The Magneto-Optical Rotatory Dispersion of Benzophenone in the $S_0 \rightarrow T$ (n-π^*) and the $S_0 \rightarrow S_1$ (n-π^*) Absorption Regions

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The magneto-optical rotatory dispersion (MORD) of benzophenone has been measured in the spectral regions corresponding to its $S_0 \rightarrow S_1$ (n-π^*) and $S_0 \rightarrow T$ (n-π^*) absorption systems. The abnormal MORD in the $S_0 \rightarrow T$ absorption region has not always been observed, contrary to the results by Shashoua, only the normal MORD has always been observed. The MORD in the $S_0 \rightarrow S_1$ (n-π^*) absorption region changes its sign at about 340 mμ and is classified as a positive ($B+C/kT$) type, according to Stephens *et al.* It has been concluded that the MORD of the $S_0 \rightarrow S_1$ transition of benzophenone occurs as a result of the n,π^* state, S_1, being mixed with the B_{2u}-analogue state, S_3, and that then the S_1 state interacts magnetically with the S_3 under an external magnetic field.

Shashoua observed the MORD of benzophenone in 1960[1] and acetophenone in 1964[2] in the spectral regions corresponding to the absorption systems of these compounds. The electronic structure of benzophenone has been investigated in detail by analyses of its absorption and emission spectra.[3,4] It is well known that the lowest excited singlet state, S_1, and the lowest triplet state, T, are both of the n-π^* type.[5,6]

Some aspects of the magnetic field on the $S_0 \rightarrow T$ transition have been studied.[7,8] More recently, Eberhardt *et al.* studied the magnetic rotation spectra of the $S_0 \rightarrow T$ absorption of several small organic compounds.[9] Therefore, it seems that the MORD in the $S_0 \rightarrow T$ absorption region should be observed, and the experiments by Shashoua seem to support this idea. However, the f value of the $S_0 \rightarrow T$ absorption of benzophenone has been reported to be 0.6×10^{-7}, [10] and this region is overlapped by the tail of the strong $S_0 \rightarrow S_1$ absorption. Therefore, there remain some questions as to the reality of the observation of the MORD in the $S_0 \rightarrow T$ region of aromatic carbonyl compounds by Shashoua. Accordingly, we undertook an MORD experiment with benzophenone in the region of its $S_0 \rightarrow T$ absorption spectrum and also studied the rotatory dispersion in the spectral region of its $S_0 \rightarrow S_1$ absorption.

Experimental

A Shimadzu spectrophotometer, model QR-50, with an accessory for the observation of natural optical rotation was modified in order to observe the magnetic optical rotation. The light source was a 500-W Xe-lamp. The magnetic field was produced with an electric magnet, its field strength being 5080 gausses at 5.0 A d.c. The strength of the field was determined form Verdet's constant (min.gauss^{-1}.cm^{-1}) of water.[11]

When $\varepsilon(\nu)$ stands for the rotation of a light frequency, ν, of two quartz plates (0.20 cm in total width) and $V(\nu)$, for that of the quartz plates plus a sample with a total optical path of 1.20 cm, the rotation of a sample, $\theta(\nu)$, can be expressed as follows:

$$\theta(\nu) = V(\nu) - \varepsilon(\nu) + \delta(\nu) \quad (1)$$

where δ is the dispersion of air exchanged for the sample (it will be neglected in this experiment). The average experimental error was $\pm 0.005°$ degrees.

For the measurement of the MORD in the $S_0 \rightarrow T$ absorption region, two solutions, consisting of 3.08% and 3.14% of benzophenone in ethanol, and a solution of 1.88% in cyclohexane were used, while for the measurement of the MORD in the $S_0 \rightarrow S_1$ absorption region, a solution of 0.1916% benzophenone in ethanol was used at 10°C, its density being 0.799 g/cc.

Results and Discussion

The magnetic rotation angle (degree) of benzophenone has been measured in the spectral region between 340 and 480 mμ, which corresponds to its $S_0 \rightarrow S_1$ and $S_0 \rightarrow T$ absorption regions. The rotation angles of the samples in the latter region, which were calculated with Eq. (1) for each wavelength, are plotted against the wavelength in Fig. 1, in which, for the sake of comparison, Shashoua's data are also plotted.

