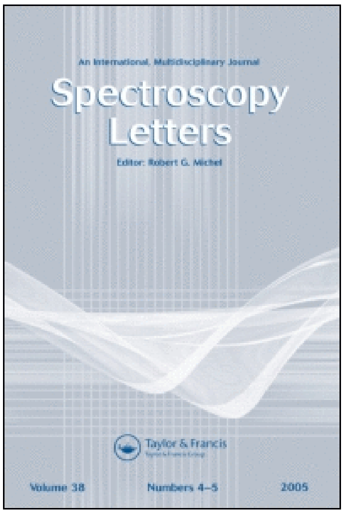

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Excited Electronic States of Pyrene and some Azapyrenes

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Excited Electronic States of Pyrene and some Azapyrenes

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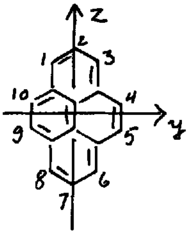
Pyrene and three azapyrenes have been studied by means of linear and magnetic circular dichroic spectroscopy. As a result, an improved understanding of the lower excited states has been reached, and a simple relation has been found between structure and MCD sign of the first two transitions in the azapyrenes.

A large number of investigations of pyrene have made an extensive characterization of four singlet-singlet transitions possible. These transitions are[1,2]: ^1L_b (27000 cm^{-1}, weak and y-polarized), ^1L_a (30000 cm^{-1}, strong and z-polarized), ^1B_b (37000 cm^{-1}, strong and y-polarized), and ^1B_a (41000 cm^{-1}, very strong and z-polarized).



In addition to these transitions π-electron calculations[3] predict that a number of symmetry-forbidden transitions should occur in the region around or below the ^1B_a-band, in agreement with the result of absorption experiments on the ^1L_b state[4]. In order to further study these transitions and to investigate the effect of aza replacement on the linear and magnetic circular dichroism of pyrene, LD and MCD spectra were obtained of pyrene, 1- and 4-azapyrene and 2,7-diazapyrene, and CI calculations in the π-electron approximation were carried out on these molecules.

The LD spectra were obtained by the stretched sheet method at low temperature using a closed-cycle helium cryostat. Further experimental details and a description of the calculations will be given elsewhere[5].

The stretched sheet spectra of 2,7 diazapyrene (see Fig. 1 for the reduced spectrum) show that the orientation factors for this molecule (K_1 = 0.53, K_2 = 0.36) are very close to those obtained for pyrene (K_1 = 0.54, K_2 = 0.32) in contrast to the results in earlier cases, where aza-replacement caused a substantial change in the orientation. For 1- and 4-azapyrene the assumption that one of the observed transitions is polarized parallel to and one perpendicular to the orientation axis gave the orientation factors K_1 = 0.55 and K_2 = 0.32, almost identical to the values for pyrene.

For the determination of reduced curves corresponding to z- and y-polarized absorption, the following equation is used[2]:

$$\underline{A} = \underline{K}^{-1}\,\underline{E}$$

where $\underline{A} = \begin{pmatrix} A_z(\lambda) \\ A_y(\lambda) \end{pmatrix}$ (absorption polarized along z and y),

$\underline{E} = \begin{pmatrix} E_{\parallel}(\lambda) \\ E_{\perp}(\lambda) \end{pmatrix}$(observed spectra), and $\underline{K} = \begin{pmatrix} K_1 & K_2 \\ \frac{1}{2}(1-K_1) & \frac{1}{2}(1-K_2) \end{pmatrix}$

(orientation factors which can be determined from the conditions $\left(\frac{dA_z}{d\lambda}\right)_{^1L_b} = \left(\frac{dA_y}{d\lambda}\right)_{^1L_a} = 0$). It can be noted that using a K_2 orientation factor corresponding to a rod-like case ($K_2 = \frac{1}{2}(1-K_1) \sim 0.23$) for the symmetrical 2,7-diazapyrene would lead to a prediction of strongly mixed polarization of the 0-0 band of the well resolved first transition (^1L_b).

Besides the four well-known transitions the LD spectrum of pyrene shows two absorption bands which through vibronic coupling might be assigned to some of the calculated forbidden transitions. The first of these, at 38000 cm^{-1}, is z-polarized, while the second, at 44000 cm^{-1}, is polarized along the y-axis. Corresponding bands are found in the absorption spectrum of 2,7-diazapyrene (bands F and H, respectively, in Fig. 1), where also the presence of a y-polarized transition (band C) and a z-polarized transition (band D) around 35000 cm^{-1} is observed. However, none of these transitions (C, D, F and H) are seen in the MCD-spectrum of the compound.

The LD and MCD spectra of 4-azapyrene also indicate the presence of one or both of the transitions C and D between the ^1L_a and ^1B_b bands, while little can be said from the spectra of 1-azapyrene. In both the unsymmetrical compounds the MCD curves have negative peaks (possitive B-terms) on each side of the ^1B_a band, corresponding to the bands F and H in Fig. 1. There seems little reason to doubt that band H is due to a separate electronic transition, while the observations on bands C, D and F in the four compounds still leave the possibility open that one or more of the bands are due to vibronic components of the well-known transitions.

