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Magnetic Circular Dichroism of Cyclic π -Electron Systems. 12.^{1,2} Aza Analogues of Phenanthrene

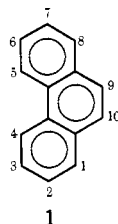
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Abstract: Magnetic circular dichroism of phenanthrene and seven of its aza analogues is reported and interpreted. An improved characterization of $\pi\pi^*$ transitions is achieved, evidence for a new low-lying $\pi\pi^*$ state in phenanthrene is presented, and a reassignment of the $\pi\pi^*$ states of the azaphenanthrenes is proposed. The perimeter model of parts 1–3 combined with the PMO approximation accounts for most of the observed signs of the lowest two bands but, with the exception of phenanthrene itself, not for those of higher energy transitions. Simple PPP calculations account well for the MCD signs of the four lowest $\pi\pi^*$ bands. Only in the case of benzo[*c*]cinnoline has an $n\pi^*$ transition been observed; its *B* term is weakly negative.

Introduction

According to the qualitative theory of the MCD signs of transitions of the L and B types in cyclic π -electron systems described in parts 1–3,^{4–6} phenanthrene and other polycyclic benzenoid hydrocarbons without a threefold or higher symmetry axis are odd-soft chromophores. Some simple consequences follow for their MCD spectra and for the effect of I and E substituents on these spectra. As noted in part 1,⁴ elsewhere in the present series we investigate the case of naphthalene, anthracene, and pyrene. In the present paper, we examine the effects of I substitution, represented by aza replacement, on MCD of phenanthrene (**1**). The MCD spectrum of **1** has been reported previously,^{7,8} and the sign of its first *B*



term has been calculated.⁸ A remeasured spectrum is included here for comparison. The MCD spectra of azaphenanthrenes have not been reported previously except for a mention in our preliminary communications.^{1,9,10} Presently, we report the spectra of three azaphenanthrenes (1-N-**1**, 4-N-**1**, 9-N-**1**) and four diazaphenanthrenes (1,8-N-**1**, 1,5-N-**1**, 4,5-N-**1**, 9,10-N-**1**).

Singlet excited states of **1** are now understood in considerable detail. The presently accepted assignment of the L and B bands was proposed by Dörr et al.,¹¹ arguing on basis of

polarized fluorescence spectra. These authors discussed in detail the relation to earlier experimental and theoretical work, such as the classical papers of Kleven and Platt¹² and of Pariser.¹³ The assignment, in particular the identification of the *B_b* band, is in agreement with measurements of linear dichroism in stretched polymer sheets.^{14–16} Theoretical and experimental work on assignment of electronic transitions was summarized in ref 14; the more recent theoretical work^{17–19} has brought no substantial changes. Well-established bands of interest here are *L_b* (short-axis polarized) near 29 000 cm^{-1} , *L_a* (long-axis polarized) near 34 000 cm^{-1} , *B_b* (short-axis) near 38 000 cm^{-1} , and *B_a* (long-axis) near 40 000 cm^{-1} . The *B* bands are so close to each other that the weaker *B_b* band is hidden in ordinary absorption spectra, but its presence is obvious in stretched-sheet spectra^{14–16} and also in the MCD spectrum.^{7,8} The former also show that the next higher region of absorption contains two intense transitions near 45 000 cm^{-1} (short-axis polarized) and 47 000 cm^{-1} (long-axis polarized), assigned as *C_b* and *C_a*, respectively. In addition to these six transitions, most calculations also predict the presence of about three or four very weak transitions at energies about 40 000–50 000 cm^{-1} . No definitive experimental evidence appears to exist for these.

The experimental^{11,15,20–22} and calculated^{11,15,21–27} absorption and polarization spectra of various aza analogues of **1** generally are in good mutual agreement. As noted in ref 22, the $\pi\pi^*$ transition energies in azaphenanthrenes are quite close to those of the parent **1**, but intensities and, if symmetry is *C_s*, also polarization directions are modified. Since the aza nitrogen breaks the alternant pairing symmetry, it is not surprising that the *L_b* transition is more intense in the heterocycles. Intensities and polarizations in diazaphenanthrenes have been discussed