It is necessary to use the specific magnetic rotation or the molar magnetic rotation in order to discuss the dispersion phenomenon in detail. The specific magnetic rotation, $[\theta]$, of a solution and the molar magnetic rotation, $[\alpha]_M$ of a solute are defined as follows:[12-14]

$$[\theta] = H\theta/\rho \quad (2)$$

$$[\alpha]_M = (10M/100k)([\theta] - k_s[\beta]) \quad (3)$$

where $[\alpha]_M$ is defined in the same way as the natural

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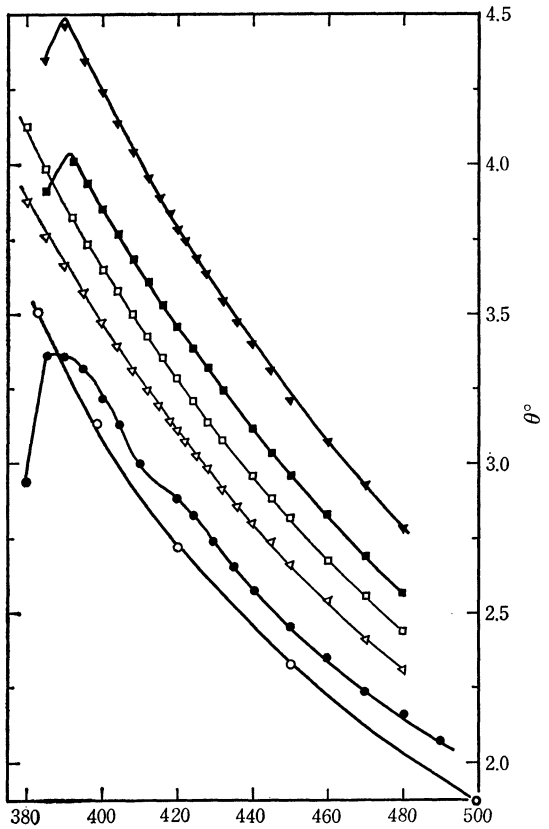

Fig. 1. The dispersion curves ($\theta°$) of benzophenone in alcohol; —○—, —●— alcohol and 2.5% benzophenone in a 5 cm cell at 30°C in 1.2×10^3 gauss by Shashoua; —□—, —■— alcohol and 3.14% benzophenone in a 5 cm cell at 11°C in 1.68×10^3 gauss; —△—, —▲— alcohol and 13.08% benzophenone 1 cm cell at 10°C in 8.06×10^3 gauss.

optical activity;[15] H is the strength of a magnetic field; ρ, the density of a solution; M, the molecular weight of the solute; k and k_s, the grams of the solute and the solvent respectively, and β, the specific rotation of the solvent. The MORD values in the region corresponding to the $S_0\rightarrow T$ and the $S_0\rightarrow S_1$ absorptions of benzophenone are shown in Fig. 2.

A. $S_0\rightarrow T$ Absorption Band. The 0–0 band of the phosphorescence spectrum of benzophenone was observed at 24,185 cm^{-1},[4] while the absorption maximum of its $S_0\rightarrow T$ transition was located at 24,300 cm^{-1}.[10] Shashoua observed an abnormal dispersion at 420 mμ[1] which he interpreted as due to the $S_0\rightarrow T$ absorption, since there is no other absorption in the region. As the interaction between a molecule in the triplet state and a magnetic field is proportional to the strength of the field, H, the MORD of benzophenone has been observed in the spectral region corresponding to the $S_0\rightarrow T$ absorption under a magnetic fields almost the same in strength and seven times as strong as that used by Shashoua. We observed no abnormal dispersion near 420 mμ in an alcoholic solution, even under 8000 gausses, nor did we do so in cyclohexane. That the rotation angles in a solution decrease in the three curves near 390 mμ to shorter wavelengths may be ascribed to experimental error, since the absorption coefficient of benzophenone increases abruptly in that region because of the presence of the $S_0\rightarrow S_1$ absorption and since the light that comes through the sample is naturally decreased in intensity. This makes the slit-width of the excitation monochromator wider and, accordingly, the measurement becomes less accurate. Therefore, it may be concluded no abnormal dispersion is observable in the $S_0\rightarrow T$ absorption region within the limits of our experiment. As is shown in Fig. 2, the molecular rotatory dispersion in the region from 390 to 430 mμ is too flat to be explained by either formula, $[\alpha]_M=A\nu^2/(\nu_0^2-\nu^2)^2$ or $[\alpha]_M=B\nu^2/(\nu_0^2-\nu^2)$.[8] Since the slope of the dispersion curve is small and the dispersion is constant at each wavelength in this region, the dispersion should be interpreted as a result of dispersions due to absorptions in the shorter wavelengths. Therefore, even if the rotation of the $S_0\rightarrow T$ transition were observable, it would be included within the limits of experimental error.

