Magnetic Circular Dichroism of Cyclic π-Electron Systems. 13.[1,2] Derivatives of Pyrene

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Abstract: Magnetic circular dichroism of pyrene and 11 of its derivatives is reported and interpreted. Two new low-energy transitions and several new high-energy transitions are detected in pyrene derivatives and, by extrapolation, in pyrene itself. The signs of $B(L_b)$, $B(L_a)$, and $B(B_b)$ are sensitive to the location and nature of substituents. They are in perfect agreement with predictions of the general qualitative theory of parts 1–3 for an odd-soft chromophore and its response to mesomeric effects of substituents.

Introduction

As discussed in more detail in parts 1–3[4–6] of this series, pyrene (**1**), like other polycyclic benzenoid hydrocarbons without a threefold or higher symmetry axis, should be an odd-soft chromophore, and MCD signs of its L and B transitions as well as their response to substitution are simply predictable. As noted in part 1,[4] we are now reporting experi-

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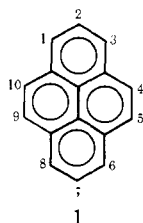
mental studies of simple and substituted aza analogues and derivatives of naphthalene, anthracene, phenanthrene, and pyrene. The present paper describes our results for fluoro, hydroxy, amino, and carbethoxy derivatives of pyrene. The MCD spectrum of pyrene has been reported previously[7] and corrected and extended in our recent study of the aza pyrenes;[8] it is included here for comparison.

Singlet excited states of pyrene have been studied in much detail. Solution absorption spectra of **1** and its alkyl derivatives[9] and fluorescence spectra,[10] single-crystal polarized absorption,[11] polarized emission in rigid glass[12] and in a liquid crystal,[13] linear dichroism of partially oriented samples obtained by photoselection[14] or in a stretched polymer,[15] and MCD of **1** and its aza analogues[7,8] have led to the following assignments of the four bands of primary interest to us: L_b, very weak, short-axis polarized with much long-axis-polarized borrowed intensity, near 27 000 cm^{-1}; L_a, strong, long-axis polarized, near 30 000 cm^{-1}; B_b, strong, short-axis polarized, near 37 000 cm^{-1}; B_a, very strong, long-axis polarized, near 41 000 cm^{-1}. There also is evidence for the existence of additional transitions. These are symmetry forbidden and not easily detected in the ordinary absorption spectrum of **1**. At least one of them lies between the L_a and B_b bands, another one between B_b and B_a, and another one is buried below B_a. Two bands at higher energies, 48 000 cm^{-1} and 51 000 cm^{-1}, have been established, and the presence of additional electronic states is suggested by $S_n \leftarrow S_1$ absorption experiments; for a recent summary, see ref 8.

The spectroscopy of substituted pyrenes has received relatively little attention. The spectrum of 1-aminopyrene (1-NH$_2$-**1**) has been compared with PPP calculations[16] and substituent shifts of the four main bands for a large number of 1-substituted pyrenes have been reported.[17]

Experimental Section and Calculations

The samples were prepared by published procedures and were purified by gradient sublimation. The measurements and calculations were performed as in part 4,[18] except that 1-OH-**1**, 1-COOEt-**1**, 2-OH-**1**, and 2-NH$_2$-**1** were measured in acetonitrile because their solubility in cyclohexane is insufficient.

Results

The results are shown in Figures 1–12. An identification of eight electronic transitions is proposed. This is less than calculated, and more than eight may well be present. However, eight seems to be the minimum number which is capable of accounting for all features in the absorption and MCD spectra, assuming the substituents cause only minor shifts in transition energies. Some transitions can be clearly identified for all of the compounds, in particular the L_b (=1), L_a ($\approx$2), B_b (=4), and B_a (=6) transitions well-known in pyrene itself, which dominate the absorption spectra. Generally, the MCD spectra are much more revealing. As expected from simple theory for an odd-soft chromophore, the signs of the MCD peaks are a sensitive function of the nature and location of substituents. The calculations are of the standard PPP type, without any optimization for MCD purposes, and, as noted in part 2,[5] are best viewed as a calculation of the difference between the spectra of substituted and parent **1**.