The most striking feature in the MCD spectra of the azapyrenes is the dependence of the signs of the ^1L_b and ^1L_a bands

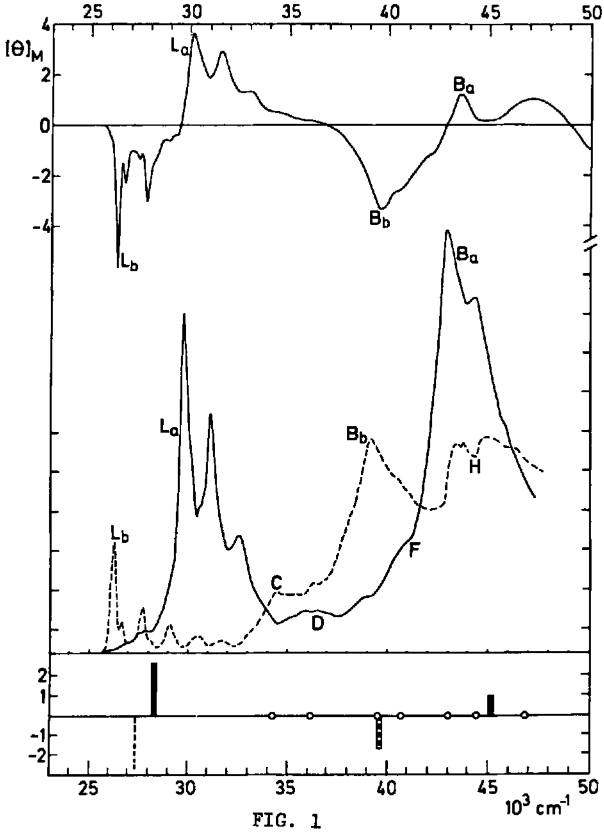


FIG. 1

2,7 diazapyrene. Top: MCD-spectrum. Center: Reduced absorption curves, z-polarized (full line) and y-polarized (broken line). Bottom: Calculated transitions (monoexcited CI in the PPP approximation[3]). Oscillator strength is indicated by line thickness and the calculated value of -B for the MCD is given by line length and direction. The circles show calculated symmetry-forbidden transitions.

on the position of aza replacement. In 1- and 4-azapyrene the MCD signs (- sign of B-term) for (^1L_b, ^1L_a) are (+,-) while the signs for 2,7-diazapyrene are (-,+). This can be understood in a simple model: Assuming that the ^1L_b and ^1L_a MCD B-terms are only due to the mutual interaction of the two transitions one has[7]:

$$B(^1L_a) = -B(^1L_b) = \mathrm{Im}\{\langle ^1L_a|\vec{m}|^1L_b\rangle \cdot \langle 0|\vec{M}|^1L_a\rangle \times \langle ^1L_b|\vec{M}|0\rangle \cdot \frac{1}{E(^1L_b)-E(^1L_a)}\}$$

The states ^1L_a and ^1L_b can be approximated by the configurations: $^1L_a = |1\to-1\rangle$ and $^1L_b = a|1\to-2\rangle - b|2\to-1\rangle$, (a=b for pyrene), where 1, 2, 3 are π-orbitals in decreasing energy order and -1, -2, -3 are π* orbitals ordered after increasing energy. For pyrene itself, as for other neutral alternant hydrocarbons with orbital pairing, the MCD-terms vanish in a PPP-model. Aza replacement in position α will remove the degeneracy of the configurations $|1\to-2\rangle$ and $|2\to-1\rangle$ and the MCD-sign will depend on which of the two configurations becomes lower in energy and gets the larger coefficient in the expression for ^1L_b. Since nitrogen is more electronegative than carbon, $|c_{\alpha,2}|>|c_{\alpha,1}|$ means that $|a|>|b|$, while $|c_{\alpha,2}|<|c_{\alpha,1}|$ means that $|a|<|b|$, where $\{c_{\alpha,i}\}$ are Hückel coefficients. Inspection of the triple product of vectors in the expression for $B(^1L_a)$ shows[7] that the sign of $B(^1L_a)$ is equal to that of $|b|-|a|$. Using this result and the Hückel coefficients for the MO's 1 and 2, it can be concluded that aza replacement in one or both of the positions 2 and 7 corresponds to the MCD signs (-,+) for (^1L_b, ^1L_a) and aza replacement in one or more of the positions 1, 3, 4, 5, 6, 8, 9, and 10 corresponds to the sign sequence (+,-),in agreement with the experimental observations.

It should be noted that the simple model can be used for other replacements or substitutions in pyrene, providing the resulting perturbations are reasonably small, and that the model can be extended to other neutral alternant hydrocarbons. For this reason such molecules have been called "soft MCD chromophores"[8] in contrast to "hard MCD chromophores", which are non-alternant or charged hydrocarbons where no similar sensitivity to substitution or replacement can be expected for the MCD B-terms.

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