Calculation of the Diamagnetic Anisotropy of Benzene by the Method of Antisymmetric Molecular Orbitals

By Saburo FUJII and Shoji SHIDA

(Received July 20, 1951)

Introduction

Cyclic molecules⁽¹⁾ composed of conjugated double bonds, such as aromatic compounds,⁽²⁾ have a remarkable degree of diamagnetic anisotropy in the directions perpendicular to the molecular planes. For instance, the observed value of the anisotropy for benzene is about -54×10^{-6} ergs per gauss per mole⁽³⁾. This phenomenon is generally recognized to be caused by the free migration of the resonating $p\pi$-electrons along the molecular network under an external magnetic field. The quantum mechanical theories of the effect in aromatic molecules have been worked out by F. London⁽⁴⁾ and by H. Brooks,⁽⁵⁾,⁽⁶⁾ who calculated the ratio of the anisotropies of the various condensed ring compounds to that of benzene. In London's theory⁽⁴⁾ based on the simple method of molecular orbitals the calculated results are in good agreement with experiments, but his theory neglects the Pauli's exclusion principle and also the correlation effects between electrons. On the other hand H. Brooks⁽⁶⁾ treated anisotropy from the standpoint of the Heitler-London-Pauling-Slater approximation including ionic structures and amended the weakness of London's method, but his results are not better than London's in spite of his great labor. Furthermore both theories can not calculate the absolute value of the anisotropy for benzene.

The present paper is an effort to treat the diamagnetic anisotropy of benzene from the standpoint of the method of antisymmetric molecular orbitals (Goeppert-Mayer and Sklar's metod⁽⁷⁾) and to calculate the absolute value of the anisotropy. The G-M-S method has given a satisfactory result in the calculation of the lower excited levels of benzene and therefore it is interesting to see what results we can get from this method for the present purpose.

The Orbitals

When the magnetic field $\mathbf{H}$ is applied in the direction perpendicular to the plane of benzene molecule, the orbital of the ν-th π-electron in the l-th energy level may be described according to London's method:

$$\left.\begin{aligned}\phi_l=(6\sigma_l)^{-\frac{1}{2}}\sum_{k=1}^{6}e^{\frac{2\pi i}{6}(kl+f)}\times e^{i[\vec{\alpha}(k)\cdot\vec{r}_\nu]}\times U_k(\nu),\\ l=0,\pm1,\pm2,3,\quad \phi_l{}^*\mp\phi_{-l}{}^{(8)},\end{aligned}\right\}\quad(1)$$

where $U_k(\nu)$ is the $2p\pi$ wave function of the k-th carbon atom at $\mathbf{H}=0$ and σ_l the normalization factor ($\sigma_l=1$ in London's paper). Also $\vec{\alpha}(k)=\frac{2\pi e}{hc}\vec{\mathbf{A}}(r_k)$, $\vec{\mathbf{A}}(r_k)$ ⁽⁹⁾ being the vector potential in the position of the k-th nucleus; $f=\frac{e}{hc}S\cdot\mathbf{H}$, S being the area of the benzene ring. Here the orbitals ϕ_l are mutually orthogonal and $U_k(\nu)$ assumed to be normalized.

If the treatment for the vector potential is similar to that in London's paper, the normalization factors σ_l are then determined by the relation:

$$\sigma_l=1+2S_1\cos\frac{2\pi}{6}(l+f)+2S_2\cdot\cos\frac{2\pi}{6}(2l+f)+(-1)^l\cdot S_3,\quad(2)$$

where

$$S_t=\int U_1(\nu)\cdot U_{1+t}(\nu)d\tau_\nu$$

(overlap integrals at $\mathbf{H}=0$).

The energy of the molecule is the lowest if the

---

(1) Cyclooctatetraene C_8H_8 is excepted: see S. Shida and S. Fujii, This Bulletin, **24**, 173 (1951).

(2) K. Lonsdale, *Reports on Progress in Physics*, **4**, 368 (1937).

