The Normal Magneto-Optical Rotatory Dispersion and the Magnetic Moment of Benzene

Yoshiya Takenoshita
Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka

(Received February 21, 1972)

The magneto-optical rotatory dispersion in the absorptionless region has been investigated with liquid benzene, and the related magnetic moment has been discussed theoretically. It has been concluded that the main contribution to the magneto-optical rotatory dispersion consists of an A term through the ${}^1A_{1g}\rightarrow{}^1E_{1u}$ transition and that the contribution from σ-electrons is never negligible. The magnetic moment in the excited state, ${}^1E_{1u}$, of benzene has been obtained as $-1.72\,\beta$ (Bohr magneton), which is about 2 or 4 times greater than the value of $-1.0\,\beta$ calculated with the FEN-model or the value of $-0.396\,\beta$ calculated by the LCAO-MO method.

The anomalous magneto-optical rotatory dispersion (MORD) and the magnetic circular dichroism (MCD) of porphyrine and other organic compounds have been studied by Shashoua and others.[1–3] The MCD's of benzene, triphenylene and coronene have been studied by Stephens *et al.*,[4] and the magnetic moment has been discussed in detail with triphenylene and coronene. No discussion has been made with benzene, however, since they did not succeed in observing the MCD of benzene in the region below 2300 Å because of the limitations of these experiments.

However, it could be possible to discuss the magnetic properties of benzene in the excited states if the normal magneto-optical rotatory dispersion (or the normal Faraday effect in an absorptionless region) would be simple enough to analyze. In 1955, Garner *et al.*[5] observed the normal MORD of liquid benzene. However, they had no intention of studying the magnetic properties of benzene itself, but those of several solute compounds dissolved in benzene. Already, in the period between 1896 and 1906, Perkin had made an extensive study of the Faraday effects of various organic compounds for the Na-D line.[6] Although his excellent experimental data have never been examined from the viewpoint of modern molecular physics, π-electrons may be expected to make an important contribution to the magnetic properties of benzene. No direct information has been obtained so far concerning the magnetic properties of benzene in the excited states.

We will try here to analyze the normal MORD of benzene and estimate its magnetic moment. The estimated value will be compared with the theoretical one, which will also be developed in this paper.

Theoretical Results of MORD

The contribution of the $a\rightarrow j$ transition to the normal MORD of isotropic molecules in a longitudinal magnetic field, H, along the $+z$ axis may be expressed as follows:[2,7,8)]

$$[\phi(a\rightarrow j)]_M = -\frac{24\boldsymbol{N}H}{\hbar c}\left[\frac{2\nu_{ja}\nu^2}{\boldsymbol{h}(\nu_{ja}^2-\nu^2)^2}A(a\rightarrow j) + \frac{\nu^2}{\nu_{ja}^2-\nu^2}\{B(a\rightarrow j)+C(a\rightarrow j)/\boldsymbol{k}T\}\right], \qquad (1)$$

where $[\phi]_{\mathrm{M}}$ is a molar magnetic rotation defined for natural optical activity,[9] where $\boldsymbol{N}$ is the Avogadro number, and where $h\nu_{ja}=W_j-W_a$ is the energy difference between the a and j states.

Assuming a random orientation of rotating anisotropic molecules, one obtains the Faraday parameters, A, B, and C, as follows:

$$A(a\rightarrow j) = (2d_a)^{-1}\sum[(j|\boldsymbol{\mu}|j)-(a|\boldsymbol{\mu}|a)] \times \mathrm{Im}\{(a|\boldsymbol{m}|j)\times(j|\boldsymbol{m}|a)\}, \qquad (2a)$$

$$B(a\rightarrow j) = (2d_a)^{-1}\sum\mathrm{Im}\{\sum_{k\neq a}(k|\boldsymbol{\mu}|a)\cdot(a|\boldsymbol{m}|j) \times (j|\boldsymbol{m}|k)/(W_k-W_a) + \sum_{k\neq j}(j|\boldsymbol{\mu}|k)\cdot(a|\boldsymbol{m}|j) \times (k|\boldsymbol{m}|a)/(W_j-W_k)\}, \qquad (2b)$$

