Magnetic Property and Resonance Character of Cycloöctatetraene (C_8H_8)

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Introduction

If cycloöctatetraene (C. O. T.) is assumed to have a regular eight-membered ring structure, it may be paramagnetic in the ground state. This has been theoretically suggested by E. Hückel(1) in his earlier quantum mechanical treatment and shown recently also by Y. Mori, I. Tanaka and S. Shida(2) from the standpoint of the antisymmetrical molecular orbital theory including electron repulsions.

On the other hand, if it is not paramagnetic but diamagnetic on account of some reasons, it will have more or less diamagnetic anisotropy due to resonance in analogy with benzene and other aromatic molecules.

In the course of the study the following fact has come to be clear that R. C. Pink(3) and W. Klemm(4) had obtained -51.9×10^{-6} and -55.6×10^{-6} respectively as the molecular diamagnetic susceptibility of C. O. T. The difference between the above two values, which is beyond the usual experimental errors in susceptibility measurements, may be considered to be dependent upon impurities in the C. O. T. used by them, and their interpretations for the magnetic property seem to be different from ours so far as we can know from the available abstracts(5) of their works.

Therefore it is worthwhile to report our new susceptibility measurements for purified C. O. T. and to describe our opinions for this magnetic property, especially for the relationship between the diamagnetic anisotropy and the resonance character, on the basis of its probable structures(6)~(11), its thermal data(12)~(14) and the quantum mechanical calculations(2), (15) on its electronic levels.

Experimental

Our apparatus for magnetic susceptibility measurements is a Weiss-Fõex type(16) with several refinements and the main part is shown diagramatically in Fig. 1.

This main part is doubly covered with glass plates to prevent it from air disturbance. Passing a constant direct current of 20 amperes through this magnet, the field strength between the pole-pieces, 17 mm. apart from each other, is about 10,000 gausses. According to the tests with several common substances this apparatus is proved to be useful with an error of 0.5 percent for determinations of mass susceptibilities of 10^{-6} order and able to detect its temperature dependence exceeding 0.5 percent over the temperature range 20° to 100°C.

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(2) Y. Mori, I. Tanaka and S. Shida, This Bulletin, **23**, 168 (1950).

(3) R. C. Pink and A. R. Ubbelohde, (a) *Nature*, **160**, 502 (1947); (b) *Trans. Faraday Soc.*, **44**, 708 (1948); (c) *Chemical Abstracts*, **43**, 2479f (1949); (d) *ibid.*, **44**, 6212f (1950).

(4) W. Reppe, "Acetylene Chemistry," 1946.

(5) References 3a, 3c, 3d, and 4.

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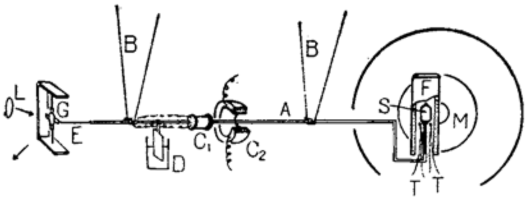

Fig. 1—Weiss-Fõex Balance: A, quartz rod; B, fine copper wire; C_1, the 1-st coil; C_2, the 2-nd coil; D, oil damper; E, magnetized needle; F, electric furnace; G, mirror suspended by fine bronz ribbon (its back is pasted with polished thin steel plate).; L, lens; M, magnet; S, sample vessel; T, thermocouple.

The C. O. T. used in the present measurement was obtained through the courtesy of Professor S. Murahashi and Dr. N. Hagiwara(17), who prepared it with the catalytic polymerization of acetylene in autoclave and purified it by means of several fractional distillations under a low pressure of nitrogen. This substance is a transparent yellow liquid (m. p. −7.5°, b. p. 95.6° at 185 mm. Hg) and stored in an evacuated tube in the dark because it becomes turbid brown in a day if opened in air. Before each measurement this substance, not including any detectable amount of styrene, was distilled several times *in vacuo* and the last middle portion always used.