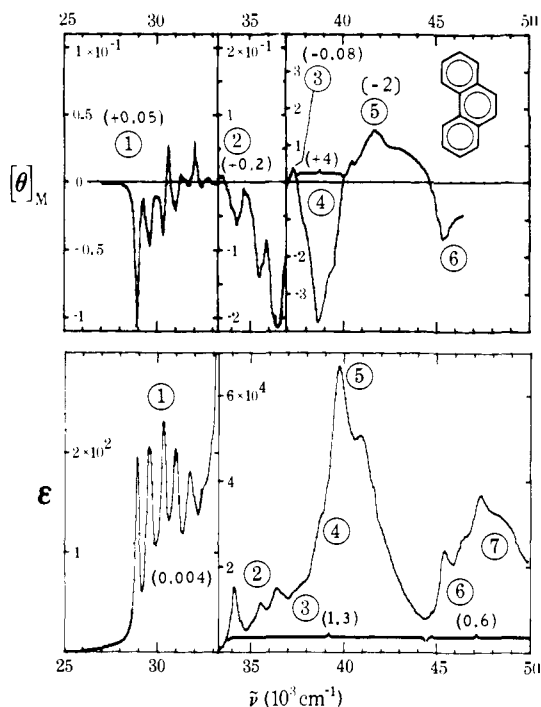


Figure 1. Phenanthrene spectra: bottom, absorption (oscillator strengths given); top, MCD (B terms in units of $10^{-3}\beta_e D^2/\text{cm}^{-1}$).

in some detail in ref 22. Koutecký²⁸ has shown how simple arguments account for the calculated effects of aza replacement on the L_b polarization direction.

The presence of a low-energy $n\pi^*$ transition in the spectrum of 9,10-N-1 is well established^{11,29-32} and agrees with calculations.²⁷ The search for $n\pi^*$ absorptions in other azaphenanthrenes has been mostly in vain.²⁹ A weak long-axis polarized feature in the absorption of 4,5-N-1 at 30 200 cm^{-1} has been tentatively attributed¹⁵ to a $n\pi^*$ transition but it seems to us that it is more likely a part of the vibronic structure of the L_b band. Also, it has been claimed³³ that weak $n\pi^*$ absorptions have been detected by a differential measurement of solvent effects in 1-N-1 (30 600 cm^{-1}), 4-N-1 (31 850 cm^{-1}), and 9-N-1 (30 600 cm^{-1}). No independent confirmation is available.

Experimental Section and Calculations

The samples were commercial and were purified by gradient sublimation. Details of the measurements and PPP calculations were the same as in part 4,³⁴ except that acetonitrile solvent was used for 4,5-N-1, whose solubility in cyclohexane is too low.

Results

The results for **1** and its aza analogues are shown in Figures 1-8. The assignments shown are based on comparison of the eight spectra and on consideration of previous work on these compounds and other azaphenanthrenes, particularly on polarized spectra where available^{15,21,22,32} (in **1**, 1 = L_b , 2 = L_a , 4 = B_b , 5 = B_a , 6 = C_b , 7 = C_a). The calculations shown used the simple standard version of the PPP model, incorporating only nearest-neighbor effects, and as discussed in more detail in part 2,⁵ they represent an approximate prediction of the difference between the aza compound and parent **1**. The calculated energies, intensities, and polarizations are in general agreement with the previous work cited above.

The B term of the only well-established $n\pi^*$ band (9,10-N-1) is negative and extremely small, similarly as in aza analogues of benzene³⁴ and naphthalene.³⁵ The MCD of the $\pi\pi^*$ region shows rich structure, showing the presence of at least seven $\pi\pi^*$ transitions but shows less variation in signs from one compound to the next than suggested by the general simple

