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DIAMAGNETIC ANISOTROPY AND MOLECULAR STRUCTURE OF ISOMORPHOUS TRIHALOGENBENZENIC CRYSTALS

MOHAMED GAAFAR

Physics Department, Faculty of Science, Alexandria University, Egypt

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Measurements of the crystal diamagnetic susceptibilities of isomorphous trihalogenbenzenic crystals $C_6H_3X_3$ (X = Cl, Br) of orthorhombic structure are reported. Molecular components, as diagonal values in crystal molecular tensor relation are deduced and their variancies are discussed. The measurements show that the molecular structure of these related crystals is of layer type, the molecules being planar in the vicinity of the (001) plane. Effects of partial substitution of halogen ions on the magnetic properties and on the packing forces of these crystals are also discussed. Reduction of the molecular anisotropies were observed and reduction of the molecular orbital areas were expected.

1. Introduction

Anisotropy properties may often be used to give direct information about the general features of structure of molecular crystals [1–3]. In some cases this information can be obtained directly from X–ray diffraction data. In some other cases , the "trial and error" structure has been obtained by an intensive study of the X-ray data, which is difficult problem involving much time and work. Any independent physical method, which indicates the approximate configuration and orientation of the molecules in the crystal is, therefore, greatly welcome. In the present measurements, a pair of isomorphous trichloro- and tribromobenzenic molecular crystals were investigated. These related crystals are of orthorhombic structure [4], with the space group $p2_12_12_1z = 4$.

The present work shows that a knowledge of the diamagnetic anisotropies of these crystals may give information concerning the configuration and orientation of the molecules and also the effect of halogen substitution on their magnetic properties.

2. *Experimental*

2.1. *Samples and measurement*

Pure crystals isomorphous pair 1,3,5 tribromobenzene $C_6H_3Br_3$ (denoted by TBB) and 1,3,5 trichlorobenzene $C_6H_3Cl_3$ (denoted by TCB) were crystallized using ethyl alcohol. They are soft needles along the [001] axis [4]. As these materials easily react with water, they stored in glass tubes and manipulated in a dry box. This was a difficult task during the measurements which were carried out in the shortest possible time. TBB crystal has the density $\rho = 2.659$ g/cm^3 and molecular weight 314.70 mols, while for the TCB crystals $\rho = 1.680$ g/cm^3 and molecular weight is 181.35 mols. Two crystals of each compound of weights varying between 8.0 and 12.0 mg were used. The measurements were carried out using the suspended method described elsewhere [1]. In this method, the crystal was suspended along one of its principal axes by very fine quartz fibre at the central point of the uniform magnetic field to avoid any complications due to lateral forces acting on the crystal. The upper end of the fine quartz fibre was attached to the center of a graduated torsion head which was used to measure the twisting angle of the quartz fibre at the balance point between the restoring couple due to the field and the crystal anisotropy. The quartz fibre was calibrated using triphenylbenzene crystal of known diamagnetic susceptibility as standard sample. The absolute accuracy of the measurements was about 2%, determined by the reproducibility in the adjustment of the sample to the place where the measurement was made.

The measurements were carried out on each of the crystals for at least three different orientations, in order to calculate the crystal magnetic anisotropies and to compare the calculated and the observed values. Each crystal was weighed accurately just before and immediately after the magnetic measurements in order to detect any volatilization of the crystal due to its rapid rotation during the experiment, and the loss of weight was subsequently checked. The sensitivity of the measuring system is approximately 10^{-6} cm^3/mole.

2.2. *Molecular values and their variances*

One should note that small experimental error in the measurements of the crystal diamagnetic susceptibilities and anisotropies may lead to relatively large uncertainties in the calculated molecular diamagnetic susceptibilities and anisotropies.

Therefore, corrections of the molecular values are very important in order to give correct information about the molecular structure. Study of diamagnetic susceptibility χ of orthorhombic crystals is based on the determination of the crystal anisotropies, $\chi_a - \chi_b = A$ and $\chi_a - \chi_c = B$, where A and B are the anisotropy values when the crystal is suspended along the c-axis and b-axis, respectively. Making use of the relations:

$$\chi_a + \chi_b + \chi_c = C \tag{1}$$

where $\chi_M = C/3$ is the gram molecular susceptibility measured by the Gouy powder method, which is described elsewhere [5], the values of χ_a, χ_b and χ_c are deduced. The molecular diamagnetic susceptibilities K_L, K_M and K_N are deduced from the relations:

$$\begin{pmatrix} \chi_a \\ \chi_b \\ \chi_c \end{pmatrix} = \begin{pmatrix} \alpha_1^2 & \alpha_2^2 & \alpha_3^2 \\ \beta_1^2 & \beta_2^2 & \beta_3^2 \\ \gamma_1^2 & \gamma_2^2 & \gamma_3^2 \end{pmatrix} \begin{pmatrix} K_L \\ K_M \\ K_N \end{pmatrix} \tag{2}$$

where α_i, β_i and γ_i are the direction cosines of the molecular principal axes with respect to the crystal axes. Substituting χ_a, χ_b and χ_c in Eq. (2) we get:

$$K_{L,M,N} = \frac{1}{3D}\left[(a_i - 2b_i + c_i)A + (a_i + b_i - 2c_i)B + (a_i + b_i + c_i)C\right]. \tag{3}$$