Discussion

Pyrene as an Odd-Soft Chromophore. Simple theory of part 2[5] predicts that in pyrene itself, μ^+ contributions to MCD vanish, and the μ^- contributions yield $B(L_b) = 0$, $B(L_a)$ small and positive (due to L_a–B_b mixing), and $B(B_b)$ and $B(B_a)$ larger and positive and negative, respectively (due to B_b–B_a mixing). This is in good agreement with the spectrum of Figure 1, except that the MCD of the L_b band, though weak, does not vanish exactly. It shows sign reversals throughout the band, due to vibronic effects, and its sign could only be calculated by a less primitive theory. The simple model further predicts that nonvanishing μ^+ contributions to MCD will appear when a perturbation produces ΔHOMO $\neq \Delta$LUMO (this is already true in **1** itself to a small degree if a more sophisticated description is used). The signs of the μ^+ contributions are given by the sign of ΔHOMO − ΔLUMO. If ΔHOMO > ΔLUMO, the contributions to the B term of the lower of the two L states (L_b) and the lower of the two B states (B_b) will be positive and those to the higher states in the pairs (L_a, B_a) negative, and the opposite will hold if ΔHOMO < ΔLUMO. As the ΔHOMO–ΔLUMO difference increases, the contributions will increase and tend to their limiting values and then probably gradually fall off again as the substituent effects become extremely strong and the perimeter orbitals too strongly perturbed. The perturbation also modifies the intrinsic μ^- con-
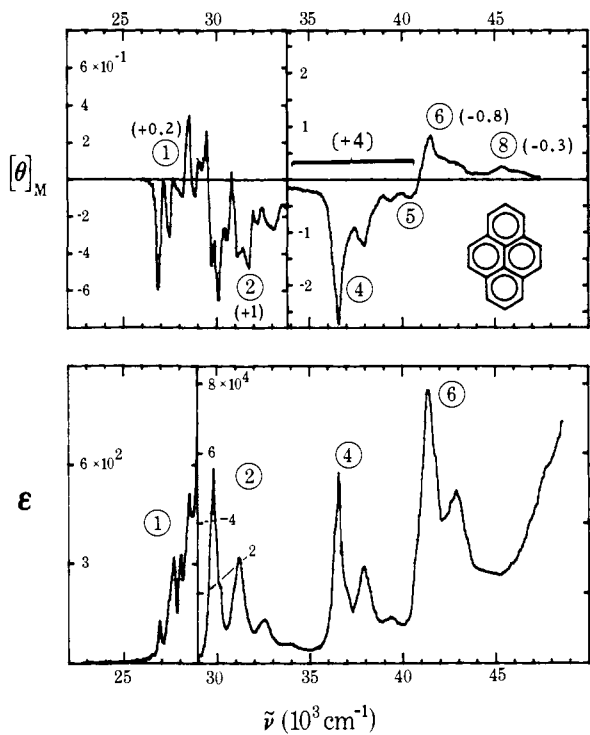
Figure 1. Pyrene spectra: bottom, absorption; top, MCD (*B* terms in units of $10^{-3}\,\beta_e\,D^2/cm^{-1}$).
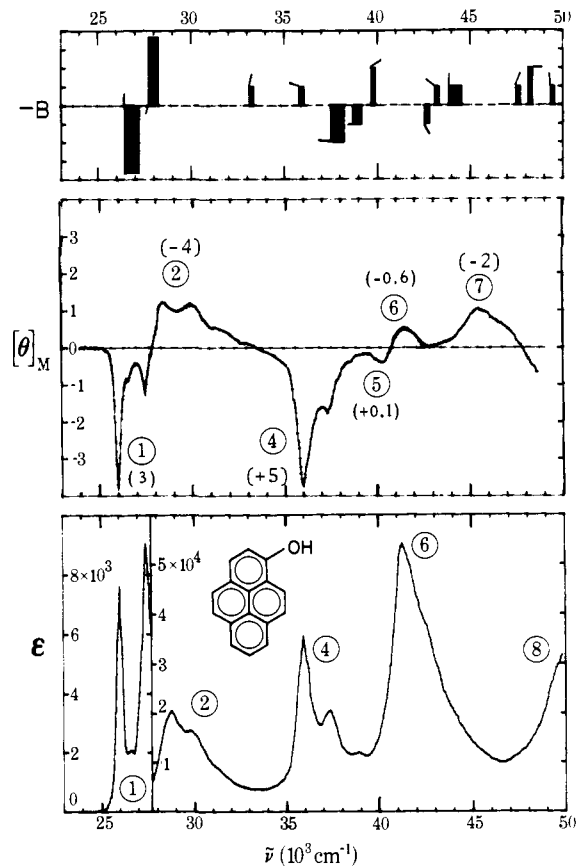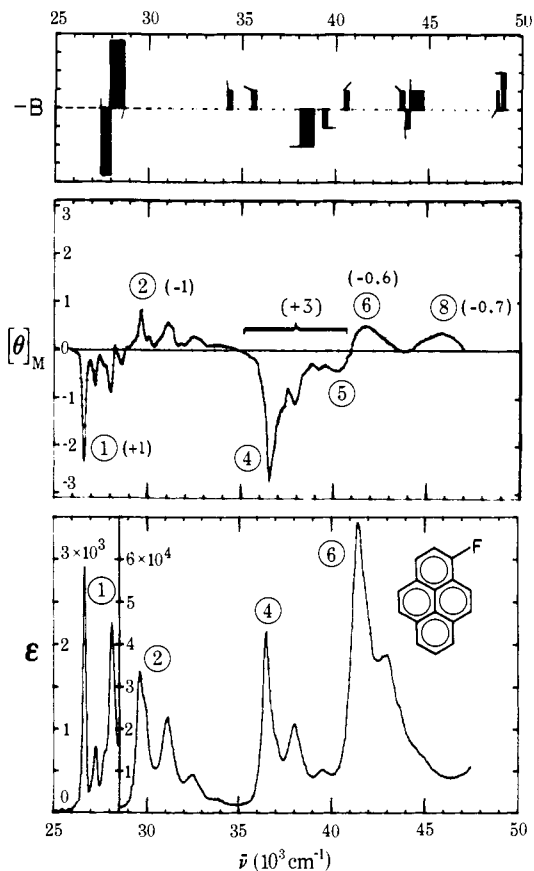