$$C(a\rightarrow j) = (2d_a)^{-1}\sum(a|\boldsymbol{\mu}|a)\cdot\mathrm{Im}\{(a|\boldsymbol{m}|j)\times(j|\boldsymbol{m}|a)\}, \qquad (2c)$$

where d_a is the degeneracy of the ground state, a, (the summations are taken over all the transitions degenerate with $a\rightarrow j$), where $\boldsymbol{m}$ and $\boldsymbol{\mu}$ $(=(\beta/\hbar)\sum(\boldsymbol{l}_i+\boldsymbol{s}_i))$ are the electric and magnetic dipole operators respectively, and where β stands for a Bohr magneton. The A, B, and C terms of Eq. (1) arise, respectively, from the Zeeman splitting of $a\rightarrow j$, the mixing of a and j with other states, k, by means of the magnetic field, and the change in the populations of the component levels of the ground state, a, due to its Zeeman splitting. Hence, A is different from zero only when a or j is degenerate, and C is different from zero only when a is degenerate.

If an imaginary term, $\mathrm{Im}\{(a|\boldsymbol{m}|j)\times(j|\boldsymbol{m}|a)\}$, in Eqs. (2a) and (2c) can be defined with a real dipole strength, D, one obtained the following:

$$D(a\rightarrow j) = (d_a)^{-1}|(a|\boldsymbol{m}|j)|^2 = 2.126\times10^6(d_a)^{-1}f_{ja}/\omega_{ja} \text{ (square of the Debye unit)}, \qquad (3)$$

---

[1] V. E. Shashoua, *J. Amer. Chem. Soc.*, **86**, 2109 (1964); *ibid.*, **87**, 4044 (1965); *Arch. Biochem. Biophys.*, **111**, 550 (1965).

[2] P. J. Stephens, W. Suëtaak, and P. N. Schatz, *J. Chem. Phys.*, **44**, 4592 (1966).

[3] B. Briat, D. A. Schooley, R. Records, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 6170 (1967).

[4] P. J. Stephens, P. N. Schatz, A. B. Retchie, and A. J. McCaffery, *J. Chem. Phys.*, **48**, 132 (1968).

[5] F. H. Garner, O. B. E., C. W. Nutt, and A. Labbauf, *J. Inst. Petrol.*, **41**, 329 (1955).

[6] W. H. Perkin, *J. Chem. Soc.*, **69**, 1025 (1896); *ibid.*, **81**, 292 (1902); *ibid.*, **89**, 849 (1906).

[7] R. Serber, *Phys. Rev.*, **41**, 489 (1932).

[8] A. D. Buckingham and P. J. Stephens, *Ann. Rev. Phys. Chem.*, **17**, 399 (1966).

[9] Formerly, molar Verdet's constant $V_{\mathrm{M}}(=-600[\phi]_{\mathrm{M}}/H)$ was used as a technical term, but recently Stephens and coworkers have been using this term.

where f_{ja} is an oscillator strength[10] and where ω_{ja} is the energy difference between j and a in cm^{-1}. Accordingly, the magnetic moment of a diamagnetic organic molecules can be estimated as follows:

$$-\mu = 2A/D, \tag{4}$$

since $(a|\boldsymbol{\mu}|a)=0$, and since, then, $C=0$.

However, the normal MORD for an arbitary wave number in the absorptionless region is naturally expressed as the summation of $[\phi(a\to j)]_{\mathrm{M}}$ over j. In a system with only one allowed electronic transition as benzene, the MORD in the absorptionless region is given as follows:

$$[\phi(\omega)]_{\mathrm{M}} = -\frac{24\boldsymbol{N}H}{c\hbar}\frac{2\omega^2}{c\boldsymbol{h}(\omega_{ja}^2-\omega^2)^2}A(a\to j) + \sum_{k\neq j}[\phi(a\to j)]_{\mathrm{M}}, \tag{5}$$

where k consists of the excited states with π and/or σ excited electrons. As the first and second terms in Eq. (1) are proportional to ω^2, the last part in Eq. (5) can be regarded for $\omega_{ka}\gg\omega$ $(k>j)$ as:

$$\sum_{k>j}[\phi(a\to k)]_{\mathrm{M}} = E\omega^2, \tag{6}$$

where E is constant and is expressed as $\sum_{k>j}2A(a\to j)/h\omega_{ka}{}^3$ and $\sum_{k>j}(B(a\to k)+C(a\to k)/\boldsymbol{k}T)/\omega_{ka}{}^2$. Then, one can estimate the values of the A term and the μ on the basis of an analysis of the normal MORD.