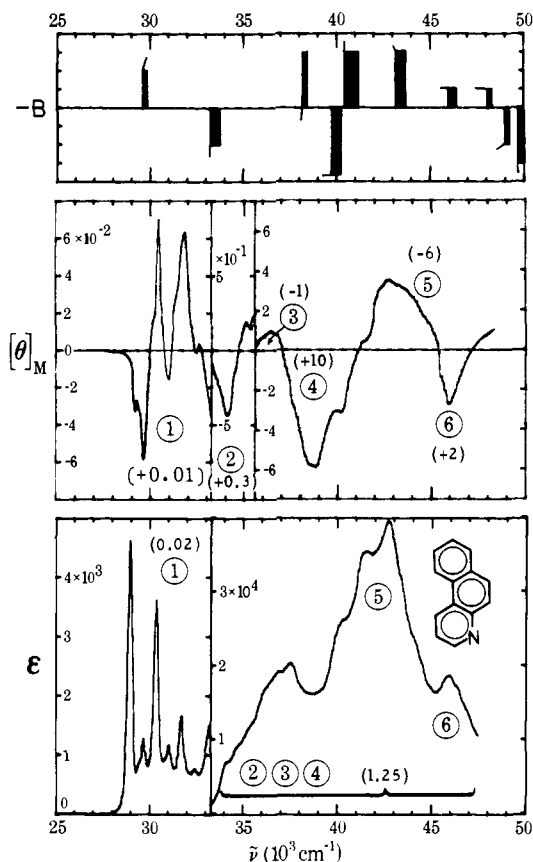


Figure 2. 1-Azaphenanthrene spectra: bottom, absorption (oscillator strengths given); center, MCD (B terms in units of $10^{-3}\beta_e D^2/\text{cm}^{-1}$); top, calculated. Calculated $-B$ values are indicated by the length of the bars (short, below 1; next, 1-3; next, 3-10; longest, over 10, in units of $10^{-3}\beta_e D^2/\text{cm}^{-1}$), calculated oscillator strengths by their three grades of thickness (less than 0.2; 0.2-0.5; over 0.5), and calculated polarizations by directions of the flags at the end with respect to the formula shown.

theory⁶ for an odd-soft chromophore. Some vibronic effects are noted in the weak MCD of the L_b transition.

Discussion

Spectral Assignments. There is no evidence for $n\pi^*$ transitions in the spectra except in the clear-cut case of 9,10-N-1. A proposal for the identification of individual $\pi\pi^*$ electronic transitions in the heterocycles is shown in Figures 2-8 (the numbers are all increased by one in the case of 9,10-N-1 because of the presence of the $n\pi^*$ band). The assignment is fairly straightforward for the first four or five transitions but only tentative in the congested higher energy region which may well contain more transitions than shown. Comparison with the published¹⁵ stretched-sheet spectra of 4,5-N-1 shows that in this case absorption in the general region of the origin of transition 1 (L_b) is short-axis polarized, as are transitions 4 (B_b) and 6 (C_b), while transitions 2 (L_a), 3, and 5 (B_a) are long-axis polarized. In 9,10-N-1, transition 2 (L_b) is known to be short-axis polarized and transition 3 (L_a) long-axis polarized.³² Similar relative polarizations were found in some other diazaphenanthrenes²² and we shall assume that they prevail throughout.

The MCD spectra make very clear the separate existence of the similarly polarized transitions 2 and 3 (3 and 4 in 9,10-N-1), which often merge in ordinary or polarized absorption spectra. In view of the generally excellent correspondence of the energies of the first few transitions in azaphenanthrenes to those in **1** itself, we propose that a transition corresponding to 3 also occurs in **1** in the region between its L and B bands, as calculated, but has so far remained unnoticed

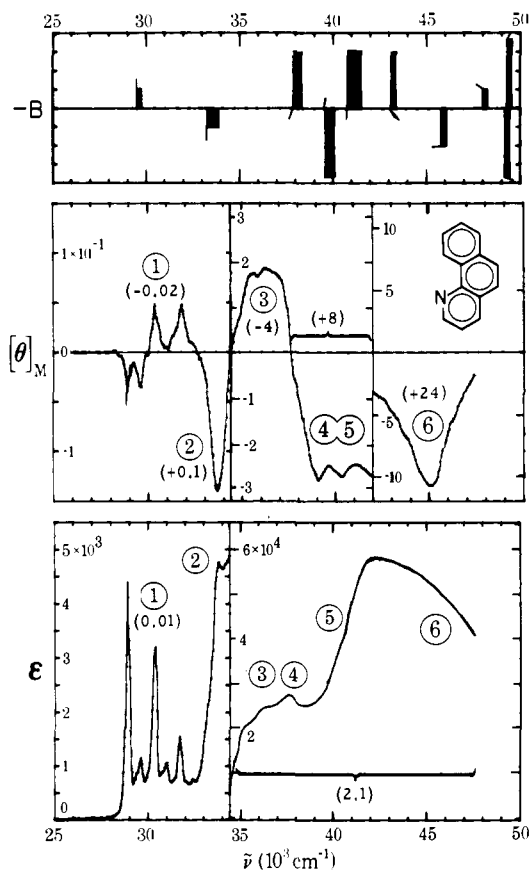


Figure 3. 4-Azaphenanthrene. See caption to Figure 2.

