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# MAGNETIC CIRCULAR DICHROISM OF SUBSTITUTED BENZENES

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The magnetic circular dichroism (MCD) spectra of a series of substituted benzenes were measured. The B values of the $^1L_b$ band of these compounds are discussed in terms of the dipole strengths and wave numbers of the $^1L_b$ and $^1L_a$ bands, and it is concluded that these B values depend mainly on the contribution of the mixing of the above two states.

Recently, Eyring et al.[1] analyzed the B values[2] of the $^1L_b$ band of homo-substituted benzenes in terms of the Petruska's theory.[3] However, since the Petruska's work was concentrated on the effects of the substituents which cause relatively small changes in the absorption spectrum of benzene, it is clear that the treatment of Eyring et al. is inadequate to explain the B values of substituted benzenes with stronger donor and acceptor groups. In this work, we have discussed the MCD spectra of such kinds of substituted benzenes and clarify the factor which affects the B values of the $^1L_b$ band.

The measurements of the MCD spectra were carried out with a JASCO model J-20 automatic recording spectropolarimeter with an electromagnet. The magnetic field was set at 14100 Gauss. The absorption spectra were taken on a Shimadzu automatic recording spectrophotometer model MPS-50L.

Since substituted benzenes investigated in this work are all of relatively low symmetry, none has any degenerate electronic states. It is apparent, therefore, that these compounds exhibit only the B term in the MCD spectra. In this case, the molar ellipticity $[\theta]_M$ (in deg·gauss$^{-1}$·cm$^2$·mole$^{-1}$) per unit magnetic field for an isolated transition a→j is given by[4]

$$[\theta(a\rightarrow j)]_M = -21.3458 \cdot B(a\rightarrow j) \cdot f(\nu,\nu_{ja}) \qquad (1)$$

where $f(\nu,\nu_{ja})$ is a frequency function which determines the band shape($\int f(\nu,\nu_{ja})d\nu=1$). $B(a\rightarrow j)$ (in Debye$^2$·Bohr magneton·cm) is a Faraday B term, and for randomly oriented molecules with non-degenerate electronic states it is given by

$$B(a\rightarrow j) = \mathrm{Im}\{\sum_{k\neq a} \langle k|\mu_m|a\rangle\cdot\langle a|\mu_e|j\rangle\times\langle j|\mu_e|k\rangle/(W_k - W_a) + \sum_{k\neq j} \langle j|\mu_m|k\rangle\cdot\langle a|\mu_e|j\rangle\times\langle k|\mu_e|a\rangle/(W_k - W_j)\} \qquad (2)$$

where $\mu_e$ and $\mu_m$ are the electric and magnetic dipole moment operators, respectively. $W_k$ is the energy of the state k. We assumed here that the transition is electronically allowed and is composed of vibronic components which are simply a

Franck-Condon progression, and that eq.(1) and eq.(2) can be used for the contributions of the whole band.

The B values of mono- and para-di-substituted benzenes have been investigated through the following procedure. For discussing the B values of the lowest excited $\pi\rightarrow\pi^*$ state, we rewrite eq.(2) as

$$\begin{aligned} B(E_0\rightarrow E_1) = {} & \mathrm{Im}\{\langle E_1|\mu_m|E_2\rangle\cdot\langle E_0|\mu_e|E_1\rangle\times\langle E_2|\mu_e|E_0\rangle/(W_2-W_1)\} \\ & + \mathrm{Im}\{\sum_{k\neq 0}\langle E_k|\mu_m|E_0\rangle\cdot\langle E_0|\mu_e|E_1\rangle\times\langle E_1|\mu_e|E_k\rangle/(W_k-W_0) \\ & + \sum_{k\neq 1,2}\langle E_1|\mu_m|E_k\rangle\cdot\langle E_0|\mu_e|E_1\rangle\times\langle E_k|\mu_e|E_0\rangle/(W_k-W_1)\} \end{aligned} \quad (3)$$

where $E_0$ and $E_k$ represent the ground and k-th excited states, respectively. $E_1$ and $E_2$ denote the $^1L_b$ and $^1L_a$ states for the present case. We assumed here that the transition moments of the $^1A\rightarrow{}^1L_b$ and $^1A\rightarrow{}^1L_a$ transitions of mono- and para-di-substituted benzenes are directed perpendicular and parallel to the molecular axis, respectively. On this assumption, the magnitude of the vector product of the $^1L_b$ and $^1L_a$ transition moments was approximated in terms of the square root of the product of the observed $^1L_b$ and $^1L_a$ dipole strengths, and the energy differences was evaluated in terms of the observed wave numbers. Thus, we defined the 'M' values to be