Magnetic Moment and Orbital Angular Momentum

The magnetic moment and electronic orbital angular momentum make discussed in 1966 by Stephens *et al.*[2] and in 1968 by Bishop and Dingle.[11] Now, the magnetic moment of benzene will be discussed. For convenience, we will take all the molecular orbital functions of benzene as real. The benzene is a regular hexagon molecule with a diamagnetic ground state, ${}^1A_{1g}$. The angular momentum vector operator can have only one non-zero component $({}^1E_{1u}x|L_z|{}^1E_{1u}y)$ in excited states which involve two allowed electric dipole transitions, $({}^1A_{1g}|m_x|{}^1E_{1u}x)$ and $({}^1A_{1g}|m_y|{}^1E_{1u}y)$.[12] Therefore, the magnetic moment of the excited state, ${}^1E_{1u}$, may be defined by:

$$\mu = -(i\beta/\hbar)({}^1E_{1u}x|L_z|{}^1E_{1u}y), \tag{7}$$

where z is the principal molecular axis; x and y, the mean basis functions transforming like the two coordinates, x and y respectively, and $\boldsymbol{L}(=\sum\boldsymbol{l}_i)$ is a total orbital angular momentum operator.

In the singly-excited configuration approximation of the MO theory, the ${}^1E_{1u}$ state $(e_{1g}{}^3, e_{2u})$ of benxene[13] is:

$$\begin{aligned}|{}^1E_{1u}x) &= \frac{1}{2}[\{y\bar{y}x\bar{\xi}\}+\{y\bar{y}\xi\bar{x}\}+\{y\bar{\eta}x\bar{x}\}+\{\eta\bar{y}x\bar{x}\}],\\ |{}^1E_{1u}y) &= \frac{1}{2}[\{y\bar{y}x\bar{\eta}\}+\{y\bar{y}\eta\bar{x}\}+\{y\bar{\xi}x\bar{x}\}+\{\xi\bar{y}x\bar{x}\}],\end{aligned} \tag{8}$$

where x and y denote e_{1g}, ξ and η e_{2u} MO's, and where the braces symbolize anti-symmetrization. By substituting Eq. (8) into Eq. (7), one obtains:

$$\mu = -(i\beta/\hbar)[(\xi|l_z|\eta) - (x|l_z|y)]. \tag{9}$$

The calculation of the magnetic moments resolves itself into the problem of the estimation of the angular momentum of each electronic molecular orbital. An electronic angular momentum is generally equal to zero for non-linear molecules, but equal to a non-zero value, $\zeta_e\hbar$,[14] corresponding to a rotation around the molecular axis, for planar cyclic molecules, which are deemed intermediate between highly symmetric molecules and less symmetrical or asymmetrical ones. In the FEN model,[15] the wave functions of the degenerate states, $\phi_n{}^+$ and $\phi_n{}^-$ with quantum numbers, $\pm|n|$, are $a_{\mathrm{B}n}\cos(k_n, x)$ and $a_{\mathrm{B}n}\sin(k_n, y)$ respectively, where $a_{\mathrm{B}n}=\sqrt{2/L}$ for $n\geq 1$ or $1/\sqrt{2}$ for $n=0$, and where $k_n=2n\pi/L$. The x, y, ξ, and η in Eqs. (6) and (7) correspond to $n=1$, -1, 2, and -2 respectively. The matrix elements of l_z are equal to $(\phi_n{}^+|l_z|\phi_n{}^-)=-in\hbar$. In the LCAO-MO treatment, on the other hand, a new problem occurs when one operates l_z on each atomic orbital. If the atomic orbitals, χ_a, are expressed with $2p$-Slater AO's and if the molecular orbitals are taken as $\phi_k=\sum C_{ka}\chi_a$, the matrix elements of l_z are given as:

$$(\phi_2|l_z|\phi_1) = \sum_{a,\,b}C_{1a}C_{2b}(\chi_b|l_z|\chi_a). \tag{10}$$

If the origin of l_z is then transferred from the center of the molecular skeleton to the middle point, P, of a bond between the A and B nuclei, as is shown in Fig. 1, one obtains:

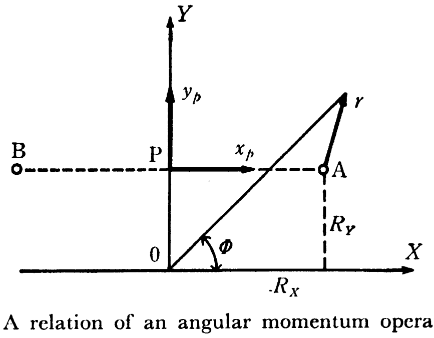

Fig. 1. A relation of an angular momentum operator with the coordinates.

$$l_z = l_z^p + i\hbar R_{\mathrm{Y}}(\partial/\partial x_p). \tag{11}$$

Since $(\chi_b|l_z{}^p|\chi_a)=0$, one obtains:

$$(\chi_b|l_z|x_a) = i\hbar R_{\mathrm{Y}}(\chi_b|\partial/\partial x_p|\chi_a). \tag{12}$$

The $R_Y\partial/\partial x_p$ operator corresponds to an infinitesimal rotation, $R_Y\delta\Phi$, and an effective component of l_z in

---

[10] C. Sandorfy, "Electronic Spectra and Quantum Chemistry," Prentice-Hall Inc., New Jersey (1964), p. 100.

[11] D. M. Bishop and T. W. Dingle, *J. Chem. Phys.*, **48**, 541 (1968).

[12] P. S. Pershan, M. Gouterman, and R. L. Fulton, *Mol. Phys.*, **10**, 397 (1966).

[13] W. E. Moffitt, *J. Chem. Phys.*, **22**, 320 (1954); R. Pariser and R. G. Parr, *ibid.*, **21**, 767 (1953).

[14] G. Herzberg, "Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand Co., New York, (1966), p. 12.

[15] K. Ruedenberg and C. W. Scherr, *J. Chem. Phys.*, **21**, 1565 (1953).

the multicenter field (see Appendix); therefore, it may express an electronic motion on a circle with a radius, R_Y, through the middle points between the A and B nuclei. For benzene, two circles are possible, since $R_Y=0$ on a connecting line through the point of origin.

If the coordinate system (x_p, y_p, z_p) is transformed to the elliptic coordinates (ξ, η, φ), one obtains:

$$R_{\mathrm{Y}}\frac{\partial}{\partial x_p}|\chi_a) = \frac{1}{2}Z_{eff}R_{\mathrm{Y}}\frac{\xi\eta-1}{\xi-\eta}|\chi_a), \tag{13}$$

and then:

$$(\chi_b|l_z|\chi_a) = \frac{\hbar}{i}\frac{p^2}{10}\frac{R_{\mathrm{Y}}}{R_{\mathrm{X}}}\exp(-p)\left(1+p+\frac{p^2}{3}\right), \tag{14}$$

where $p=Z_{eff}R_{ab}/2$ in atomic units.

Consequently, we can estimate and compare both the magnetic moments calculated experimentally from Eq. (6) and those calculated theoretically from Eqs. (9), (10), and (14) for some planar molecules. We shall discuss a normal MORD and a magnetic moment in the next section.

Results and Discussion

The normal MORD of liquid benzene, which is observed at 10°C with the same apparatus as was described in one of the present author's previous paper,[16] is shown in Fig. 2, which also gives the result estimated from the Verdet constant by Garner *et al.*[5] assuming a temperature of 20°C.