due to its low intensity (as mentioned below, it may actually be discernible in the MCD spectrum of **1**). The existence of a long-axis-polarized transition corresponding to 3 in **1** itself has been suspected for some time since such a transition is present in carbazole and related heterocycles.¹⁶

The assignment of transitions 1 and 2 (2 and 3 in 9,10-N-**1**) to L_b and L_a , respectively, is clear-cut in the azaphenanthrenes of C_{2v} symmetry. Of course, in those of C_s symmetry, the two L bands may be mutually mixed.^{22,28} The identification of the B_b band with transition 4 (5 in 9,10-N-**1**) is also trouble-free. On the other hand, while in the parent **1** the B_a band is clearly identified with a transition corresponding to our no. 5, and the state corresponding to our no. 3 is of the "minus" type and not even observed in absorption spectra, in the azaphenanthrenes the two transitions mix and share the B_a character. This is suggested by inspection of CI wave functions calculated in ref 22 and presently by us and by the observed sharing of intensity and polarization¹⁵ by the two transitions. Transition no. 3 has been previously assigned²² as B_a and no. 5 as very strongly shifted C_a , so that the orders of the two B states and of the two C states were reversed with respect to **1** itself, but this appears less reasonable to us. In azaphenanthrenes of C_s symmetry, aza substitution can also mix the B_b state (no. 4) with either of the two states which share " B_a " character (nos. 3, 5), so that in these compounds, these three nearly isoenergetic states of the basic chromophore **1** are mixed. As might be expected, this intervention of another low-energy state into the L, B sequence of four states in a molecule of C_{2v} symmetry spells disaster for attempts to use the simple theory of parts 1-3⁴⁻⁶ to predict MCD signs of the $G \rightarrow B$ transitions.

The assignment of transitions 6 and 7 of the azaphenanthrenes (7 and 8 in 9,10-N-**1**) to the C_b and C_a states, respectively, in close analogy to **1**, appears quite straightforward once it is accepted that transition 5 now shares its B_a character with transition 3. All of these assignments are in good agreement

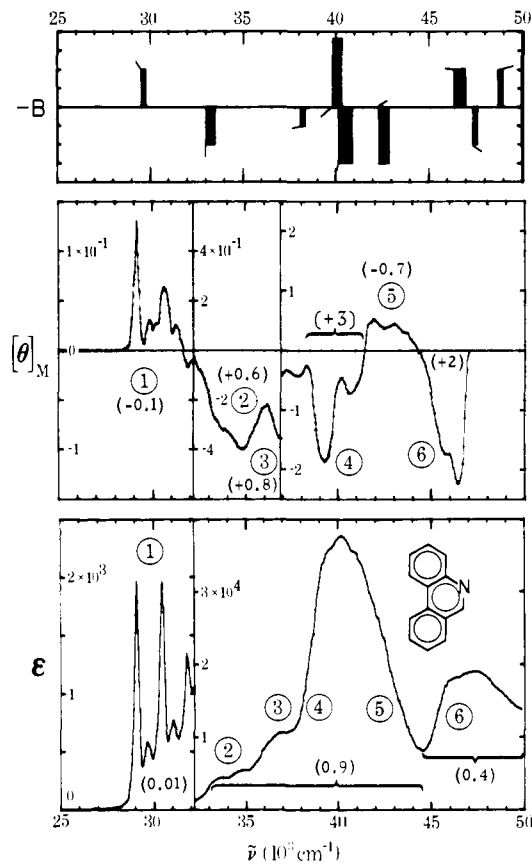


Figure 4. 9-Azaphenanthrene. See caption to Figure 2.

with calculations, which also suggest one to three additional weak bands just below 50 000 cm^{-1} . However, if our previous experience³⁶ on molecules of this size is any guide, results of the present type of calculations are quite unreliable in this high-energy region, since introduction of doubly excited configurations will cause considerable changes. Experimental assignments are also difficult because of the lack of well-developed spectral features.