The variances of these values are:

$$\sigma^2 K_{L,M,N} = \frac{1}{9D^2}\left[(a_i - 2b_i + c_i)^2\sigma^2 A + (a_i + b_i - 2c_i)^2\sigma^2 B + (a_i + b_i + c_i)^2\sigma^2 C\right]$$

where

$$D = \begin{vmatrix} \alpha_1^2 & \alpha_2^2 & \alpha_3^2 \\ \beta_1^2 & \beta_2^2 & \beta_3^2 \\ \gamma_1^2 & \gamma_2^2 & \gamma_3^2 \end{vmatrix}$$

and

$$a_i = \beta_j^2\gamma_k^2 - \gamma_j^2\beta_k^2,$$

$$b_i = \gamma_j^2\alpha_k^2 - \alpha_j^2\gamma_k^2,$$

$$c_i = \alpha_j^2\beta_k^2 - \beta_j^2\alpha_k^2$$

with

$(i = 1,\, j = 2,\, k = 3)$ along L-direction,
$(i = 2,\, j = 3,\, k = 1)$ along M-direction,
$(i = 3,\, j = 1,\, k = 2)$ along N-direction.

Also, the variance of the molecular anisotropy:

$$\Delta K = \frac{K_L + K_M}{2} - K_N \tag{4}$$

is given by:

$$\begin{aligned}
\sigma^2(\Delta K) &= \frac{1}{9D^2}\left\{\left[\frac{1}{2}(a_1 - 2b_1 + c_1) + \frac{1}{2}(a_2 - 2b_2 + c_2)\right.\right. \\
&- \left.(a_3 - 2b_3 + c_3)\right]^2 \sigma^2 A + \left[\frac{1}{2}(a_1 + b_1 - 2c_1)\right. \\
&+ \left.\frac{1}{2}(a_2 + b_2 - 2c_2) - (a_3 + b_3 - 2c_3)\right]^2 \sigma^2 B \\
&+ \left.\left[\frac{1}{2}(a_1 + b_1 + c_1) + \frac{1}{2}(a_2 + b_2 + c_2) - (a_3 + b_3 + c_3)\right]^2 \sigma^2 C\right\}.
\end{aligned}$$

The case when large molecular susceptibility variances accur is when the ratios of the direction cosines nearly satisfy the relation $\alpha_1^2 : \beta_1^2 : \gamma_1^2 \approx \alpha_2^2 : \beta_2^2 : \gamma_2^2$ i.e. when the denominator determinant D is very small and consequently the variances are large.

3. Results and discussion

The crystal diamagnetic anisotropies of the isomorphous trichloro- and tribromobenzene were measured. The results are listed in Table 1.

TABLE 1.
Crystal diamagnetic anisotropies (in units of 10^{-6} cm^3/mole*).*

Crystal	Crystal anisotropy		
	$\chi_b - \chi_a$	$\chi_a - \chi_c$	$\chi_b - \chi_c$
TBB	10.96 ± 0.08	28.90 ± 0.38	39.86 ± 0.15
TCB	11.16 ± 0.06	25.36 ± 0.36	36.51 ± 0.18

To get the values of the crystal diamagnetic susceptibilities χ_a, χ_b and χ_c relation (1)

$$\chi_{M} = \frac{1}{3}\left(\chi_a + \chi_b + \chi_c\right)$$

was used, where χ_M was measured several times by the familiar Gouy powder method. The results are listed in Table 2.

TABLE 2.
Crystal diamagnetic susceptibilities (in units of -10^{-6} cm^3/mole).

Crystal	Crystal anisotropy			Mean value
	χ_a	χ_b	χ_c	χ_M
TBB	124.99 ±1.03	114.03 ± 0.84	153.89 ± 1.32	130.97 ± 0.91
TCB	108.28 ± 0.98	97.13 ± 0.72	133.64 ± 1.14	113.02 ± 0.87

The results show small axial anisotropy ($\chi_a - \chi_b$) in the (001) plane and large χ_c in the normal direction. This behaviour suggests, however, that the mean molecular plane lies nearer to the (001) plane in each of these compounds. Intense X-ray reflection near the (001) plane [4], may confirm this result. The value of the small inclined angle of the mean molecular plane to (001) plane in the two compounds will be discussed latter. The calculated direction cosines α_i, β_i and γ_i (i =1, 2, 3) of the molecular axes L, M, N, referred to the principal axes a, b and c [4], are given in Table 3, where L joins one halogen atom to the midpoint of the other two in the molecular plane, M is normal to L in the molecular plane, N is normal to the $L - M$ plane, as shown in Fig.1.