Assuming the contribution from only one electronic transition to the normal MORD and modifying Eqs. (1), (5), and (6), one can obtain:

$$\omega^2 = \omega_{ja}^2 - (A_0+B_0)^{1/2}\omega/[\phi]_{\mathrm{M}}^{1/2}, \tag{15}$$

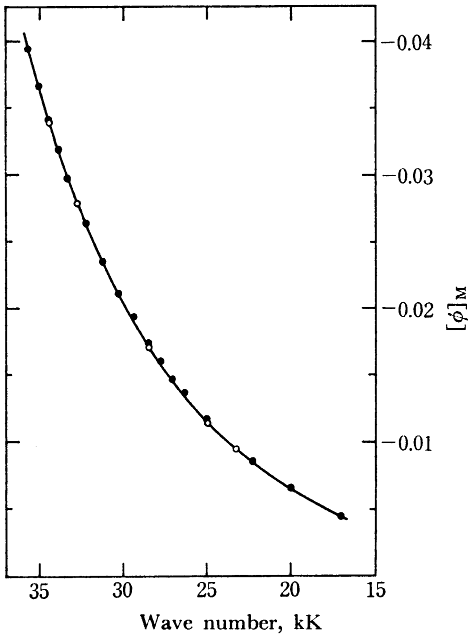

Fig. 2. The MORD (deg·*l*/*m*·mol·gauss) of benzene; dark circles are taken in this work and white ones show the data by Garner *et al.* (Ref. 5).

$$\omega^2 = \omega_{ja}^2 - A_0^{1/2}\omega/([\phi]_{\mathrm{M}}-E\omega^2)^{1/2}, \tag{16}$$

where $A_0=21.346\times 2\omega_{ja}|A(a\rightarrow j)|$, where $B_0=21.346\times B(a\rightarrow j)(\omega_{ja}^2-\omega^2)+\sum_{k>j}[\phi(a\rightarrow k)]_{\mathrm{M}}(\omega_{ja}^2-\omega^2)^2$, where ω is expressed in cm^{-1}, and where the factor 21.346 is the value of $(24\boldsymbol{N}/c\hbar)$ when $\boldsymbol{m}$ stands for the Debye unit, and μ, the Bohr magneton.

From Eq. (15), it may be seen that the curve of $\omega/[\phi]_{\mathrm{M}}^{1/2}$ *vs.* ω^2 is nearly a straight line; it is shown in Fig. 3(a). The deviation, increasing with a decrease in the ω^2 value from the straight line, shows that no terms except for $A(a\rightarrow j)$ are always completely negligible because of the behavior of B_0. A tangent, $A_0^{1/2}$, of the line becomes apparently greater, so the extrapolated resonance absorption, 59,500 cm^{-1}, may be assigned to the $^1A_{1g}\rightarrow{}^1E_{1u}$ transition (54,500 cm^{-1}).[17] It should, however, be stressed that the contributions of σ-electrons to the MORD are never negligible.

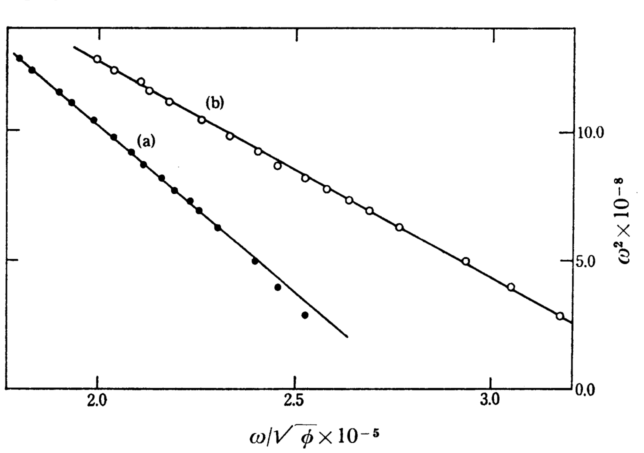

Fig. 3. Diagrams plotted (*a*) $\omega/([\phi]_M)^{1/2}$ and (*b*) $\omega/([\phi]_M-E\omega^2)^{1/2}$ *vs.* ω^2 for benzene.