Our measured value of the mass susceptibility of this C. O. T. at 30° is

$$(-0.518\pm0.003)\times10^{-6}$$

hence the molecular susceptibility

$$(-53.9\pm0.3)\times10^{-6}$$

This value is between those obtained by W. Klemm and by R. C. Pink. In the measurement of the temperature dependence of susceptibility for this substance the experiment was carried out with the sample distilled in an evacuated small glass vessel for susceptibility measurement and the correction for the vessel was done under the condition of it being evacuated. The magnitude of force acting on the sample liquid in a non-homogeneous magnetic field depends sharply upon the volume and the position which are occupied by the sample between both pole-pieces. Therefore the magnitudes of force acting on the constant mass at various temperatures are, though slightly, detectably different from each other owing to the volume change with temperature of the sample liquid. The fact indicates that the relation between the magnetic force and the volume of sample is necessary to be determined in this experiment. The correction(18) for the effect described above was also taken into account in the present measurement.

According to these three measurements the temperature dependence of the mass susceptibility of C. O. T. could not be detected over the temperature range 30° to 80°C. with an experimental error of 0.5 percent.

Discussion

Though we cannot determine the reliable order for the three different values of the mass susceptibility of C. O. T. because the detailed reports on W. Klemm's and R. C. Pink's experiments cannot be obtained, this substance is now clearly proved to have a temperature independent diamagnetism and therefore the possibility of a spin paramagnetism, as suggested by E. Hückel, excluded. Our purpose for the measurement of the temperature dependence of this diamagnetism was to examine the possibility of a small energy difference between the diamagnetic ground state and the lowest triplet one as well as that of a mixture of diamagnetic and spin paramagnetic isomers, this latter one being assumed in the first report(3a) by R. C. Pink and A. R. Ubbelohde. But our result does not support these possibilities.

Next it is important to consider the diamagnetic anisotropy of this molecule in comparison with aromatic and hetero-cyclic ones composed of conjugated double bonds, for the previous authors(3),(4) did not pay any attention to this property. The diamagnetic anisotropy of ring-shaped molecules composed of conjugated double bonds is generally recognized to be induced by the free migration of resonating $p\pi$ electrons along the molecular network under an external magnetic field, and therefore it can be represented qualitatively with circulating electric currents along the molecular network. The molecular structure of C. O. T. has not yet been determined definitely, but the most probable one may be D_{2d}(9)∼(11), while D_{4d}(6),(7) and D_4(8) are also recently reported by different authors.

Then, with these structures and the models shown in Fig. 2, the anisotropic parts to x and y directions may be nearly negligible because each component of the diamagnetic currents is canceled out vectorically by oneself from the above view-point.

According to this consideration the molecular susceptibilities to the both directions have to be equally 4/3 times of that of benzene, *i. e.*, about -49.7×10^{-6}. Then, from the experimental mean molecular susceptibility -53.9×10^{-6} and the values to x and y directions, the

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(17) The members of the Institute of Scientific and Industrial Research, University of Osaka.

(18) This correction was obtained by the use of toluene. The mass susceptibility of toluene has not a temperature dependence exceeding 0.5 percent over the temp. range 10° to 50°. (G. F. Boeker, *Phys. Rev.*, **43**, 756 (1933)).

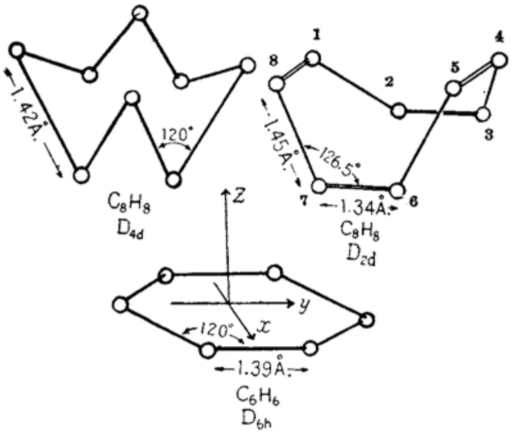

Fig. 2.

anisotropic part[19] to z-direction is estimated as about -12.6×10^{-6} per mole, that is, about 23 percent of that of benzene. This estimated anisotropy is very small in spite of the fact that this molecule has eight pπ electrons and larger projected area on the xy plane than that of benzene.