MCD Signs: Phenanthrene. The MCD spectrum of **1** itself (Figure 1) conforms nicely to expectations⁵ for an odd-soft chromophore, which are $B(L_b) = 0$, $B(L_a) > 0$ (weak), $B(B_b) > 0$, and $B(B_a) < 0$. The observed MCD of the L_b band is weak and dominated by vibronic effects; the other observed signs are as expected. In absorption, there is no evidence for a transition corresponding to transition 3 of the azaphenanthrenes, predicted by most calculations to be approximately degenerate with the B bands. In MCD, its existence might be responsible for the positive peak at 37 400 cm^{-1} between the negative L_a and B_b bands as suggested in Figure 1. This interpretation has been proposed independently by Thulstrup.³⁷

MCD Signs: Azaphenanthrenes. According to the simple theory of parts 1-3,⁴⁻⁶ introduction of substituents into an odd-soft chromophore will introduce μ^+ contributions to the B terms, whose signs will depend on the sign of the difference $\Delta\text{HOMO} - \Delta\text{LUMO}$. If this difference is positive, the contributions to the lower of the L bands and the lower of the B bands will be positive and those to the upper bands negative; if the difference is negative, the opposite will hold. The contributions to $B(L_b)$ and $B(L_a)$ are predominantly due to L_a-L_b mixing [the contribution to $B(L_b)$ is reduced by the effect of L_b-B_a mixing, which is normally much smaller]; because of the relatively large L_a-L_b separation in **1**, these contributions should be rather weak. The contributions to $B(B_b)$ and $B(B_a)$ are predominantly due to B_b-B_a mixing. Since these two states are almost degenerate in **1**, these contributions should be ab-

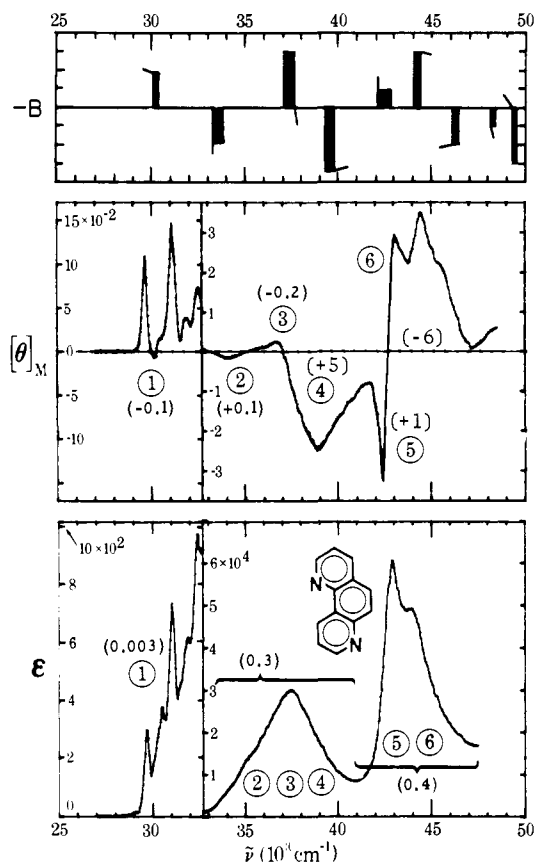


Figure 5. 1,5-Diazaphenanthrene. See caption to Figure 2.

normally large—but so is, of course, the inherent μ^- contribution in **1** itself which depends inversely on the same B_b - B_a separation.

As we have seen above, however, in **1** the aza replacement will produce another large effect: it will transfer much of the B_a character from transition 5 to transition 3, and thus produce a new moderately intense band in close vicinity of transitions 2 and 4. Moreover, the two C states, not considered in the simple theory, are nearby in energy and have high intensity. The simple perimeter model is clearly incapable of predicting or rationalizing the effects of mutual mixings of the closely spaced five states 3, 4, 5, 6, and 7, leaving the MCD signs of transitions 1 and 2 as the only ones we can presently understand in simple terms. If the symmetry is C_{2v} , the emergence of strong transition 3 near transition 2 will not affect $B(2)$, since transitions 2 and 3 have the same polarization. It will, however, affect $B(1)$. In the first approximation, we shall assume that it will effectively bring the B_a - L_b separation close to the L_a - L_b separation and thus largely cancel the expected substituent effect on the L_b band. If the symmetry is C_s , the new strong transition 3 may affect both $B(1)$ and $B(2)$. The existence of two opposed contributions to $B(L_b)$ is indicated both by the unusually small magnitude of this B term in the aza heterocycles and by the sign reversal through the band in the cases of 1-N-1, 4-N-1, and 4,5-N-1.

