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A CNDO STUDY ON THE $n \rightarrow \pi^*$ CONTRIBUTION TO MCD IN AZA ANALOGUES OF ANTHRACENE

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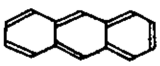
Abstract —— Magnetic circular dichroism of aza analogues of anthracene was interpreted on the basis of the CNDO/S method. Magnetic coupling of the lowest $n \rightarrow \pi^*$ state with the lowest $\pi \rightarrow \pi^*$ state was suggested to be of appreciable importance in acridine, phenazine and benz[a]acridine.

Magnetic circular dichroism (MCD) of acridine (**2**) and phenazine (**3**) has been successfully interpreted[1] in terms of an MO consideration for the response of an odd-soft chromophore to substituent effects[2,3,4]. The signs of Faraday B terms associated with the lower $\pi \rightarrow \pi^*$ transitions in **2** and **3** are calculated within the framework of the PPP method to give an agreement with observation[1].

It seems to be beyond doubt that the strong absorption and MCD bands observed in the UV region of aza analogues of anthracene are $\pi \rightarrow \pi^*$ in origin[5]. Accordingly the magnetic coupling between the lower $\pi \rightarrow \pi^*$ excited states is considered to give dominant contribution to the MCD B values, while appreciable contribution of the lowest $n \rightarrow \pi^*$ excited state to the lowest $\pi \rightarrow \pi^*$ transition in aza analogues of benzene and those of naphthalene is pointed out in recent MCD works[6,7].



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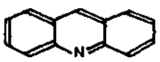

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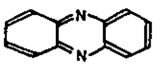

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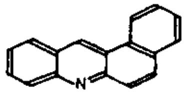

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The purpose of this paper is to calculate the Faraday B values based on the CNDO/S method[8] in order to see to what extent the lowest $n \rightarrow \pi^*$ state contributes to MCD of the lower $\pi \rightarrow \pi^*$ transitions in aza analogues of anthracene.

CNDO/S calculations were carried out as in our previous papers[6,7]. Configuration interaction (CI) among singly excited configurations below 10 eV was taken into account. Using wavefunctions and excitation energies after CI, magnetic rotational strengths B were evaluated according to the equation

$$B(j\leftarrow a) = \mathrm{Im}\{\sum_{k\neq a} (\langle k|\vec{\mu}|a\rangle\cdot\langle a|\vec{M}|j\rangle\times\langle j|\vec{M}|k\rangle)/(E_k - E_a) + \sum_{k\neq j} (\langle j|\vec{\mu}|k\rangle\cdot\langle a|\vec{M}|j\rangle\times\langle k|\vec{M}|a\rangle)/(E_k - E_j)\}$$

where $\langle a|\vec{M}|j\rangle$ and $\langle j|\vec{\mu}|k\rangle$ stand for electric and magnetic moments, respectively. Although the sum in the equation should be taken over all electronic states, the sum is severely truncated because of the approximate LCAO MO method employed in the present calculation. Actually the sum was taken over 100 electronic states and, hence, the origin dependency was minimized by taking the charge distribution of the ground state into account according to the proposal by Caldwell *et al*[9].

We have measured MCD spectra of **1**, **2**, **3** and benz[a]acridine (**4**). However, the MCD spectra of **1**[1, 10-13], **2** and **3**[1] have been already reported. We include only the spectrum of **4** and that of **2** for a comparison.

Experimental MCD spectra of **2** and **4** are represented in Fig. 1 and Fig. 2, respectively. Observed MCD spectrum of **2** in the energy region 25000 ∿ 35000 cm^{-1} is in complete agreement with that by Steiner and Michl[1], clarifying the ^1L_a and ^1L_b bands in **2**. Instead of a single negative peak at 40000 cm^{-1} in the previous work, **2** exhibits MCD with fine structure in the present work corresponding to the strongest absorption which comprises the ^1B_a and ^1B_b transitions. The MCD spectral profile of **2** in solution looks similar with that of **4** which exhibits unfortunately no distinct MCD in the energy region higher than 35000 cm^{-1}, however.