Figure 2. 1-Fluoropyrene spectra: bottom, absorption; center, MCD (*B* terms in units of $10^{-3}\,\beta_e\,D^2/cm^{-1}$); top, calculated. Calculated $-B$ values are indicated by the length of the bars (short, below 1; next, 1-5; next, 5-10; longest, over 10, in units of $10^{-3}\,\beta_e\,D^2/cm^{-1}$), calculated oscillator strengths by their three grades of thickness (less than 0.1, 0.1-0.5, over 0.5), and calculated polarization directions by directions of the flags at the end with respect to the formula shown.
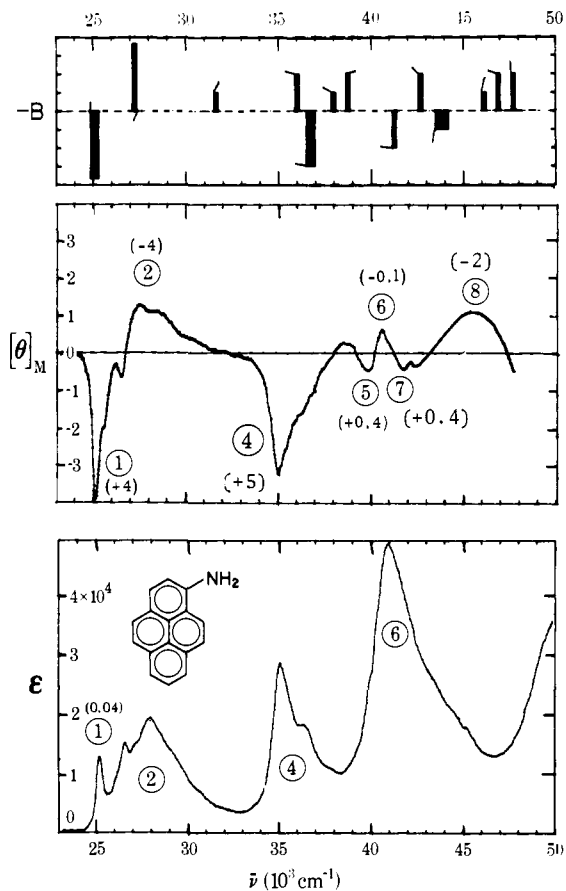

Figure 3. 1-Hydroxypyrene. See caption to Figure 2.

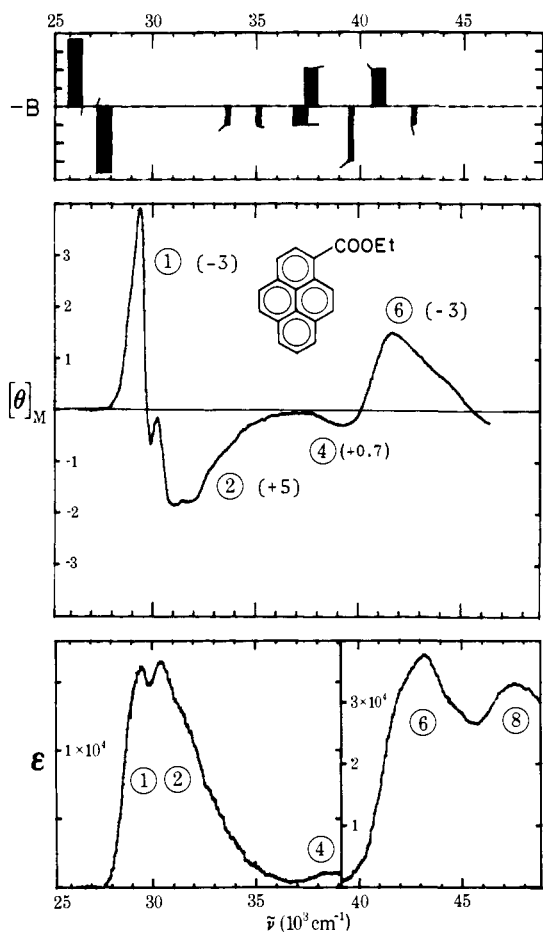**Figure 4.** 1-Aminopyrene. See caption to Figure 2.