(3) K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc. London*, **156 A**, 597 (1937).

(4) F. London, *J. phys.*, **8**, 397 (1937).

(5) H. Brooks, *J. Chem. Phys.*, **9**, 463 (1941).

(6) H. Brooks, *J. Chem. Phys.*, **8**, 939 (1940).

(7) M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

(8) $\phi_l{}^*$ is the complex conjugate of ϕ_l. $\phi_l{}^*=\phi_{-l}$ for $\mathbf{H}=0$.

(9) If the direction perpendicular to the molecular plane is chosen to be Z-axis,

$$\vec{\mathbf{A}}=(A_x,A_y,A_z)=\left(-\frac{1}{2}y\mathbf{H},\frac{1}{2}x\mathbf{H},0\right).$$

orbitals $\phi_0, \phi_1, \phi_{-1}$ contain two electrons each; the perturbation energy caused by the magnetic field is usually very small. Therefore it is not necessary, for the present purpose, to consider the excited levels $l=\pm 2, 3$. Then the eigenfunction of the lowest state in this order of approximation is represented by

$$\Psi_0=\phi_0(1)\phi_0(2)\phi_1(3)\phi_1(4)\phi_{-1}(5)\phi_{-1}(6).$$

Also the total spin function in this state is the product

$$\chi_0=\alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6),$$

for the lowest state is experimentally diamagnetic.

The totally antisymmetric eigenfunction for this state is then obtained as follows,

$$\boldsymbol{\Psi}_0=(6!)^{-1/2}\sum_p(-1)^p\mathbf{P}(\Psi_0\chi_0), \tag{3}$$

where $\mathbf{P}$ is the permutation operator.

The Calculation of Energy in a Magnetic Field

The Hamiltonian for the benzene molecule in the magnetic field may be written(4), (7):

$$\mathcal{H}=\sum_\nu\left\{\frac{h^2}{8\pi^2m}\left(\frac{1}{i}\vec{\nabla}_\nu+\vec{\alpha}_\nu\right)^2+\sum_\kappa V_{\nu k}\right\}+\sum_{\substack{\nu=1\\ \mu<\nu}}^{6}\frac{e^2}{r_{\nu\mu}}, \tag{4}$$

where $\vec{\alpha}_\nu=\frac{2\pi e}{hc}\vec{\mathbf{A}}_\nu$, $\vec{\mathbf{A}}_\nu$ being the vector potential which acts in the ν-th electron. V_{2k} is the potential of the k-th carbon nucleus acting on the ν-th lelctron and may be represented as follows,

$$V_{\nu k}=\mathbf{H}_{\nu k}-\int\frac{e^2}{r_{\nu\mu}}U_k^2(\mu), \tag{5}$$

where $\mathbf{H}_{\nu k}$ is the potential of the neutral carbon atom. The average value of the Hamiltonian $\mathcal{H}$ in this state is given by

$$E=\iint\cdots\int\boldsymbol{\Psi}_0^*\mathcal{H}\boldsymbol{\Psi}_0\,d\tau_1d\tau_2\ldots d\tau_6. \tag{6}$$

If we put

$$\left.\begin{aligned}\mathcal{E}_l&=\int\phi_l^*(\nu)\left\{\frac{h^2}{8\pi^2m}\left(\frac{1}{i}\vec{\nabla}_\nu+\vec{\alpha}_\nu\right)^2\right.\\&\qquad\left.+\sum_\kappa V_{\nu k}\right\}\phi_l(\nu)d\tau_\nu,\\ \gamma_{ll'}&=\int\frac{e^2}{r_{\nu\mu}}[\phi_l(\nu)\phi_l^*(\nu)][\phi_{l'}(\mu)\phi_{l'}^*(\mu)]d\tau_\nu d\tau_\mu,\\ \delta_{ll'}&=\int\frac{e^2}{r_{\nu\mu}}[\phi_l(\nu)\phi_{l'}^*(\nu)][\phi_{l'}(\mu)\phi_l^*(\mu)]d\tau_\nu d\tau_\mu,\end{aligned}\right\} \tag{7}$$