$$|\langle E_0|\mu_e|E_1\rangle\times\langle E_2|\mu_e|E_0\rangle/(W_2-W_1)| \simeq \sqrt{D_1\cdot D_2}/\Delta\nu \equiv M \quad (4)$$

where $D_1$, $D_2$ and $\Delta\nu$ represent the dipole strengths of the excited $E_1$,$E_2$ states, and the difference of their wave numbers, respectively. The dipole strength is expressed as $D(a\rightarrow j)=|\langle a|\mu_e|j\rangle|^2$. To obtain the dipole strengths from the observed spectra, the overlapping absorption bands were resolved into each component by the use of a Du Pont 310 Curve Resolver, assuming a Gaussian band shape. The examples of such operation are shown in Fig.1 and Fig.2. The dipole strengths were determined by the approximate relation,[5] $D(a\rightarrow j)=(9.1834\cdot 10^{-3}/\nu_0)\cdot\int\varepsilon d\nu$. As for the B values, they were determined by the method of moments. The zeroth moment of the MCD satisfies the relation,[5] $B(a\rightarrow j)=-(1/33.53)\cdot\int([\theta(a\rightarrow j)]_M/\nu)d\nu$. Usually, the dielectric field effect is corrected by taking a ratio of $B(a\rightarrow j)$ to $D(a\rightarrow j)$. However, this was not done in this work, since such operations produced little influences on our conclusions.

The absolute B values of mono- and para-di-substituted benzenes were plotted against the 'M' values defined by eq.(4), and good linear correlations were obtained. The results are shown in Fig.3. It seems to be able to classify roughly the plots in Fig.3 into two groups. The compounds of the first group correspond to substituted benzenes with donor groups(plots of (1)-(12)), and the compounds of the second group, to those with acceptor groups(plots of (13)-(22)). This fact implies that the values of the term, $|\mathrm{Im}\langle E_1|\mu_m|E_2\rangle|$, which can be considered to be approximately represented by the gradients of the linear correlation curves in Fig.3, are different between the above two groups. The origin of such difference, however, is not clear at present, and further investigations should be required. In the case of the second group, the plots of nitrobenzene and its derivatives seem to somewhat deviate from a correlation. This may be ascribed to the strong overlapping MCD bands of opposite signs. From the fact mentioned above, it is concluded that the B value of the lowest excited $\pi\rightarrow\pi^*$ state depends mainly on the mixing of the $^1L_b$ and $^1L_a$ states.

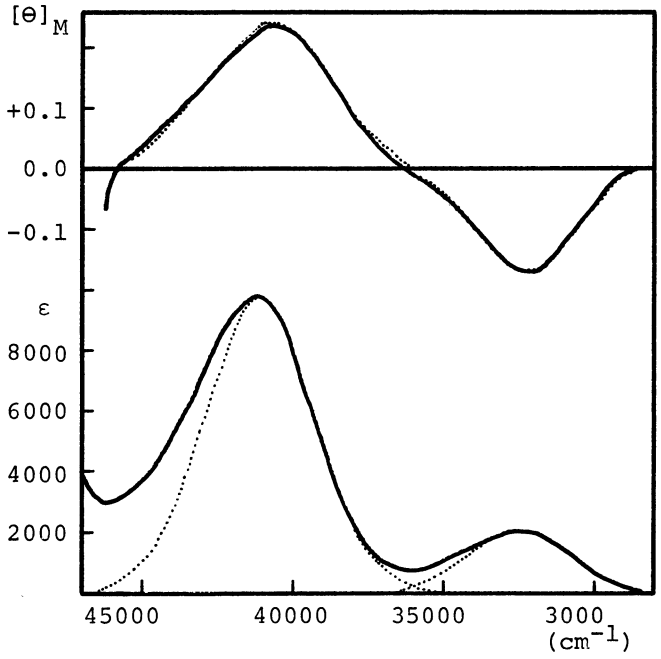



Fig.1. MCD and absorption spectra of para-phenylenediamine. (The solvent used was ethanol)