The aza analogues of anthracene exhibit positive first and negative second MCD extrema (see Fig. 1 and Fig. 2), where heavy overlapping is apparent. No curve fitting procedure has been carried out because of this reason.

Theoretical transition energies, oscillator strengths and magnetic rotational strengths are summarized and listed in Table 1 along with experimental values[14]. Calculated excitation energies are in fairly good agreement with the observed transition energies. The present calculation predicts the direction of polarization in agreement with that clarified from the analysis of dichroic spectra for **1**, **2** and **3**[15]. The sign of the observed MCD in **2**, **3** and **4** are well reproduced by the present calculation, although B values for transitions of higher energy are calculated to be small. This may be modified by the use of the dipole length method. The observed MCD spectra are considered to be assigned to the $\pi \to \pi^*$ transitions.

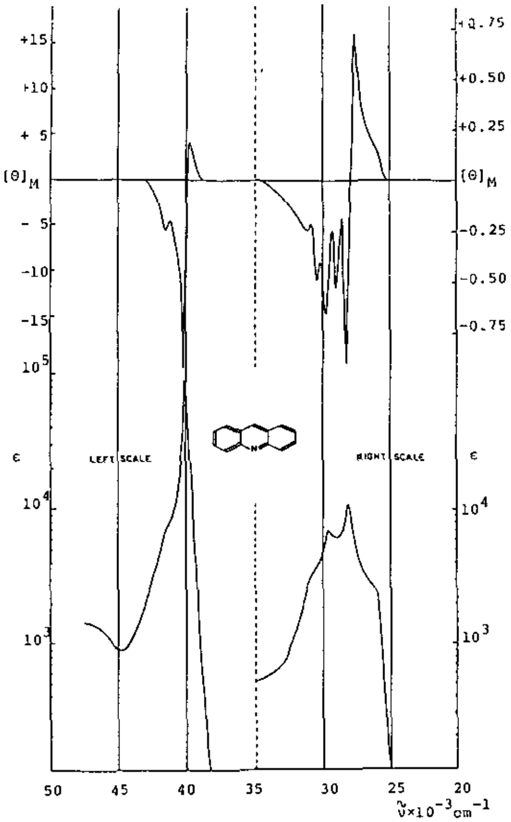

Fig. 1 Absorption(bottom) and MCD(top) spectra of acridine in ethanol at room temperature.

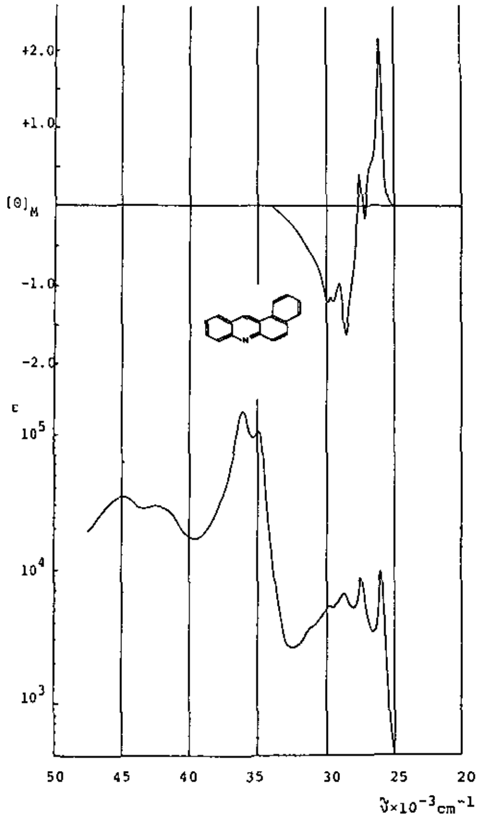

Fig. 2 Absorption(bottom) and MCD(top) spectra of benz[a]acridine in ethanol at room temperature.