Figure 5. 1-Carbethoxypyrene. See caption to Figure 2. In the calculation of polarization directions, the carbonyl oxygen of the carbethoxy group pointed up in the formula given.
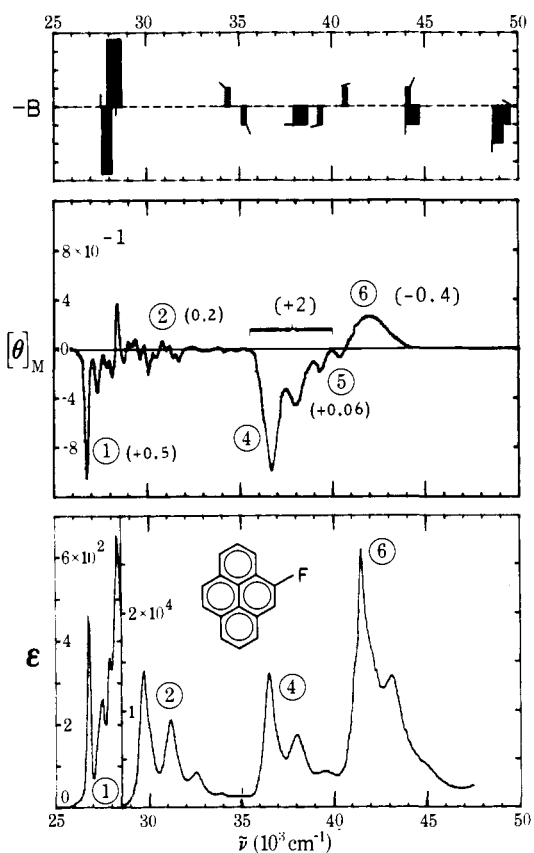

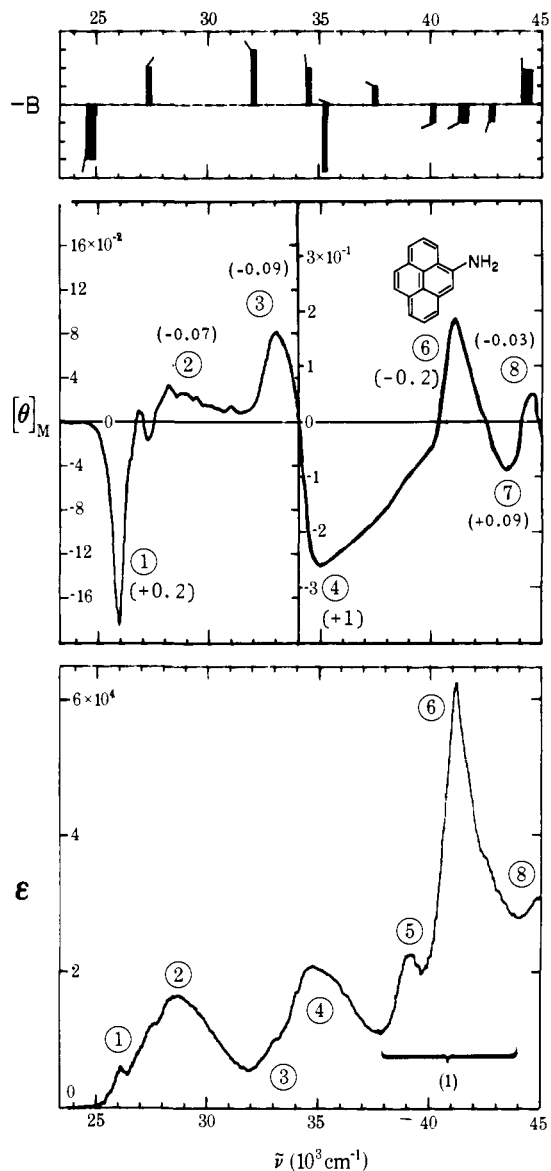**Figure 6.** 4-Fluoropyrene. See caption to Figure 2.

Figure 7. 4-Aminopyrene. See caption to Figure 2.

tribution somewhat, but this should be a negligible change compared with the introduction of nonvanishing μ^+ terms.