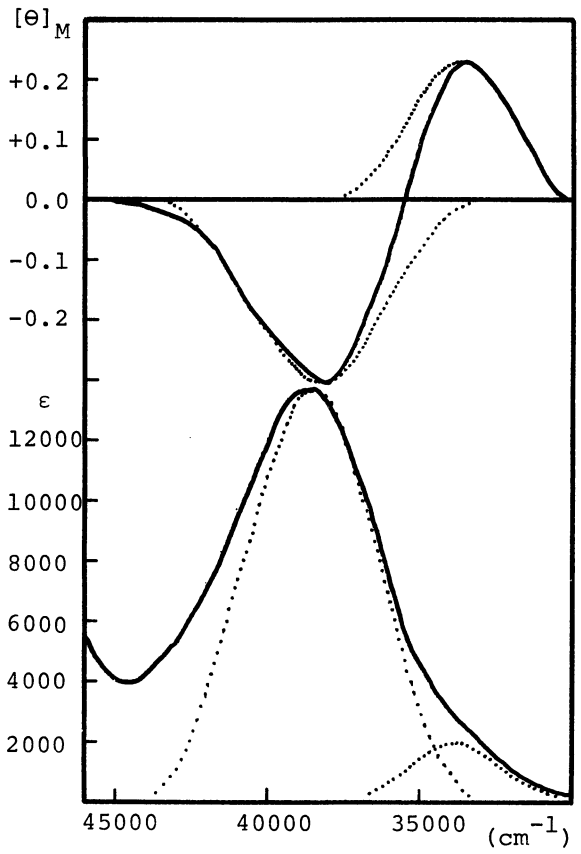
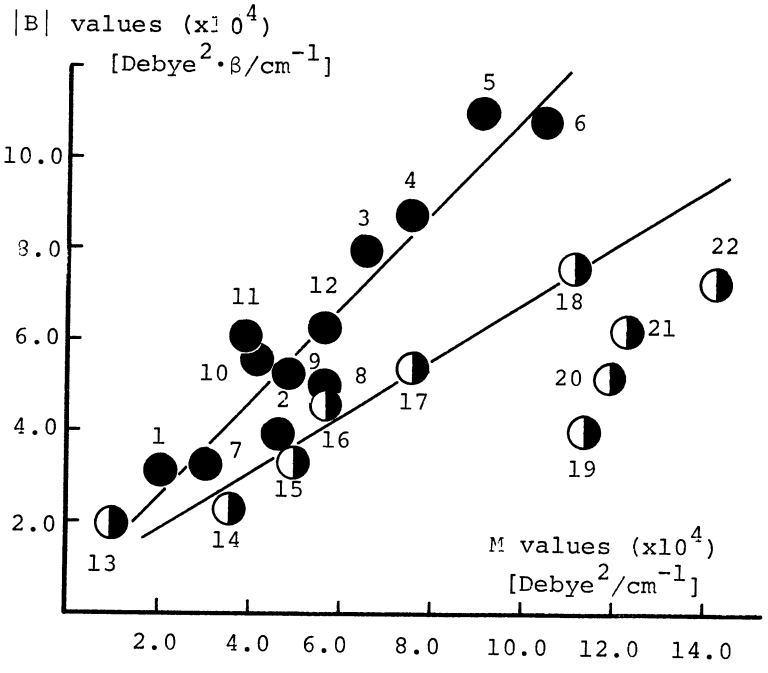



Fig.2. MCD and absorption spectra of para-nitrobenzoicacid. (The solvent used was ethanol)

Fig.3. Plots of the absolute B values against the M values. (The solvent used was ethanol)

(1) -$OCH_3$
(2) -$NH_2$
(3) -$N(CH_3)H$
(4) -$N(C_2H_5)H$
(5) -$N(CH_3)_2$
(6) -$N(C_2H_5)_2$
(7) -p-$OH,CH_3$
(8) -p-$(OH)_2$
(9) -p-$CH_3,NH_2$
(10) -p-$OH,OCH_3$
(11) -p-$(OCH_3)_2$
(12) -p-$(NH_2)_2$
(13) -$CONH_2$
(14) -COOH
(15) -$COCH_3$
(16) -CHO
(17) -p-$(COOH)_2$
(18) -p-$(CHO)_2$
(19) -$NO_2$
(20) -p-$(NO_2)_2$
(21) -p-$NO_2$,COOH
(22) -p-$NO_2$,$COCH_3$



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