The polarized spectra of a single crystal of 3 have been measured at low temperature to find n → π* band at around 420 nm[16]. The dichroic spectra using PVA sheets were not successful to observe the n → π* band of 3 because of its low intensity[15]. Although the n → π* transition is theoretically predicted to take place at the lowest energy in 2 and 3, the present measurement of MCD of 3, even at high concentration, clarifies no distinct MCD in the wavelength region longer than 400 nm under external magnetic field applied.

In Table 2 theoretical contribution of the low-lying excited electronic states to the magnetic rotational strengths is summarized and compared with the net B values summed over 100 electronic states. From Table 2 it is clear that the major part (90 ∿ 100 %) of the calculated Faraday B value for each transition comes from the magnetic coupling among few low-lying excited states. The larger the energy gap in the preceding equation, the smaller becomes the contribution of the high-lying excited states to the magnetic rotational strengths associated with the low energy

Table 1

Calculated transition energies, $\Delta\tilde{\nu}$, oscillator strengths, f, and Faraday B terms, B, on the basis of the CNDO/S method.

Compound	Symmetry	Theoretical			Experimental	
		$\Delta\tilde{\nu}/10^3\mathrm{cm}^{-1}$	f	$B/10^5$	$\Delta\tilde{\nu}/10^3\mathrm{cm}^{-1}$	$B/10^5$
1	$B_{2u}(\pi \rightarrow \pi^*)$	27.8	0.32	+437	26.1	+ 115
	$B_{3u}(\pi \rightarrow \pi^*)$	31.3	0.04	-496	27.8	
	$B_{3u}(\pi \rightarrow \pi^*)$	42.2	2.98	+245	38.9	+1208
	$B_{2u}(\pi \rightarrow \pi^*)$	51.9	0.27	-158		
2	$A_2\ (n \rightarrow \pi^*)$	27.1	0.002	- 86		+ 75
	$A_1\ (\pi \rightarrow \pi^*)$	27.8	0.281	-170	25.7	
	$B_2\ (\pi \rightarrow \pi^*)$	31.7	0.042	+429	28.1	
	$B_2\ (\pi \rightarrow \pi^*)$	41.8	2.770	- 35	39.4	+1211
	$A_2\ (n \rightarrow \pi^*)$	45.4	0.002	+ 65		
	$A_1\ (\pi \rightarrow \pi^*)$	45.5	0.023	-153	45.5	
3	$B_{1u}(n \rightarrow \pi^*)$	20.1	0.001	- 17		+ 297
	$B_{2u}(\pi \rightarrow \pi^*)$	26.4	0.249	- 753	26.6	
	$B_{3u}(\pi \rightarrow \pi^*)$	30.2	0.304	+1069	28.2	
	$B_{3u}(\pi \rightarrow \pi^*)$	41.8	2.505	- 98	39.4	+ 516
	$B_{2u}(\pi \rightarrow \pi^*)$	46.1	0.058	- 282	45.5	
4	$A'\ (\pi \rightarrow \pi^*)$	29.4	0.308	-2343	26.3	+ 288
	$A''\ (n \rightarrow \pi^*)$	29.5	0.001	+ 51		
	$A'\ (\pi \rightarrow \pi^*)$	30.3	0.169	+2832	29.0	
	$A'\ (\pi \rightarrow \pi^*)$	36.5	1.326	- 127	36.7	
	$A'\ (\pi \rightarrow \pi^*)$	38.8	0.076	-1374		
	$A'\ (\pi \rightarrow \pi^*)$	39.9	0.570	+1488		

transitions. That the sum is truncated in the practical use of the equation is considered to be trivial, although CI must be included to fair extent so as to evaluate better values of matrix elements and also to obtain reasonable excitation energies. *There is an appreciable contribution from the magnetic coupling of the* lowest n → π^* state ($1A_2$ in **2** and $1B_{1u}$ in **3**) with the lowest $\pi \rightarrow \pi^*$ state ($1A_1$ in **2** and $1B_{2u}$ in **3**). It should be noted that the contribution of the n → π^* state

Table 2
Contribution to the Faraday B term of the low-lying $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states.