Inspection of Hückel coefficients shows that positions 1, 3, and 9 are dominant ($c_1^2 > c_2^2$) and position 2 and, more weakly, position 4 subdominant ($c_1^2 < c_2^2$). When the inductive effect of the aza nitrogen on adjacent carbons is included in the considerations as in part 5,⁴ the conclusions are unchanged, except that replacement in position 1 now should have almost no effect. A +I effect in a dominant position should cause $\Delta\text{HOMO} < \Delta\text{LUMO}$; in a subdominant position, $\Delta\text{HOMO} > \Delta\text{LUMO}$. Agreement with experimental signs of the two L transitions is mostly good but not without exceptions. In 1-N-1 (Figure 2), 1,5-N-1 (Figure 5), 1,8-N-1 (Figure 6),

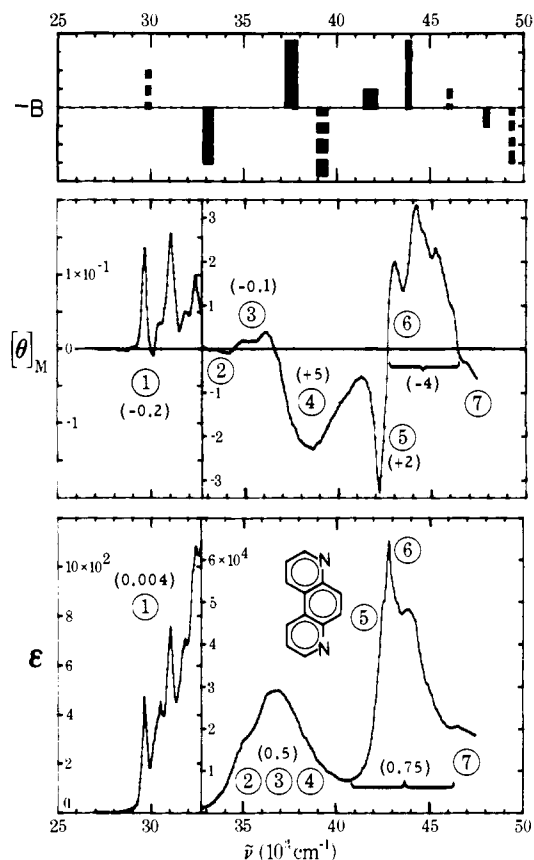


Figure 6. 1,8-Diazaphenanthrene. See caption to Figure 2. Solid bars indicate vertical polarization and broken bars horizontal polarization with respect to the formula shown.

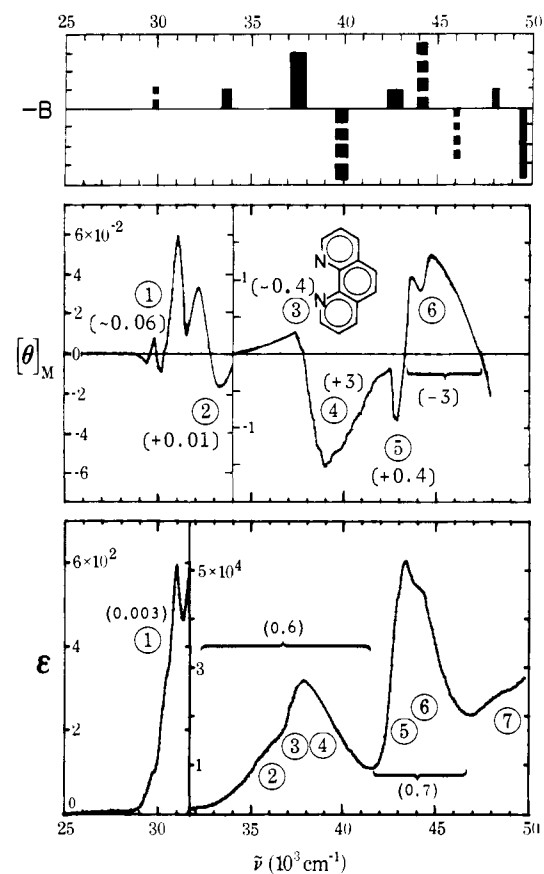


Figure 7. 4,5-Diazaphenanthrene. See captions to Figures 2 and 6.