then the total energy in the magnetic field $\mathbf{H}$ is

$$\begin{aligned}E&=(2\mathcal{E}_0+2\mathcal{E}_1+2\mathcal{E}_{-1})\\&\quad+\iint\cdots\int\boldsymbol{\Psi}_0^*\left(\sum_{\substack{\nu=1\\ \mu<\nu}}^{6}\frac{e^2}{r_{\nu\mu}}\right)\boldsymbol{\Psi}_0d\tau_1d\tau_2\ldots d\tau_6\\&=(2\mathcal{E}_0+2\mathcal{E}_1+2\mathcal{E}_{-1})+(\gamma_{00}+4\gamma_{01}+4\gamma_{0-1}\\&\quad+4\gamma_{1-1}+\gamma_{11}+\gamma_{-1-1}-2\delta_{01}-2\delta_{0-1}-2\delta_{1-1}).\end{aligned} \tag{8}$$

In the expansion of the integrals $\mathcal{E}$, γ, δ in terms of $\mathbf{H}$ and integrals over the atomic eigenfunctions U_k, we must treat the integrals of the form

$$\begin{aligned}\iint e^{i[\overrightarrow{\alpha(k)-\alpha(l)}\cdot\vec{r}_\nu]}U_k(\nu)\,U_l(\nu)\frac{e^2}{r_{\nu\mu}}\,e^{i[\overrightarrow{\alpha(m)-\alpha(n)}\cdot\vec{r}_\mu]}\\ \times U_m(\mu)U_n(\mu)d\tau_\nu\,d\tau_\mu.\end{aligned} \tag{9}$$

The rigorous calculations of these integrals are complicated. Therefore, for the first approximation, $\vec{r}_\nu$ is replaced by $\frac{1}{2}(\vec{R}_k+\vec{R}_l)$ where the product $U_k(\nu)U_l(\nu)$ has the maximum value, and $\vec{r}_\mu$ by $\frac{1}{2}(\vec{R}_m+\vec{R}_n)$ in the similar manner. Here $\vec{R}_k$, $\vec{R}_l$, $\vec{R}_m$ and $\vec{R}_n$ represent the position vectors of the correspondingly numbered nuclei. This approximation(10) may be adequate, because $e^{i[\overrightarrow{\alpha(k)-\alpha(l)}\cdot\vec{r}_\nu]}$, $e^{i[\overrightarrow{\alpha(m)-\alpha(n)}\cdot\vec{r}_\mu]}$ do not make large changes in the ranges of $\vec{R}_k\sim\vec{R}_l$ and $\vec{R}_m\sim\vec{R}_n$ respectively. Using this approximation, we then obtain

$$\begin{aligned}\gamma_{ll'}=\frac{1}{6\sigma_l\cdot\sigma_{l'}}\Big[&(A_0+2A_1+2A_2+A_3)\\&+2(B_1+B_2+B_3)\left\{\cos\frac{2\pi}{6}(l+f)+\cos\frac{2\pi}{6}(l'+f)\right\}\\&+2(C_1+2C_2+2C_3+C_4)\left\{\cos\frac{2\pi}{6}(l+l'+2f)\right.\\&\qquad\left.+\cos\frac{2\pi}{6}(l-l')\right\}\\&+2(F_1+2F_2+2F_3+F_4)\left\{\cos\frac{2\pi}{6}(2l+f)\right.\\&\qquad\left.+\cos\frac{2\pi}{6}(2l'+f)\right\}\end{aligned}$$

---

(10) This approximation is analogous to the one used by F. London in the calculation of the resonance integral of π-electron in a magnetic field.