Comp.								Sum	Net
		$1B_{2u}$	$1B_{3u}$	$2B_{3u}$	$2B_{2u}$				
1	$1B_{2u}$	0	+ 458	- 64	0			+ 394	+ 437
	$1B_{3u}$	- 458	0	0	- 37			- 495	- 496
	$2B_{3u}$	+ 64	0	0	+ 170			+ 234	+ 245
	$2B_{2u}$	0	+ 37	- 170	0			- 133	- 158
		$1A_2$	$1A_1$	$1B_2$	$2B_2$	$2A_2$	$2A_1$		
2	$1A_2$	0	- 84	0	0	0	0	- 84	- 86
	$1A_1$	+ 84	0	- 383	+ 133	0	0	- 166	- 170
	$1B_2$	0	+ 383	0	0	0	0	+ 379	+ 429
	$2B_2$	0	- 133	0	0	+ 5	+ 76	- 52	- 35
	$2A_2$	0	0	0	- 5	0	+ 70	+ 64	+ 65
	$2A_1$	0	0	+ 4	- 76	- 70	0	- 141	- 153
		$1B_{1u}$	$1B_{2u}$	$1B_{3u}$	$2B_{3u}$	$2B_{2u}$			
3	$1B_{1u}$	0	- 12	0	0	0		- 12	- 17
	$1B_{2u}$	+ 12	0	- 980	+ 217	0		- 751	- 753
	$1B_{3u}$	0	+ 980	0	0	- 29		+ 951	+1069
	$2B_{3u}$	0	- 217	0	0	+ 227		+ 10	- 98
	$2B_{2u}$	0	0	+ 29	- 227	0		+ 198	- 282
		$1A'$	$1A''$	$2A'$	$3A'$	$4A'$	$5A'$		
4	$1A'$	0	- 87	-2472	+ 116	0	+ 29	-2413	-2343
	$1A''$	+ 87	0	- 33	0	0	0	+ 54	+ 51
	$2A'$	+2472	+ 33	0	+ 250	- 42	+ 108	+2821	+2832
	$3A'$	- 116	0	- 250	0	+ 241	+ 28	- 97	- 127
	$4A'$	0	0	+ 42	- 241	0	-1294	-1493	-1374
	$5A'$	- 29	0	- 108	- 28	+1294	0	+1129	+1488

takes place in such a fashion as to decrease the magnitude of the Faraday parameter associated with the lowest $\pi \rightarrow \pi^*$ transitions in **2** and **3**. Further the $n \rightarrow \pi^*$ state exhibits the magnetic coupling preferably with the lowest $\pi \rightarrow \pi^*$ state in **2** and **3**. This is because the lowest $\pi \rightarrow \pi^*$ state has nonzero transition density at the nitrogen atom resulting in $\mathrm{Im} \langle \text{lowest } \pi \rightarrow \pi^* | \vec{\mu} | \text{lowest } n \rightarrow \pi^* \rangle \neq 0$. Although the π-electron approximation has interpreted well the Faraday B term of many organic molecules and their ions, the present results show the significant contribution of the lowest $\pi \rightarrow \pi^*$ transition to the B term in **2** and **3** is derived from the magnetic mixing of the lowest $n \rightarrow \pi^*$ state with the lowest $\pi \rightarrow \pi^*$ state, as found in the lowest transition of indole[17] and that of aza analogues of naphthalene[7]. The PPP method is considered to be valid for the $\pi \rightarrow \pi^*$ transitions which take place at apart from the $\sigma \rightarrow \pi^*$ type transitions. On the other hand, inclusion of the $\sigma \rightarrow \pi^*$ state is necessary when the relatively stronger $\sigma \rightarrow \pi^*$ type transitions lie near by the $\pi \rightarrow \pi^*$ transition of interest.

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