# Short Communications

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## Diamagnetic anisotropy of symm. $C_6H_3Br_3$, $C_6H_3Cl_3$ and of $B\text{–}B_3N_3H_3Cl_3$.

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1:3:5-$C_6H_3Cl_3$ and 1:3:5-$C_6H_3Br_3$ are isomorphous and their crystal structures have been determined by H. J. Milledge & L. M. Pant (*Acta Cryst.*, in press). The Cl compound is not very stable and the measurements of magnetic anisotropy were made on $C_6H_3Br_3$ (by E. W. Toor, using the Krishnan-Rabi method), giving

$$\chi_a-\chi_b=-9{\cdot}6,\quad \chi_a-\chi_c=26{\cdot}1,\quad \chi_b-\chi_c=35{\cdot}7$$
$$(10^{-6}\ \text{c.g.s.e.m.u.})\ .$$

Using Pascal's addition data, the mean susceptibility would be

$$\bar{\chi}=-138{\cdot}0=\tfrac{1}{3}(\chi_a+\chi_b+\chi_c)\ .$$

This would give

$$\chi_a=-132{\cdot}5,\quad \chi_b=-123,\quad \chi_c=-158{\cdot}5$$
$$(10^{-6}\ \text{c.g.s.e.m.u.})\ .$$

The direction cosines of the molecular axes $L, M, N$ are as follows ($L$ is along one Cl–Cl direction, $N$ normal to molecule):

| | | | | | |
|---|---|---|---|---|---|
| $L_a$ | 0·0235 | $M_a$ | 0·8808 | $N_a$ | —0·4731 |
| $L_b$ | 0·9976 | $M_b$ | 0·0087 | $N_b$ | 0·0685 |
| $L_c$ | 0·0645 | $M_c$ | −0·4735 | $N_c$ | −0·8784 |

From the relations

$$\chi_a=K_L(L_a)^2+K_M(M_a)^2+K_N(N_a)^2\quad \text{etc.}$$

we obtain

$$K_L=-123,\quad K_M=-122,\quad K_N=-170$$
$$(10^{-6}\ \text{c.g.s.e.m.u.})\ .$$

Hence the molecular anisotropy $\Delta K=47$, which may be compared with $\Delta K=60$ (Pacault *et al.*, 1956; Hoarau *et al.*, 1956) for benzene and $C_6(CH_3)_6$ and 40·5 for 1:4-$C_6H_4O_2$. To judge from this limited amount of evidence, the total $\pi$-electron orbital area has been reduced by partial substitution.

Owing to difficulties of manipulation the diamagnetic susceptibilities of single crystals of 1:3:5-$C_6H_3Cl_3$ have not been measured. The difference in susceptibility between 3 Br and 3 Cl, as estimated from a series of pairs of similar compounds, is about $26{\cdot}10^{-6}$. (This, however, includes a wide margin of error). On this basis the molecular susceptibilities of the Cl compound would be −97, −96, −144. This may be compared with the molecular susceptibilities of cyanuric trichloride (Lonsdale, 1936) which are −70·9, −71·2, −101·3, giving $\Delta K=30{\cdot}3$.

The diamagnetic anisotropies of *B*-trichloroborazole have also been measured by E. W. Toor. This was a difficult task, as the material easily reacts with water and has to be manipulated in a dry-box and the crystals enclosed in glass capillaries. Two specimens gave similar results, which are quoted here; a third gave entirely different values, the reason for which is not understood. The structure has been determined by Coursen & Hoard (1952).

The magnetic data are

$$\chi_b-\chi_c=13{\cdot}6,\quad \chi_a-\chi_c=9{\cdot}8,\quad \chi_b-\chi_c=3{\cdot}3\ (10^{-6})$$

but these values may be too small, on account of difficulties in the measurement of the crystal weight. Pascal's constants would give $\bar{\chi}=-103{\cdot}4$ and hence

$$\chi_a=-101{\cdot}4,\quad \chi_b=-97{\cdot}6,\quad \chi_c=-111{\cdot}2\ (10^{-6})\ .$$

From Coursen & Hoard's co-ordinates we find

| | | | | | |
|---|---|---|---|---|---|
| $L_a$ | 0 | $M_a$ | −0·8862 | $N_a$ | −0·4632 |
| $L_b$ | 1 | $M_b$ | 0 | $N_b$ | 0 |
| $L_c$ | 0 | $M_c$ | 0·4632 | $N_c$ | −0·8862 |

which give

$$K_L=-97{\cdot}6,\quad K_M=-97{\cdot}3,\quad K_N=-115{\cdot}3\ (10^{-6})$$

and hence $\Delta K=18$.

If Pascal's values of the additive constants give $\bar{\chi}$ ten per cent (say) too low, then these figures would be changed to −107·9, −108·0, −125·2; $\Delta K=17{\cdot}2$.

If, on the other hand, the measured crystal anisotropies are all 20 per cent too low, $K_L, K_M, K_N$ become −96·5, −96·6, −117·1 respectively and $\Delta K=20{\cdot}5$. The diamagnetic anisotropy, therefore, is about 40 per cent of that of $C_6H_3Br_3$ or about 30 per cent of that of benzene.

This, however, cannot be taken as a measure of the diamagnetic anisotropy of borazole itself, since this may well be *more* reduced by substitution than is that of benzene. In fact it seems possible that the reduction in molecular diamagnetic anisotropy might be a good way of measuring the degree of aromatic character of derivatives of conjugated ring compounds. More measurements of diamagnetic anisotropy of heavy atom compounds of known structure could usefully be made to test this suggestion.

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