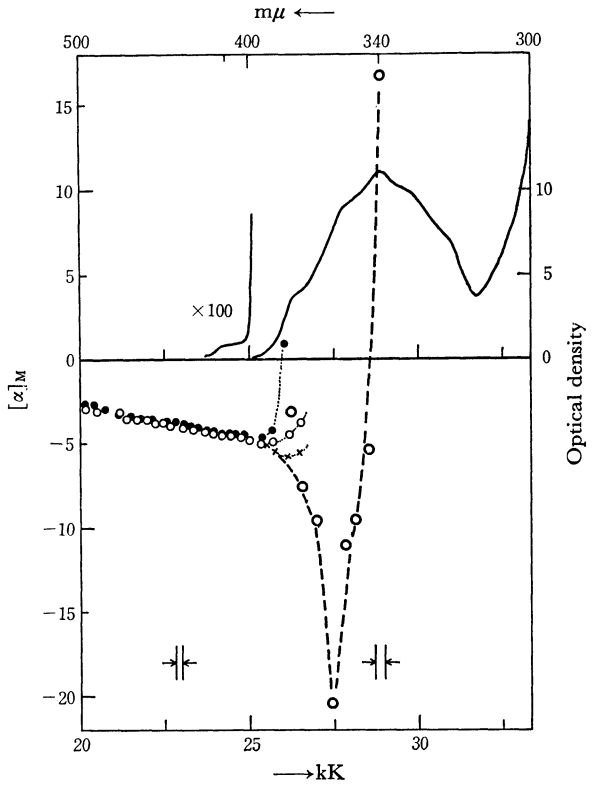

Fig. 2. The MORD and the absorption spectrum of benzophenone ○○○....., ●●●....., -⊙-⊙- in alcohol; ...×... ...×... in cyclohexane.

Theoretically speaking, the dispersion due to the $S_0\rightarrow T$ absorption could be classified as to the A-type.[16] It is, however, impossible to discuss quantitatively the order of the magnitude of the MORD of the $S_0\rightarrow T$ transition according to the results of this experiment. It should be noted that no abnormal MORD, but only a normal MORD, is observed in this region.

B. n–π^* ($S_0\rightarrow S_1$) Absorption Band. The absorption spectrum of benzophenone between 390 and 310 mμ is shown in Fig. 2. The MORD of the n–π^* absorption

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region corresponding to the wavelength of the absorption maximum changes in sign at about 340 mμ, it may be interpreted as an I type, according to Shashoua,[2] or as a positive $(B+C/kT)$ type, according to Stephens *et al.*[17] As benzophenone is diamagnetic in the ground state, C is equal to zero.

Then, assuming a damped-oscillator model, according to Stephens *et al.*,[17,18] one obtains the following values:

$$[\alpha]_{M\,max} = 10 - 20\ \text{deg}\cdot l/\text{m.mol},\ \Gamma_{01} = 1.1 - 0.9\ \text{kK},$$

$\omega_{01}=28.7$ kK,

therefore, $B(S_0\rightarrow S_1)=1.8-1.5\times10^{-2}d^2\beta/\text{cm}^{-1}$ where Γ means a damping constant; ω_{01}, an energy difference in cm^{-1} between the S_0 and S_1 states, d, a dipole moment in Debye units, and β, a Bohr magneton.