$$
\begin{aligned}
&+4(J_1+J_2+J_3)\Big\{\cos\frac{2\pi}{6}(2l+l'+2f)\\
&+\cos\frac{2\pi}{6}(l+2l'+2f)+\cos\frac{2\pi}{6}(2l-l')\\
&+\cos\frac{2\pi}{6}(2l'-l)\Big\}+6\{(-1)^{l}+(-1)^{l'}\}\cdot D\Big],
\end{aligned}
\tag{10}
$$

$$
\begin{aligned}
\delta_{ll'}=\frac{1}{6\sigma_l\cdot\sigma_{l'}}\Big[&\Big\{A_0+2A_1\cos\frac{2\pi}{6}(l-l')\\
&+2A_2\cos\frac{4\pi}{6}(l-l')+(-1)^{l-l'}A_3\Big\}\\
&+4B_1\Big\{\cos\frac{2\pi}{6}(l+f)+\cos\frac{2\pi}{6}(l'+f)\Big\}\\
&+4B_2\Big\{\cos\frac{2\pi}{6}(2l-l'+f)+\cos\frac{2\pi}{6}(2l'-l+f)\Big\}\\
&+4B_3\Big\{(-1)^{l-l'}\cos\frac{2\pi}{6}(l+f)\\
&\qquad+(-1)^{l'-l}\cos\frac{2\pi}{6}(l'+f)\Big\}\\
&+2\Big\{C_1+2C_2\cos\frac{2\pi}{6}(l-l')+2C_3\cos\frac{4\pi}{6}(l-l')\\
&\qquad+(-1)^{l-l'}\cdot C_4\Big\}\Big\{1+\cos\frac{2\pi}{6}(l+l'+2f)\Big\}\\
&+4\{F_1+(-1)^{l-l'}F_4\}\cos\frac{2\pi}{6}(l+l'+f)\\
&+4\{F_2+(-1)^{l-l'}\cdot F_3\}\Big\{\cos\frac{2\pi}{6}(2l+f)\\
&\qquad+\cos\frac{2\pi}{6}(2l'+f)\Big\}\\
&+4\{J_1+(-1)^{l-l'}\cdot J_3\}\Big\{\cos\frac{2\pi}{6}(2l'+l+2f)\\
&\qquad+\cos\frac{2\pi}{6}(2l+l'+2f)+\cos\frac{2\pi}{6}l+\cos\frac{2\pi}{6}l'\Big\}\\
&+4J_2\Big\{(-1)^{l}\cos\frac{4\pi}{6}f+(-1)^{l'}\cos\frac{4\pi}{6}f\\
&\qquad+\cos\frac{2\pi}{6}(2l-l')+\cos\frac{2\pi}{6}(2l'-l)\Big\}\\
&+D\cdot\{(-1)^{l}+(-1)^{l'}\}\cdot\Big\{1+2\cos\frac{2\pi}{6}(l-l')\\
&\qquad+2\cos\frac{4\pi}{6}(l-l')+(-1)^{l-l'}\Big\}\Big],
\end{aligned}
\tag{11}
$$

where

$$
\left.
\begin{aligned}
A_i&=\iint U_1^2(\nu)\frac{e^2}{r_{\nu\mu}}U^2{}_{1+i}(\mu)d\tau_\nu\, d\tau_\mu,\\
B_i&=\iint U_1(\nu)U_6(\nu)\frac{e^2}{r_{\nu\mu}}U_i^2(\mu)d\tau_\nu\, d\tau_\mu,\\
C_i&=\iint U_1(\nu)U_2(\nu)\frac{e^2}{r_{\nu\mu}}U_i(\mu)U_{1+i}(\mu)\, d\tau_\nu\, d\tau_\mu,\\
D^{(11)}&=\iint U_1(\nu)U_4(\nu)\frac{e^2}{r_{\nu\mu}}U_i^2(\mu)d\tau_\nu\, d\tau_\mu,\\
F_i&=\iint U_1(\nu)U_3(\nu)\frac{e^2}{r_{\nu\mu}}U^2{}_{1+i}(\mu)d\tau_\nu\, d\tau_\mu,\\
J_i&=\iint U_1(\nu)U_2(\nu)\frac{e^2}{r_{\nu\mu}}U_i(\mu)U_{2+i}(\mu)d\tau_\nu\, d\tau_\mu.
\end{aligned}
\right\}
\tag{12}
$$

