atom perimeter case, is responsible for the fourth transition in **1**[3] and **2**[4] and contributes heavily to the N transition in fluoranthene and benzofluoranthenes.[6,7] Analogous configurations must be expected in other pericondensed hydrocarbons of this type. Since the additional orbital typically consists of a grand mixture of contributions from the ϕ, **s**, and $-$**s** orbitals of the initial components, it is difficult to correlate states such as K and N with the states of the perimeter and to use the simple model of part 1[2] for sign prediction. At times, magnetic mixing of the L ($\simeq L_1$) and M ($\simeq L_2$) states, for which we have just derived signs as a function of structure [$(4N + 1)$ vs. $(4N + 3)$ perimeter] may not even dominate the signs of their B terms because of interference by mixing with the newly present states such as K and N. For hydrocarbons related to **1** and **2**, it turns out that the K band is very weak and has no discernible effect on the B terms of transitions L and M, but the N band is often strong and the M–N mixing at times significant, as is discussed in more detail in parts 17[6] and 18.[7]

Substituent Effects on MCD Signs of L and B States of 1. Comparison of Figures 1–5 with the MCD spectra of **1** and 1,2-Br-**1** shown in ref 3 shows that the $-$,$-$,$+$,$+$ sign pattern of the first four B terms survives intact, even in the presence of quite drastic perturbations which modify the shape of the absorption and MCD spectra almost beyond recognition, and is truly inherent to this negative-hard MCD chromophore. Neither a change in the $+$E or $-$E nature of a substituent in position 1 nor a change in the position of attachment of a $-$E substituent makes any difference for the signs. This stands in remarkable contrast to the behavior of structurally closely related soft chromophores, such as naphthalene,[14] in which the same substituents dominate the MCD sign pattern. Clearly, the theoretical distinction between hard and soft chromophores has a good counterpart in reality, and equally clearly, **1** is a true nonalternant hydrocarbon (this was in dispute some time ago[8]). The sign pattern for the L and M bands can be expected to remain unchanged until a perturbation is found which reverses the sign of ΔHOMO $- \Delta$LUMO; the constancy of the signs of the first and the fourth transition does not follow from the simple theory.

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$_2$O$_3$-**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

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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 (4*N* + 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