On the other hand, the estimated resonance energy of this compound is also small and about 2.9 kcal. per mole, it being about 7 percent of that of benzene. It is calculated from the following thermal data determined recently;

$$8\text{C(graphite)}+4\text{H}_2\text{(gas)}=\text{C}_8\text{H}_8\text{(liquid)} + (60.82\pm0.32)\ \text{kcal./mole}^{(13)},$$

the heat of vaporization of liquid C_8H_8 is 10.300 $\pm$0.075 kcal./mole[14] and the bond energies[20]

$$\begin{cases} \text{C}-\text{C} \ldots\ 60.3 \text{ kcal. per mole} \\ \text{C}=\text{C} \ldots 102.9 \ \text{,,} \quad \text{,,} \quad \text{,,} \\ \text{C}-\text{H} \ldots\ 87.15 \ \text{,,} \quad \text{,,} \quad \text{,,} \ . \end{cases}$$

R. C. Pink and A. R. Ubbelohde[3a] have obtained 25.4 kcal./mole for this resonance energy. The old value used by them for the heat of formation of this compound is considered to have some uncertainty and therefore their question that C. O. T. is magnetochemically aliphatic rather than aromatic in spite of its considerable resonance energy may not be fit. From these relationships between resonance energies and diamagnetic anisotropies of C. O. T. as well as aromatic and hetrocyclic molecules composed of conjugated double bonds we can understand that the larger anisotropy a molecule has, the more remarkable its resonance character is. This phenomenon can be explained qualitatively from the quantum mechanical view-point by the fact that these two properties are both directly related to the resonance integrals of pπ electrons.

According to the atomic and molecular orbital calculations[2], [15] on the electronic levels of this molecule the exchange or resonance integrals between any adjacent carbon atoms in the case of D_{4d} and these between the 1-st and 2-nd carbon atoms in D_{2d} in Fig. 2 are smaller than those of benzene. Also the calculated resonance energy[2] in the case of D_{2d} on the basis of the L-C-A-O approximation is 2.7 kcal./mole, it being consistent with the value estimated from thermochemical data.

Therefore the small anisotropy of this molecule can be also explained by the fact that the small resonance integral means the difficulty of free migration of pπ electrons along the molecular network under an external magnetic field. Then it is interesting to discuss this anisotropic part on the basis of Langevin's classical theory[21] and the molecular orbital method by F. London.[22] The latter obtained an excellent agreement with experiments in the calculation of the anisotropies of aromatic molecules. According to P. Langevin the anisotropic part of a simple ring-shaped molecule with n migrating pπ electrons can be written

$$\Delta\chi_M = -\frac{Ne^2}{4\pi mc^2}\sum^{n}\overline{r_i^2} \quad \ldots\ldots\ldots (1)$$

where N is the Avogadro number and $\overline{r_i^2}$ mean square radius of the i-th migrating pπ electron along the molecular ring.

In the cases of benzene, pyridine, furane, pyróle, thiophene and cyclopentadiene, all of which have plane structures and relatively large resonance energies, the calculated anisotropies[23] from Eq. (1) are in agreement with the values estimated from the Pascal additivity law within the maximum error of about 10 percent. However, the calculated values for C. O. T. as D_{4d} and D_{2d} are -103.7×10^{-6} and -155.6×10^{-6} respectively, and obviously they are quite different from the value estimated by us, *i. e.*, -12.6×10^{-6}. Hence Langevin's theory may be applied only to the molecule with a plane structure and a remarkable resonance character.

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Now we shall apply the London theory to this molecule to see what results we can get from this method. If the field perturbation is neglected, his theory is reduced to a simple type of the one-electron approximation, and then the ground electronic states calculated in this case are illustrated in Fig. 3.

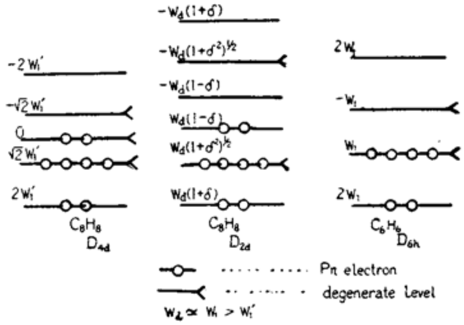

Fig. 3.

In Fig. 3 it is shown that both D_{2d} and D_4 structures are diamagnetic but D_{4d} should have a spin paramagnetism owing to a degenerate level occupied by only two electrons and so the calculation of the anisotropic part for D_{4d} may be meaningless. Therefore we shall calculate the anisotropy in the case of D_{2d}, and the present calculation follows, for the convenience' sake, the same notation and procedure as London's paper.