Also, since $e^{i[\vec{\alpha}(k)\cdot\vec{r}]}U_k(\nu)$ is taken to be an atomic eigenfunction in the magnetic field **H**, the relation

$$
\begin{aligned}
&\left\{\frac{h^2}{8\pi^2m}\left(\frac{1}{i}\vec{\nabla}_\nu+\vec{\alpha}_\nu\right)^2+V_{\nu k}\right\}e^{i[\vec{\alpha}(k)\cdot\vec{r}_\nu]}U_k(\nu)\\
&\qquad=W_{2p}'e^{i[\vec{\alpha}(k)\cdot\vec{r}_\nu]}U_k(\nu)
\end{aligned}
\tag{13}
$$

holds, where W_{2p}' is the energy of a $2p$ electron which is in the valence state and in the magnetic field **H**. Hence $\mathcal{E}_l$, the energy of the orbital in (1), is expanded in the form

$$
\begin{aligned}
\mathcal{E}_l=W'_{2p}-\frac{2}{\sigma_l}\Big[&\left(Q+A_1+A_2+\frac{1}{2}A_3\right)\\
&+(R_1+2R'_1+B_1+2B_2+2B_3)\cos\frac{2\pi}{6}(l+f)\\
&+(R_2+R'_2+F_1+F_2+2F_3+F_4)\cos\frac{2\pi}{6}(2l+f)\\
&+(-1)^{l}\cdot\left(2R'_3+\frac{5}{2}D\right)\Big],
\end{aligned}
\tag{14}
$$

where

$$
\left.
\begin{aligned}
Q&=-\int\mathbf{H}_{\nu1}U^2{}_2(\nu)d\tau_\nu,\\
R_i&=-\int\mathbf{H}_{\nu1}U_1(\nu)U_{1+i}(\nu)d\tau_\nu,\\
R'_i&=-\int\mathbf{H}_{\nu1}U_2(\nu)U_{2+i}(\nu)d\tau_\nu.
\end{aligned}
\right\}
\tag{15}
$$

The functions U_k used for the numerical calculation of the integrals are $2p\pi$ hydrogen-like functions

$$
U(r,\theta,\varphi)=\sqrt{\frac{Z^5}{32\pi}}\cdot r\cdot\sin\theta\cdot\cos\varphi\cdot e^{-\frac{Zr}{2}},
$$

where the effective nuclear charge Z is chosen to be 3.18(12) as usual. The distance between neighboring carbon atoms is 1.39 Å. The numerical values of $A_i, B_i, C_i, D_i, F_i, J_i, R_i, R_i'$, and S_i are collected in Table 1. These adopted

---

(11) Here D represents D_i, but the values of D_i for all of i are the same.

(12) C. Zener, *Phys. Rev.*, **36**, 51 (1930).

data are selected by U. Mori(13), who has recalculated the numerical values of the above integrals from Parr-Crawford's(14) and Kotani-Amemiya-Simose's(15) tables and with A. London's approximation method(16).

Table 1

$A_0=16.9301$ e.V.
$A_1=$ 9.0232 e.V.
$A_2=$ 5.6669 e.V.
$A_3=$ 4.9744 e.V.
$B_1=$ 3.3184 e.V.
$B_2=$ 1.8681 e.V.
$B_3=$ 1.4227 e.V.
$C_1=$ 0.9516 e.V.
$C_2=$ 0.6769 e.V.
$C_3=$ 0.4357 e.V.
$C_4=$ 0.3831 e.V.
$F_1=$ 0.5208 e.V.
$F_2=$ 0.3888 e.V.
$F_3=$ 0.2790 e.V.
$F_4=$ 0.2503 e.V.