TABLE 3.
Mean values of the direction cosines of both isomorphous TCB and TBB.

	a	b	c
L	α_1 = 0.0240 ± 0.0031	β_1 = 0.9975 ± 0.0035	γ_1 = 0.0648 ± 0.0021
M	α_2 = 0.8810 ± 0.0037	β_2 = 0.0082 ± 0.0002	γ_2 = -0.4737 ± 0.0062
N	α_3 = 0.4729 ± 0.0033	β_3 = 0.0681 ± 0.0026	γ_3 = -0.8780 ± 0.6641

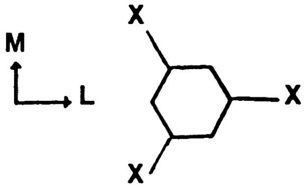

Fig.1. Structural formula of $C_6H_3X_3$ (X = Cl, Br).

The molecular diamagnetic susceptibilities K_L, K_M, K_N and anisotropy ΔK were calculated using Eqs. (3) and (4), respectively. The results are given in Table 4.

TABLE 4.
Molecular magnetic susceptibilities and anisotropies (in units of -10^{-6} cm^3/mole).

Molecule	Molecular values			Anisotropy
	K_L	K_M	K_N	ΔK
TBB	113.92 ±0.82	113.21 ± 1.02	166.02 ± 0.97	52.46 ± 0.03
TCB	97.02 ± 0.63	97.87 ± 0.71	144.31 ± 0.58	46.87 ± 0.07
Benzene*	34.59 ± 0.82	34.53 ± 0.07	95.35 ± 0.59	60.79± 0.06

* Reference [6]

It was mentioned that in the investigated crystals, the molecular planes lie in the vicinity of the (001) plane, but with different angles of inclination. The angles were deduced from relations:

$$\begin{aligned}\chi_c &= K_{\parallel}\sin^2\theta + K_{\perp}\cos^2\theta \\ &= K_{\parallel} + (K_{\perp} - K_{\parallel})\cos^2\theta\end{aligned}$$

where $K_{\parallel} = (K_1 + K_2)/2$ and $K_{\perp} = K_N$. For TBB $\theta = 28.72^o$, and for TCB $\theta = 28.50^o$, in agreement with the results obtained from X-ray measurements ($\theta \approx 27^o$) [4]. The coincidence of the maximum value of the molecular diamagnetic susceptibility in the normal direction of the molecular plane with the minimum molecular optical refractivity in that direction for these crystals [6] shows that the molecular structure may be of the layer type [7]. X-ray investigation may confirm these results [4].

Partial substitutions of halogen ions (Br or Cl) in the benzenic skeleton show different effects on the magnetic properties of these crystals. Substitution of Br ions increases the molecular diamagnetic susceptibilities more than the Cl ions do. This may be due to the difference of the spreading effect of their electron clouds [7]. Magnetic contributions of bonds C-Br and C-Cl were calculated in relation to the benzenic molecule, (see Table 4). The results are listed in Table 5, together with the contribution of these bonds to their molecular anisotropies ($K_{\parallel} - K_{\perp}$).

TABLE 5.

Molecular magnetic contribution of bonds relative to benzenic molecule (in units of -10^{-6} cm^3/mole).

Bond	Molecular components		Anisotropy
	$K_{\parallel}$	$K_{\perp}$	$K_{\parallel} - K_{\perp}$
C-Br	26.33 ±0.91	23.56 ± 0.81	2.77 ± 0.03
C-Cl	20.99 ± 0.08	16.32± 0.05	4.65 ± 0.05

On the other hand, halogen substitution leads to a reduction of molecular anisotropies and, hence, implies a force constraining π-electrons to occupy plane orbits whose effective orbital area is smaller than that of the normal area of benzene molecule. The reduction of the effective orbital area in the case of TCB is larger than that in TBB. Different degrees of packing forces were expected. Reduction of bond lengths of benzene ring would find an equivalent explanation [1]. This reduction might be a good way of measuring the degree of aromatic character of derivatives of conjugated ring compounds

4. *Conclusions*

The molecular structures of the studied isomorphous trihalogenbenzenic crystals are of layer type and the molecular plane in each of them is inclined to the (001) plane at angle $\theta \approx 28.5^o$. Substitution with Br or Cl ions cause different magnetic effects due to the difference of the spreading effect of their electron clouds.

Reduction of the molecular anisotropies leads to the reduction of molecular orbital area of π-electrons and gives information concerning the packing forces and the effect of substitution on the ring conjugation, especially when correlated with the changes in bond lengths.

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DIJAMAGNETSKA ANIZOTROPIJA I MOLEKULSKA STRUKTURA IZOMORFNIH KRISTALA TRIHALOGENBENZENA

Prikazuju se rezultati mjerenja dijamagnetske susceptibilnosti izomorfnih kristala trihalogenbenzena. Mjerenja pokazuju slojevitu molekulsku strukturu ispitivanih kristala. Raspravlja se utjecaj djelomične zamjene halogenih iona na magnetska svojstva i molekulsku strukturu tih kristala.