The estimation of the sign of ΔHOMO − ΔLUMO in an odd-soft chromophore as a function of the nature and location of substituents by means of the PMO theory has been discussed in part 3.[6] It was concluded that in a dominant position κ, characterized by Hückel (or SCF) MO coefficients $c_{\kappa,1}^2 >$ $c_{\kappa,2}^2$, +E substitution induces ΔHOMO $<$ ΔLUMO and −E substitution induces ΔHOMO $>$ ΔLUMO, while in a subdominant position, characterized by Hückel coefficients $c_{\kappa,1}^2$ $< c_{\kappa,2}^2$, the effects of +E and −E substitution are reversed. The effects increase in magnitude as the difference $|c_{\kappa,1}^2 - c_{\kappa,2}^2|$ increases. Other factors being equal, for substitution in a dominant position, a stronger E effect leads to a larger ΔHOMO-ΔLUMO difference and thus bigger contributions to the B terms. For subdominant positions, this is only true as long as the E effect is relatively weak. If it becomes sufficiently strong, the magnitude of the substituent-induced contribution to the B terms starts to decrease again, then reaches a borderline point where it goes through zero (at this point the molecule is a zero-soft or an even-soft chromophore, depending on its symmetry). For even stronger E substituents it increases again, but with reversed sign, i.e., as if the position of substitution were of the dominant type or as if the hydrocarbon were
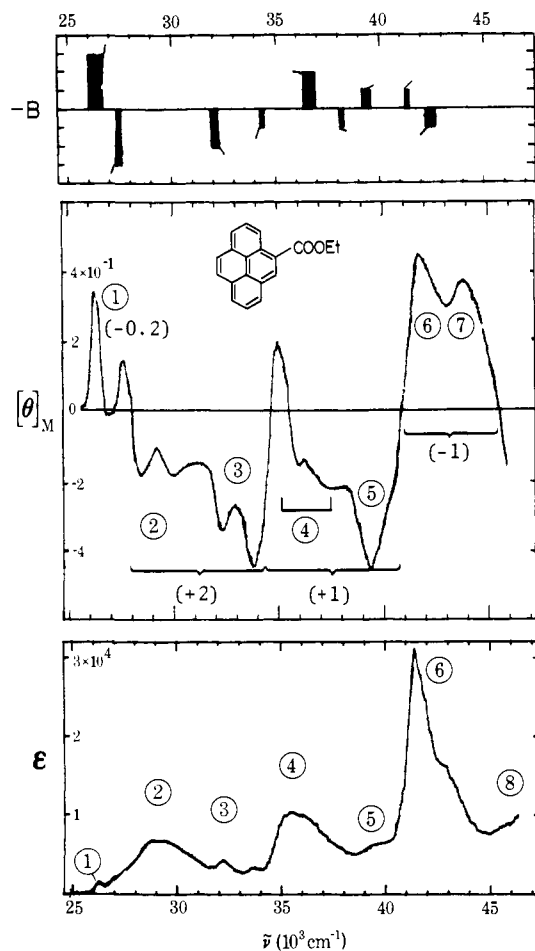
Figure 8. 4-Carbethoxypyrene. See caption to Figure 2. In the calculation of polarization directions, the carbonyl oxygen of the carbethoxy group pointed up in the formula given.

a monocyclic [$4N$ + 2]annulene. The location of the borderline point depends on the position of substitution as well as the hydrocarbon. For monosubstitution in naphthalene position 2 the OH substituent lies on one and the $NHCOCF_3$ substituent on the other side. For monosubstitution in anthracene position 2 the point is closely approached but not reached even for the stronger NH_2 substituent.

The experimental results shown in the figures are in excellent agreement with expectations for both L bands and the B_b band. The high-energy B_a band is surrounded by transitions not considered in the simple model, so that the failure in its case is not surprising.

L_b, L_a, and B_b Bands: 1-Substitution. Position 1 is strongly dominant ($c_{1,1}^2 = 0.14$, $c_{1,2}^2 = 0.03$). For the $-E$ substituents, F, OH, and NH_2 (Figures 2-4), we observe $B(L_b) > 0$, $B(L_a)$ < 0, and $B(B_b) > 0$, increasing from F to OH but no longer from OH to NH_2, suggesting that the limiting value has already been reached for OH substitution. The intrinsic positive μ^- contribution to $B(L_a)$ is clearly overridden already by the weak substituent effect of fluorine. It is likely that the weaker $-E$ effect of methyl would compensate it very nearly to zero and produce vibronic MCD sign alternation in this band.

For the $+E$ substituent $COOC_2H_5$ (Figure 5), we observe the opposite first two MCD effects: $B(L_b) < 0$ and $B(L_a) >$ 0, as expected, but $B(B_b) > 0$ and $B(B_a) < 0$, as in pyrene itself, indicating that the substituent (undoubtedly partially twisted out of the molecular plane) is not strong enough to override the stronger intrinsic μ^- contributions to the B terms of the B bands.