According to theory of the Faraday effect, the B term has been given as follows:

$$B(S_0\rightarrow S_1) = \sum_{k\neq1} \boldsymbol{M}_{1k}\cdot(\boldsymbol{R}_{01}\times\boldsymbol{R}_{k0})/(\omega_k-\omega_1) + \sum_{k\neq0} \boldsymbol{M}_{k0}\cdot(\boldsymbol{R}_{01}\times\boldsymbol{R}_{1k})/\omega_k, \quad (4)$$

where the subscripts 0, 1, and k mean the ground, the n, π^* excited, and the kth excited states respectively, and where M and R stand for a magnetic and an electric dipole moment vector respectively.

It has recently been reported by Hoffman *et al.*[19] that the both phenyl rings of benzophenone are twisted out of the >C=O plane by 38° from the CNDO-MO calculations. Therefore, it is reasonable to discuss those states with C_2 symmetry. Therefore, the $S_0\rightarrow S_1$ transition is allowed in itself. Vala and Tanaka[20] pointed out, on the basis of their study of the polarized absorption spectra of the 4,4'-dichlorobenzophenone crystal, that there are four states in the 300—230 mμ region, that is, two CT states and two B_{2u}-analogue states, and that the transition moments from the ground state to the one of the former and to the one of the latter are parallel to the z or C=O axis. The order of these four states and the polarization data of these transitions would seem to be inconsistent with the polarization spectra reported by Shimada and Goodman.[5] However, if it is taken into account that these two sets of results are not essentially inconsistent with each other because of the difference in the experimental conditions, it may be concluded that the S_3 state corresponds to one of the B_{2u}-analogues and that the $S_0\rightarrow S_3$ involves two components parallel to the x and the z axes. (By the way, S_2 corresponds to one of the CT states.) Therefore, one obtains:

$$B(S_0\rightarrow S_1) = \sum^{B}\{M^y_{1k}R^z_{01}R^x_{k0}-M^x_{1k}R^z_{01}R^y_{k0}\}/(\omega_k-\omega_1) + \sum^{B}\{M^y_{k0}R^z_{01}R^x_{1k}-M^x_{k0}R^z_{01}R^y_{1k}\}/\omega_k. \quad (5)$$

The R^y_{k0} and R^y_{1k} matrix elements[21] are much smaller than R^x and R^z. As for the R^y_{1k} matrix element, although the S_k–S_1 transitions are not always negligible, the k states must be transformed like the x-coordinate. Therefore, the M^y_{k0} magnetic monents are nearly equal to zero. The main terms of $B(S_0\rightarrow S_1)$ are, then, as follow:

$$B(S_0\rightarrow S_1) = M^y_{13}R^z_{01}R^x_{30}/(\omega_3-\omega_1) + (\text{the similar terms for } k>3). \quad (6)$$

When $\omega_1=26.58$ kK, $\omega_3=39.00$ kK, $f_{10}=0.0029$, and $f_{30}=0.42$, assuming that $|R^z_{01}R^x_{30}|=(|R^z_{01}|^2\cdot|R^x_{30}|^2)^{1/2}=(f_{10}\cdot f_{30}/\omega_1\omega_3)^{1/2}$ and $|M^y_{13}|=10^{-1}-10^{-2}$, the order of the magnitude of the triple scalar products is $10^{-3}-10^{-4}$. It may be said that this order of magnitude is considerably close to our experimental value of $B(S_0\rightarrow S_1)$.

Finally, it can be concluded from the above discussions of the C_2 approximation that the MORD of the $S_0\rightarrow S_1$ transition (n–π^* absorption) of benzophenone occurs as a result of the perturbing state, S_3, being mixed into the S_1 state; then, the magnetic dipole transition is allowed through the magnetic dipole interactions between the S_3 and the S_1 states by the perturbation of the external magnetic field.

Although benzophenone is not a good example for discussing the properties of aromatic molecles by means of the MORD observation, it should be noted that some interesting characteristics of the MORD of benzophenone have been discussed. However, it is impossible to go further until more detailed data are accumulated.

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