If $\left(\frac{x_k+x_l}{2}\pm\xi_{kl},\ \frac{y_k+y_l}{2}\pm\eta_{kl}\right)$ are two xy-coordinates where the overlap between Pz wave functions in the k-th and the l-th carbon atoms is maximum, and we put

$$\theta_{kl}=\frac{\pi e}{hc}\left[(x_k-x_l)\eta_{kl}-(y_k-y_l)\xi_{kl}\right],$$

then the anisotropic part due to a pπ electron in the p-th energy state is expressed as follows:

$$\chi_p=-|W_d|\times\left\{\frac{(\theta_d^2+\delta^2\theta_s^2)+\left(\frac{\pi^2e^2S^2}{16h^2c^2}+\theta_d^2+\theta_s^2\right)\delta\cos\frac{2\pi}{4}p}{\left(1+2\delta\cos\frac{2\pi}{4}p+\delta^2\right)^{1/2}}+\frac{\left(\frac{\pi^2e^2S^2}{16h^2c^2}+\theta_d^2+\theta_s^2\right)\delta^2\sin^2\frac{2\pi}{4}p}{4\left(1+2\delta\cos\frac{2\pi}{4}p+\delta^2\right)^{3/2}}\right\},\quad\cdots(2)$$

where $\theta_d=\theta_{81}$, $\theta_s=\theta_{12}$, $\delta=W_s/W_d<1$. S is the projected molecular area on the xy-plane and W_s, W_d are the resonance integral between the 1-st and the 2-nd carbon atoms and the one between the 1-st and the 8-th carbon atoms respectively. Here the positions of carbon atoms are denoted as shown in Fig. 2.

Therefore the total anisotropic part to z-direction is

$$\begin{aligned}\varDelta\chi_M&=2(\chi_{-1}+\chi_0+\chi_1+\chi_2)\\&=-4|W_d|\left[\delta^2\left(\frac{\pi eS}{2hc}\right)^2\left\{\frac{1}{(1+\delta^2)^{3/2}}-\frac{1}{1-\delta^2}\right\}+\theta_d^2+\frac{\theta_d^2+\delta^2\theta_s^2}{(1+\delta^2)^{1/2}}\right].\quad\cdots\cdots\cdots\cdots(3)\end{aligned}$$

Using the numerical data measured by K. Hedberg and V. Shomaker(11) we obtain $S=7.9(\text{Å}.^2)$, $|\theta_d|=0.32\left(\frac{2\pi e}{hc}\right)$ (Å.²) and $\theta_s\doteqdot0$. Then assuming $\delta=0.4$(2) we obtain

$$\varDelta\chi_{C_8H_8,D_{2d}}=+0.26|W_d|\left(\frac{2\pi e}{hc}\right)^2,\quad\cdots(4)$$

while for benzene

$$\varDelta\chi_{C_6H_8,D_{6h}}=-5.75|W_1|\left(\frac{2\pi e}{hc}\right)^2,\qquad W_1\simeq W_d.$$

Eq. (4) indicates the anisotropic part for D_{2d} being weak paramagnetic and furthermore Eq. (3) represents that the anisotropy becomes more paramagnetic as δ approches to 1 over 0.4.

These results are obviously in contradiction with experiments and physical aspects. The calculated results in the case of D_4 are identical with that of D_{2d}, though the numerical values of W_d, δ, S, δ_d and θ_s are different from those in D_{2d}. Considering the above discussions both of Langevin's theory and London's method in the original form cannot explain the small diamagnetic anisotropy of C. O. T. quantitatively or even qualitatively. The question why the London's method cannot apply to this molecule with his original procedure is remained unsolved and under investigation.

Summary

We have obtained -53.9×10^{-6} at 30° as the molecular diamagnetic susceptibility of purified cycloöctatetraene, and its temperature dependence exceeding 0.5 percent over the temperature range 30° to 80° has not been detected. The diamagnetic anisotropy of this molecule has been estimated -12.6×10^{-6} per mole on some assumptions, and the resonance energy 2.9 kcal. per mole from the thermal data.

The relationship between the small anisotropy and the weak resonance character of this

molecule has been discussed and explained qualitalively on the basis of the quantum mechanical considerations. Langevin's theory and the original procedure of London's method have been found to be unsuitable for the explanation of this small anisotropy.

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