L_b, L_a, and B_b Bands: 4-Substitution. Position 4 is again dominant, but more weakly so ($c_{4,1}^2 = 0.09$, $c_{4,2}^2 = 0.02$). It
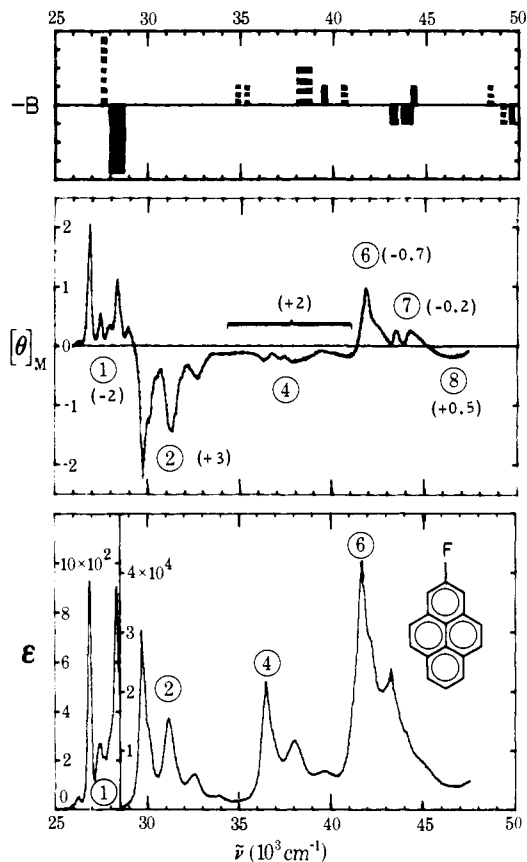

Figure 9. 2-Fluoropyrene. See caption to Figure 2. Solid bars indicate vertical polarization and broken bars horizontal polarization with respect to the formula shown.
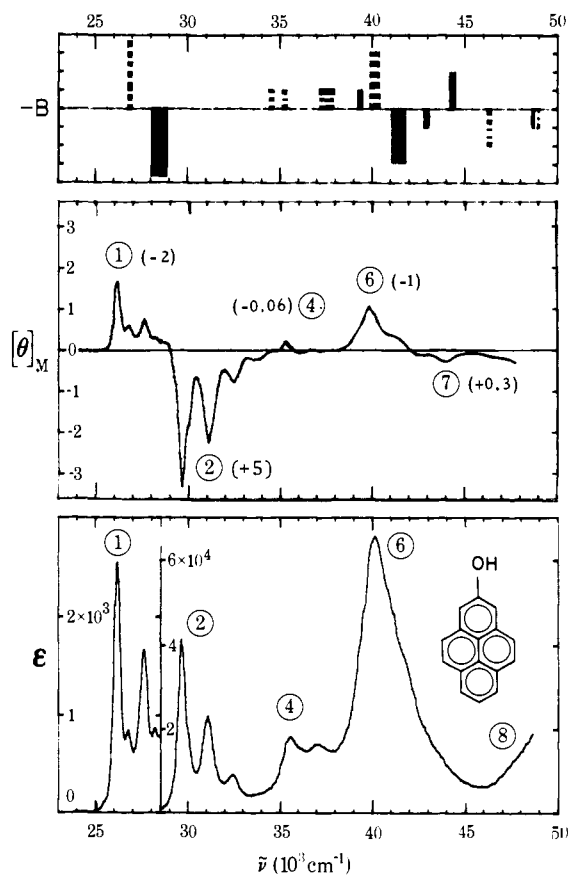

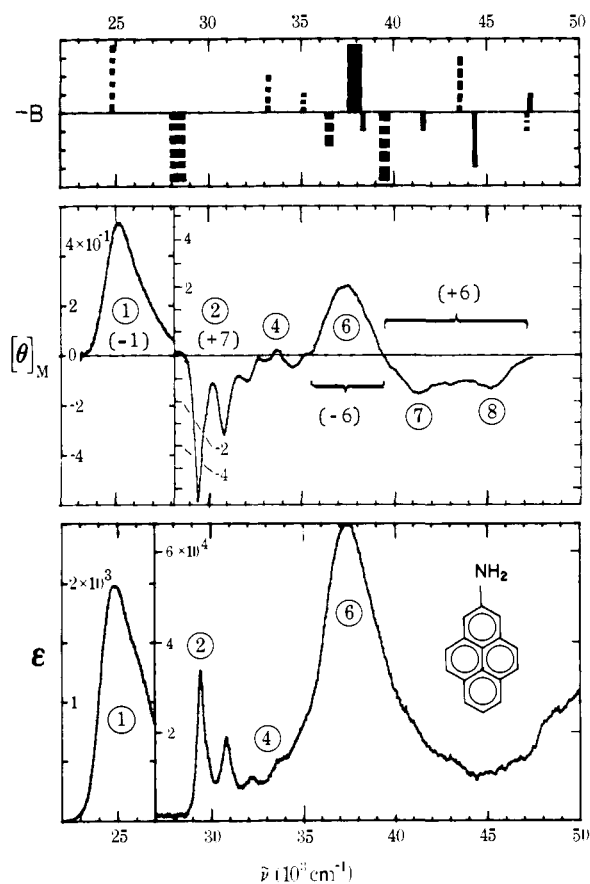Figure 10. 2-Hydroxypyrene. See captions to Figures 2 and 9.