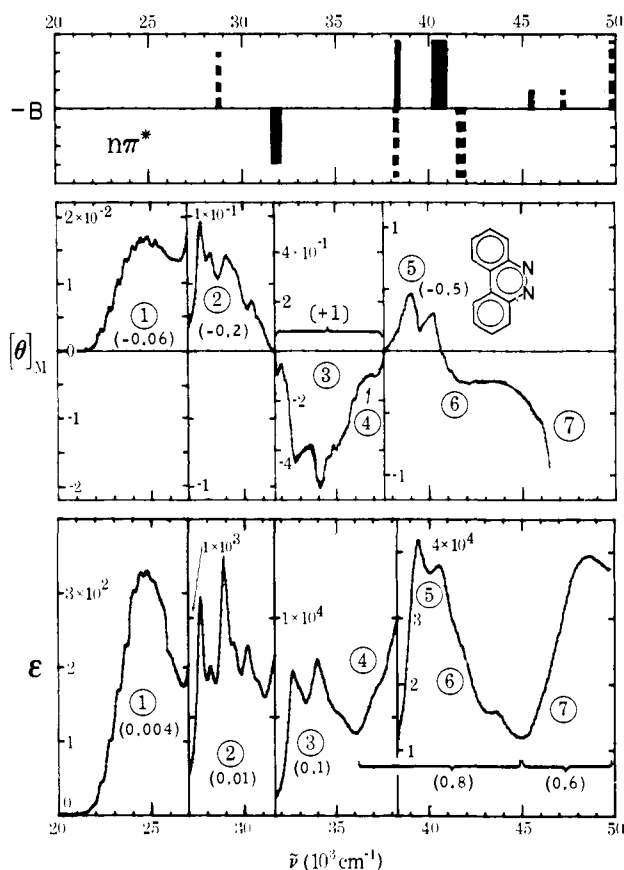


Figure 8. 9,10-Diazaphenanthrene. See captions to Figures 2 and 6.

9-N-1 (Figure 4), and 9,10-N-1 (Figure 8) the simple argument predicts $B(L_b) < 0$ and $B(L_a) > 0$, and this is observed, except that the origin though not the bulk of the L_b band in 1-N-1 is of the wrong sign. In 4-N-1 (Figure 3) and 4,5-N-1 (Figure 7), we expect $B(L_b) > 0$ and either $B(L_a)$ negative or at least less positive than in **1** itself. The latter situation is indeed observed for $B(L_a)$, but the sign of $B(L_b)$ agrees with theory only in the region of the origin and is opposite throughout much of the band.

While the simple first-order theory is clearly not adequate for the higher B terms of the azaphenanthrenes, a simple PPP calculation of nearest-neighbor contribution, whose results are shown in the figures, gives a reasonable account of most of the MCD signs for the first four transitions. It predicts almost vanishing B terms for the L_b band of 4-N-1 and for both L bands of 4,5-N-1, with signs opposite to those obtained from the simple approach, and thus in agreement with those of the bulk of the band though not the origin.

Conclusions

There is good evidence for the existence of a previously unobserved excited singlet state of **1** near $37\,400\text{ cm}^{-1}$. The MCD signs of **1** are in perfect agreement with the perimeter model of parts 1–3.^{4–6} For its aza analogues, the agreement is good for the two lowest transitions, with some exceptions related to sign reversals throughout the L_b band, but not for the higher energy transitions, and the azaphenanthrenes appear to be close to the limit of applicability of the simple theory. The difficulties may be blamed on several factors. These are the large number of transitions below $50\,000\text{ cm}^{-1}$, along with the only moderately high symmetry of **1** (C_{2v}), and the large separation of the L_b and L_a bands, due to the small value of the energy difference of the orbitals 1 (HOMO) and 2. As for the effects of E substitution, which we have not studied experi-

mentally, the proximity of energies of orbitals 1 and 2 makes it likely that in the subdominant positions (2 and, perhaps, 4) it will be relatively easy to reach the border line at which the substituent effect reverts to the signs normally expected for substitution in a dominant position.

It is heartening that even in this rather demanding case already the very simplest PPP calculation taking only nearest-neighbor interactions and not optimized for MCD in any way accounts quite well for the signs of the lowest four transitions. It is to be hoped that the performance will be only improved upon introduction of nonneighbor interactions and of the refinements inherent in all-valence electron methods.

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