According to the method of Perkin,[6] we can approximately estimate the ratio of the contribution by π and σ electrons. Perkin reported that, from the results of the Faraday effects of various organic compounds, the molecular rotation can be assumed to consist of rotations of constituent atoms. For example, the molecular rotation of the benzene skeleton, $[\mathrm{C_6H_6}^{6+}]_{\mathrm{M}}^{\mathrm{D}}$, is proportional to the difference, $[\mathrm{C_6H_{12}}]_{\mathrm{M}}^{\mathrm{D}}-6[\mathrm{H}^+]^{\mathrm{D}}=4.140$,[18] and the ratio of the contributions of the π and σ electrons is approximately equal to 7 : 4. Then, let us assume that the contributions of the electrons correspond to the E term in Eqs. (6) and (16). When $E=5.74\times 10^{-12}$ for $E\omega_{\mathrm{D}}^2=0.165\times 10^{-2}$ (deg·*l*/*m*·mol·gauss), the curve of $\omega/([\phi]_{\mathrm{M}}-E\omega^2)^{1/2}$ *vs.* ω^2 becomes almost straight, as is shown in Fig. 3(b). Since the straightness of the curve is very good, it is confirmed that the normal MORD of benzene has a large A term with one transition and that the other

---

16) Y. Takenoshita and Y. Kanda, This Bulletin, **44**, 2293 (1971).

17) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).

18) $[\mathrm{C_6H_6}]_{\mathrm{M}}^{\mathrm{D}}=11.284$, $[\mathrm{C_6H_{12}}]_{\mathrm{M}}^{\mathrm{D}}=5.664$ and $[\mathrm{H}]^{\mathrm{D}}=0.254$. See Ref. 6. These values are defined with a dimensionless term, $V_{\mathrm{M}}=[V]_{\mathrm{M}}d_w/M_w r_w$, where r_w, d_w and M_w are the magnetic rotation per cm per gauss and the density and the molecular weight of water respectively. The MORD $[\phi]_{\mathrm{M}}$ values are obtained through the multiplication of a factor, $-M_w r_w/600d_w=0.0003938$, to V_{M}.

Table 1. Faraday parameters of benzene

A_0 $\times 10^{-7}$	Res. abs. cm^{-1}	A $(d^2\beta)$[a]	D (d^2)[a]	Magnetic moment (β)[a]		
				Exp.	FEN	LCAO-MO
7.04	54280	30.4	35.3[b]	−1.72	−1.0	−0.396

a) d is expressed in Debye unit and β is a Bohr magneton.
b) Calculated from $f=0.94$ and $\omega=56{,}300\,\text{cm}^{-1}$ in Ref. 17.

terms are negligible in $([\phi]_M - E\omega^2)$. The extrapolated resonance absorption 54,280 cm^{-1}, is closer to 54,500 cm^{-1} than to the 59,500 cm^{-1} obtained by Eq. (15); therefore, the transition may be assigned to $^1A_{1g}\rightarrow{}^1E_{1u}$. The normal MORD of benzene, certainly, depends mainly on the π electronic structures. According to Stephens *et al.*,[4] this can naturally be predicted for coronene, which has a much greater value of the circular dichroism of the $^1A_{1g}\rightarrow{}^1E_{1u}$ transition than that of the $^1A_{1g}\rightarrow{}^1B_{2u}$ or $^1B_{1u}$ transition.

Therefore, the magnetic moment is given as -1.72β, with an f value of 0.94[19] (Table 1), and may be assigned to the excited degenerate state, $^1E_{1u}$. This observed moment is rather greater than the values of -1.0β for the FEN model or -0.396β for LCAO-MO when $r_{CC}=1.39$ Å, $Z_{eff}=3.25$, and the molecular orbitals without zero-differential overlap approximation[20] are used. This means that the observed magnitude of the A term is much greater than the theoretical values. Therefore, this probably means that the ratio, 7.144/11.284, of the contributions to the MORD by π-electrons used is too great, or that the observed A value consists of not only $A(^1A_{1g}\rightarrow{}^1E_{1u})$ but also of some terms for the other transitions. However, it is confirmed at last that there is a large A value. The existence of the large A value proves that the absorption band at 54,500 cm^{-1} has two symmetrical doublet transition moments, $(0|m_x|x)$ and $(0|m_y|y)$; this supports the conventional assignment of the β-band to $^1E_{1u}$.[4,12,21,22] It may be predicted that both the abnormal MORD and the MCD of the $^1A_{1g}\rightarrow{}^1E_{1u}$ transition of benzene may be assigned to the positive A type in Stephens' classification[2] or to the III type of Shashousa's[1].