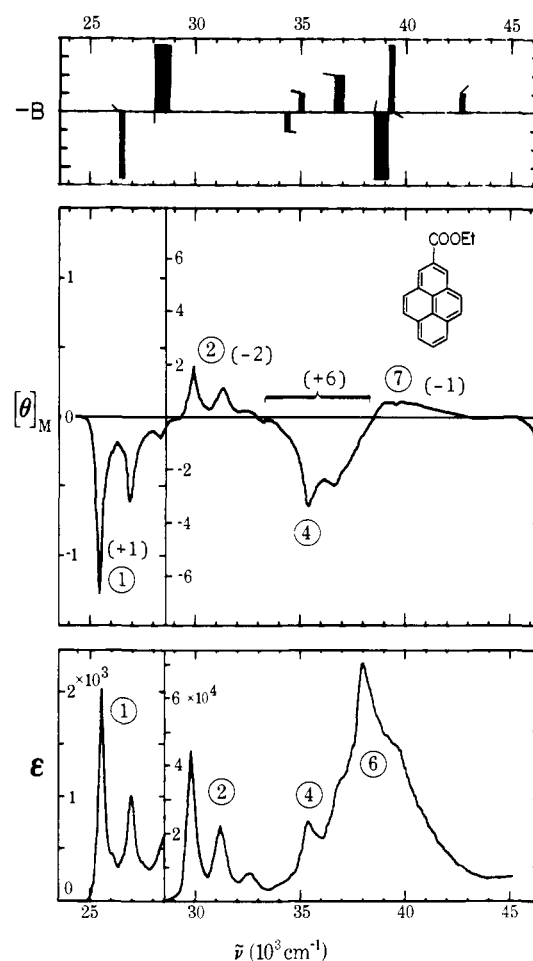Figure 11. 2-Aminopyrene. See captions to Figures 2 and 9.

Figure 12. 2-Carboethoxyprene. See caption to Figure 2. In the calculation of polarization directions, the carbonyl oxygen of the carbethoxy group pointed to the right in the formula given.

is satisfying to note that the effects of fluoro and amino substitution in this position of $B(L_b)$, $B(L_a)$, and $B(B_b)$ are weaker replicas of their effects in position 1 (compare Figure 6 with Figure 2 and Figure 7 with Figure 4). In 4-F-1, $B(L_a)$ is almost exactly compensated to zero by the substituent effect. 4-Substitution further differs from 1-substitution in that it clearly brings out the presence of transition 3 in MCD (positive) and, to a lesser degree, in absorption spectra.

For the +E substituent carbethoxy (Figure 8), we observe once again that 4-substitution has effects on $B(L_b)$ and $B(L_a)$ similar to those of 1-substitution, but weaker. Transition 3 is again seen clearly in MCD (now negative) and also quite distinctly in absorption. Its presence complicates the MCD of the B_b band: as in 1-COOEt-1, in B_b-B_a mixing the intrinsic μ^- contributions to the B terms of the B bands apparently dominate over the weak substituent-induced μ^+ contributions and $B(B_b) > 0$ and $B(B_a) < 0$, but now the origin (but not the bulk) of the B_b band, which is very close to transition 3, apparently also receives a large negative contribution to its B term from mixing with the latter, so that MCD of transition B_b is bisignate.

L_b, L_a, and B_b Bands: 2-Substitution. Position 2 is of the subdominant type ($c_{2,1}^2 = 0.0$ and $c_{2,2}^2 = 0.18$). For the −E substituents F, OH, and NH_2 (Figures 9–11), the expected substituent-induced contributions $B(L_b) < 0$ and $B(L_a) > 0$ are observed. Their magnitudes grow from F to OH and then decrease on going to NH_2, apparently since the border line for switchover to dominant behavior has been approached. This is as expected, except that $B(L_b)$ is much smaller than $B(L_a)$ in the amine, not unlike the case of 2-aminoanthracene.[19] This difference may not only be due to the intrinsic positive μ^- contribution to $B(L_a)$, which certainly explains part of it, but also to the way in which the L_b-L_a and L_b-B_a mixing partially cancel in their effect on $B(L_b)$ while the contributions from

L_b-L_a and L_b-B_a mixing add up in their effect on $B(L_a)$.[5] In 2-NH_2-1, the L_b-L_a separation is only smaller by a factor of 2 than the L_b-B_a separation, while in 2-OH-1, the factor is 4. In 2-OH-1, L_a lies closer to L_b than to B_b; in 2-NH_2, the reverse is true. However, since the L_a-L_b and L_a-B_b mixings act in the same sense, the effect on L_a is small. In all three compounds, the intrinsic positive value of $B(B_b)$ is compensated almost exactly to zero by the substituent-induced μ^+ contribution which has the expected negative sign. This is a stronger substituent effect than observed in naphthalene[20] and anthracene,[19] where neither subdominant −E substitution nor dominant +E substitution managed to override the intrinsic sign of $B(B_b)$.

For the +E substituent, carbethoxy (Figure 12), $B(L_b) > 0$, $B(L_a) < 0$, and $B(B_b) > 0$, as expected.