D $=0.1622$ e.V.
J_1 $=0.1354$ e.V.
J_2 $=0.0911$ e.V.
J_3 $=0.0725$ e.V.
Q $=0.8542$ e.V.
R_1 $=1.8880$ e.V.
R_2 $=0.1080$ e.V.
$R_1'=0.0387$ e.V.
$R_2'=0.0318$ e.V.
$R_3'=0.0316$ e.V.

$S_1=0.2600$
$S_2=0.0388$
$S_3=0.0179$

The Calculation of Anisotropy

When the magnetic field **H** is applied in the direction parallel to the molecular plane, neither $\gamma_{ll'}$ nor $\delta_{ll'}$ depends on **H**, and in the expansion of ε_l only the term W_{2p}' remains unchanged as the function of **H**, since $f=0$ in this case. Therefore the anisotropy in the direction perpendicular to the molecular plane may be written:

$$\begin{aligned}\Delta\chi_{\perp}&=-\left[\frac{\partial^2}{\partial H^2}(E-E^0)\right]_{E\to 0}\\&=-\left[\frac{\partial^2}{\partial H^2}(2\varepsilon_0+2\varepsilon_1+2\varepsilon_{-1}-6W'_{2p})\right]_{H\to 0}\\&\quad-\left[\frac{\partial^2}{\partial H^2}\left(\iint\cdots\int\boldsymbol{\psi}_0^*\left(\sum_{\substack{\nu=1\\ \mu<\nu}}^{6}\frac{e^2}{r_{\nu\mu}}\right)\right.\right.\\&\qquad\left.\left.\times\boldsymbol{\psi}_0 d\tau_1 d\tau_2\ldots\ldots d\tau_6\right)\right]_{H\to 0}, \quad (16)\end{aligned}$$

where E^0 is E in the case of which **H** is

Table 2

	A	B	C
$-\left[\frac{\partial^2}{\partial H^2}(\epsilon_0-W'_{2p})\right]_{H\to 0}$	$+4.157\left(\frac{2\pi eS}{6hc}\right)^2$,	$-2.092\left(\frac{2\pi eS}{6hc}\right)^2$,	$-2.456\left(\frac{2\pi eS}{6hc}\right)^2$,
$-\left[\frac{\partial^2}{\partial H^2}(\epsilon_{\pm 1}-W'_{2p})\right]_{H\to 0}$	+8.221 〃	−5.160 〃	−5.712 〃
$-\left[\frac{\partial^2\gamma_{00}}{\partial H^2}\right]_{H\to 0}$	−1.675 〃	+0.034 〃	+0.034 〃
$-\left[\frac{\partial^2\gamma_{0\pm 1}}{\partial H^2}\right]_{H\to 0}$	−2.664 〃	+0.041 〃	+0.041 〃
$-\left[\frac{\partial^2\gamma_{1-1}}{\partial H^2}\right]_{H\to 0}$	−3.158 〃	+0.110 〃	+0.110 〃
$-\left[\frac{\partial^2\gamma_{11}}{\partial H^2}\right]_{H\to 0}=-\left[\frac{\partial^2\gamma_{-1-1}}{\partial H^2}\right]_{H\to 0}$	−7.231 〃	−0.512 〃	−0,512 〃
$-\left[\frac{\partial^2\delta_{0\pm 1}}{\partial H^2}\right]_{H\to 0}$	+0.109 〃	−0.225 〃	−0.225 〃
$-\left[\frac{\partial^2\delta_{1-1}}{\partial H^2}\right]_{H\to 0}$	+0.665 〃	−0.319 〃	−0.319 〃
$-\left[\frac{\partial^2}{\partial H^2}(2\epsilon_0+2\epsilon_1+2\epsilon_{-1}-6W'_{2p})\right]_{H\to 0}$	+41.198 〃	−24.824 〃	−27.760 〃
$-\left[\frac{\partial^2}{\partial H^2}\left(\iint\cdots\int\boldsymbol{\psi}_0^*\left(\sum_{\substack{\nu=1\\ \mu<\nu}}^{6}\frac{e^2}{r_{\nu\mu}}\right)\boldsymbol{\psi}_0 d\tau_1 d\tau_2\ldots d\tau_6\right)\right]_{H\to 0}$	−51.853 〃	+ 1.840 〃	+ 1.840 〃
$-\left[\frac{\partial^2}{\partial H^2}(E-E^0)\right]_{H\to 0}$	−10.65 〃	−22.98 〃	−26.00 〃
Calculated anisotropy. (ergs per gauss per mole)	-16.2×10^{-6}	-35.1×10^{-6}	-40.0×10^{-6}
$\frac{\text{Calculated value}}{\text{Experimental value}}\times 100$, %	30	65	74