It should be noted that the main component of the MORD is estimated experimentally in spite of difficulties in analyzing normal MORD. We shall not discuss further the magnetic properties of benzene, especially its magnetic moment, until the MCD or the abnormal MORD of benzene has been measured in its absorption regions. The normal MORD of benzene is never simple to analyze in its structure since a normal MORD depends on many transitions.

Finally, it should be noted that the MORD in the S-T absorptional region of benzene[23] has never been observed either with or without O_2-gases.

The author would like to thank Professor Yoshiya Kanda of his laboratory for his guidance, and Professor On Matsumura and Professor Yoshio Shibuya of the Department of Physics, Kyushu University, for providing him with the electric magnet.

Appendix

According to Bishop and Dingle, an electronic angular momentum operator[11] in the multicenter field of molecular orbitals has an effective component to atomic orbital, $|\chi_a)$ as follows:

$$\partial/\partial\phi\,|\chi_a) = -\frac{1}{2}Z_a \sin\theta_a(R_X \sin\varphi_a - R_Y \cos\varphi_a)\,|\chi_a), \tag{A.1}$$

where r_a, θ_a, and φ_a denote the polar coordinates at the nuclei A; the other notations are shown in Fig. 4. This can be easily proved to coincide with the operator reported by Stephens *et al.*[2] In Eq. (A. 1), as $\sin\theta_a \cos\varphi_a$ and $\sin\theta_a \sin\varphi_a$ can be put at x_a/r_a and y_a/r_a respectively, one obtaines:

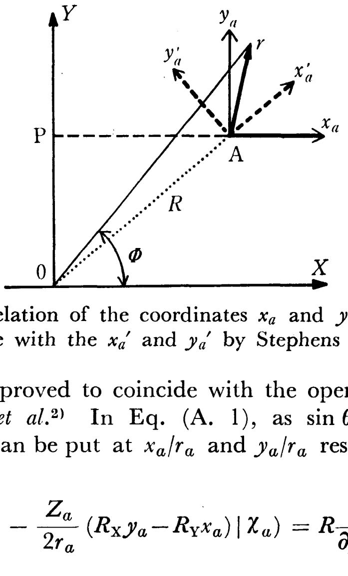

Fig. 4. A relation of the coordinates x_a and y_a by Bishop and Dingle with the x_a' and y_a' by Stephens *et al.*

$$\frac{\partial}{\partial\phi}|\chi_a) = -\frac{Z_a}{2r_a}(R_X y_a - R_Y x_a)\,|\chi_a) = R\frac{\partial}{\partial y_a'}|\chi_a). \tag{A.2}$$

If the atomic orbitals are expressed with Slater orbitals, which have no factor for φ in the conforcal elliptic coordinate system, the integration of Eq. (A. 2) for φ agreeds with Eq. (13). In the multicenter field of molecular orbitals, therefore, the effective component of l_z may be obtained with Eq. (12).

---

[19] K. Kimura and S. Nagakura, *Mol. Phys.*, **2**, 117 (1965).

[20] If the MO's calculated with a zero-differential overlap approximation are used, the expected value $(\phi_i|l_z|\phi_i)$ is zero when the bond-length is limited to zero and is, therefore, physically meaningless.

[21] E. Clar, "Aromatiche Kohlenwasserstoffe," 2nd ed. Julius Springer Verlag, Berlin, (1952).

[22] J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949); R. C. Nelson and W. T. Simpson, *ibid.*, **23**, 1146 (1955); J. Petruska, *ibid.*, **34**, 1111 and 1121 (1961); E. W. Thulstrup, *Int. J. Quantum Chem.*, **3s**, 641 (1970).

[23] A. Sklar, *J. Chem. Phys.*, **5**, 699 (1937); G. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **69**, 994 (1945); A. Pitts, *J. Chem. Phys.*, **18**, 1416 (1950); D. Evans, *J. Chem. Soc.*, **1957**, 1351; *Nature*, **176**, 777 (1955); D. Craig, J. Hollas, and G. King, *J. Chem. Phys.*, **29**, 974 (1958).