Other Transitions. The MCD effect of the other transitions observed in the spectra of substituted pyrenes are either not described properly by the simple theory ($B_a = 6$), or not described at all (3, 5, 7, . . .). Full PPP calculations predict such a multitude of transitions near and above the B_a band that a meaningful comparison is impossible. It is, however, of interest that in addition to doing quite well for the L and B transitions, they also predict correctly that transition 3 should be intensified in 4-substituted pyrenes and that it should have a negative B term in 4-NH_2-1 and a positive one in 4-$COOC_2H_5$-1. Actually, the calculations predict two weak transitions in this region, and these may well be present, but our experiments do not prove their existence. However, the experimental data clearly demand the existence of at least one such transition, and by extrapolation back to unsubstituted pyrene, we can state

with confidence that its unobserved third excited singlet state lies near 34 000 cm^{-1}, between the L_a and B_b bands. The existence of this state has been recently deduced from a study of azapyrenes,[8] and may be of interest for interpretation of two-photon absorption work.

Similarly, our data also show quite unambiguously the presence of a transition near 40 000 cm^{-1} (transition 5) in pyrene derivatives and, again by extrapolation, in pyrene itself. The existence of this weak transition has been suspected for some time[15] and was substantiated also in our MCD study of azapyrenes.[8] About four weak transitions are calculated in this region by the PPP method.

Finally, and not surprisingly, our MCD data show that the absorption region of the B_a transition is composite and contains several transitions. These may correlate with some of the four mentioned above, with another four or so calculated at somewhat higher energies, or with transitions into states of partially doubly excited nature which do not appear in the simple PPP approximation used here.

Conclusions

The simple theory of parts 1-3[4-6] accounts well for the qualitative features of the MCD spectrum of pyrene and, even semiquantitatively, for the substituent effects on the L_b, L_a, and B_b bands. The experimental data permit a conclusive identification of two new transitions near 34 000 cm^{-1} and near 40 000 cm^{-1} in pyrene derivatives and, by extrapolation, in pyrene itself, as well as a more tentative identification of several new excited states at higher energies.

References and Notes

(1) Presented at the First Chemical Congress of the North American Continent, Mexico City, Mexico, Nov 30–Dec 5, 1975; International Symposium on Atomic, Molecular, and Solid-State Theory, Sanibel Island, Fla., Jan 18–24, 1976; the 2nd International Congress of Quantum Chemistry, New Orleans, La., Apr 19–24, 1976; the Nobel Workshop on Molecular Optical Dichroism and Chemical Applications of Polarized Spectroscopy, Lund, Sweden, Oct 25–27, 1976; and the Third International Symposium on Novel Aromatic Compounds, San Francisco, Calif., Aug 22–26, 1977.
(2) Part 12: M. Vašak, M. R. Whipple, and J. Michl, *J. Am. Chem. Soc.*, preceding paper in this issue.
(3) (a) University of Utah. (b) Swiss National Foundation Fellow, 1975–1977. (c) Aarhus University.
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Magnetic Circular Dichroism of Cyclic π-Electron Systems. 14.[1] Derivatives of Azulene

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Abstract: Magnetic circular dichroism of five alkylazulenes is reported. Analysis of the results leads to a reassignment of the sign of the *B* term of the fourth singlet–singlet transition (B_a) and confirms the presence of two new excited states at 40 000 and 46 000 cm^{-1}. Standard PPP calculations are in good agreement with the results and indicate that the state at 40 000 cm^{-1} is predominantly doubly excited (HOMO,HOMO → LUMO,LUMO). Regardless of the position of alkyl substitution, the MCD signs agree with those of azulene itself and with the theory of parts 1–3. The region of the L_a band is the most sensitive to perturbation, as expected for weak substituents on a chromophore which is intermediate between positive-hard and even-soft.

Introduction

MCD properties of alkyl derivatives of azulene are of interest for testing the simple qualitative theory of MCD signs of transitions involving the L and B states of a π-electron perimeter, presented in parts 1–3 of this series.[3-5] This theory introduced the distinction between hard (ΔHOMO $\neq$ ΔLUMO) and soft (ΔHOMO = ΔLUMO) MCD chromophores, based on their expected response to perturbations [ΔHOMO = $|E(a) - E(s)|$ and ΔLUMO = $|E(-a) - E(-s)|$, where the MO's **a, s, −a, −s** are derived from the four frontier orbitals of the π-electron perimeter as described in more detail in parts 1–3[3-5]]. The existence of several types of soft chromophores was predicted. In parts 4–14 of this series, we probe substituent effects on various kind of chromophores derived from an uncharged perimeter. The response of double-soft chromophores to mesomeric (E) and inductive (I) effects was discussed in part 4.[6] The response of odd-soft chromophores was examined in parts 7,[7] 8,[8] 9,[9] 10,[10] 11,[11] 12,[12] and 13.[1] In parts 5[13] and 6[14] and in the present paper, we consider even-soft chromophores, and in the remainder of this series, we focus attention on hard chromophores.