---

(13) One of the members in our laboratory.

(14) R. G. Parr and B. L. Crawford, *J. Chem. Phys.*, **16**, 1049 (1948); C. C. J. Roothaan and R. G. Parr, *J. Chem. Phys.*, **17**, 1001 (1949).

(15) M. Kotani, A. Amemiya and T. Shimose, *Proc. Phys.-Math. Soc. Japan*, **20**, extra number I (1938); **22**, extra number I (1940).

(16) A. London, *J. Chem. Phys.*, **13**, 396 (1945).

applied in the direction parallel to the molecular plane. The results of numerical calculations are given in Table 2. Column A in Table 2 represents the result obtained when only the types of integrals used in Goeppert-Mayer and Sklar's paper(7) are adopted. Column B is the result when all the remaining types of integrals except R_2, R'_1, R'_2, and R'_3 in Table 1 are used. Column C is derived by the use of all the integrals in Table 1.

Considerations

The best result obtained in this manner is -40×10^{-6} ergs per gauss per mole, it being about 74 percent of the experimental value -54×10^{-6}. The physical contradiction appears in the case of column A, where the contribution of $\mathcal{E}_l$ to the anisotropy is paramagnetic and that of repulsions between electrons diamagnetic, in spite of the fact that the former and the latter must be physically diamagnetic and paramagnetic respectively. But this contradiction is removed in columns B and C by the use of the integrals neglected in column A, and the numerical results become better. It is natural that the calculated result approaches more and more to the experimental value as the approximation used becomes of higher order. If the approximate methods used in this paper are not unreasonable, the above considerations may be useful in the criticism of the ground states calculated by the G-M-S method and it may be concluded that the energy level $^1A_{1g}$ in their original paper is unsuitable. On the other hand we have been also taught the fact that the anisotropy is largely enhanced by the orbital effects and slightly diminished by the correlation effects between π-electrons. Thus, the reason why good results were obtained by F. London's method neglecting the correlation effects between π-electrons may be understood to some extent.

Recently the conception of configurational interaction has been introduced by Craig(17) into the antisymmetric molecular orbital treatment of the absorption spectra of benzene. According to his paper there are four A_{1g} states including the ground state (at $\mathbf{H}=0$) described in the present paper, and the interactions among this set of A_{1g} states depress the lowest of them by about 2 e.V. Therefore it is interesting and may be valuable to note that the problems of anisotropy are treated with the introduction of configurational interaction.

Summary

The absolute value of the diamagnetic anisotropy of benzene was calculated by the method of antisymmetric molecular orbitals. The value obtained was about -40×10^{-6} ergs per gauss per mole, it being about 74 percent of the experimental value.

It was found that the anisotropy was largely enhanced by orbital effects and slightly diminished by correlation effects between π-electrons.

The authors wish to express their thanks to Mr. U. Mori for his co-operation in the discussion of the atomic integrals. They also thank the Department of Education for the Scientific Research Encouragement Grant.

Laboratory of Physical Chemistry,
Tokyo Institute of Technology (Tokyo Kōgyo Daigaku), Tokyo.

---

(17) D. P. Craig, *Proc. Roy. Soc. London*, **200 A**, 747 (1950).