CRYSTALLOGRAPHY

Intermolecular Distances and Diamagnetic Anisotropy in Crystals as Measures of the Polarity of Benzene and Borazole Substituents

THE structures of 1:3:5-trichlorobenzene and of B.B.B-trichloroborazole have been analysed, and although not isomorphous they are in many respects very similar[1,2]. Both are nearly layer structures. The direction cosines of the molecular axes L (along one Cl-Cl direction), M, and N (normal to the ring) are as follows (at 20°C.) :

		L_a +0·0368	M_a −0·9070	N_a −0·4232
$C_6H_3Cl_3$		L_b +0·9965	M_b +0·0058	N_b +0·0838
		L_c +0·0758	M_c +0·4193	N_c −0·9021
		L_a 0	M_a −0·8862	N_a −0·4632
$B_3N_3H_3Cl_3$		L_b 1	M_b 0	N_b 0
		L_c 0	M_c +0·4632	N_c −0·8862

The intramolecular distances are :

$C_6H_3Cl_3$		$B_3N_3H_3Cl_3$	
Mean Cl–Cl	5·354 A.	Mean Cl–Cl	5·498 A.
Mean Cl–C	1·711 A.	Mean Cl–B	1·753 A.
Mean C –C	1·387 A.	Mean B–N	1·415 A.

Both molecules are plane to within the limits of experimental error, and the rings are regular hexagons to within 0·04 A. in bond-lengths, and 2·5° in bond-angles.

Coursen and Hoard[2] have argued, on the basis of the above bond-lengths, that B-trichloroborazole shows no evidence for any reduction in the double-bond character of the ring in favour of a large contribution from a structure of type II such as was suggested by Wiberg[3] and supported by the spectral studies of Rector, Schaeffer and Platt[4].

(I)   (II)
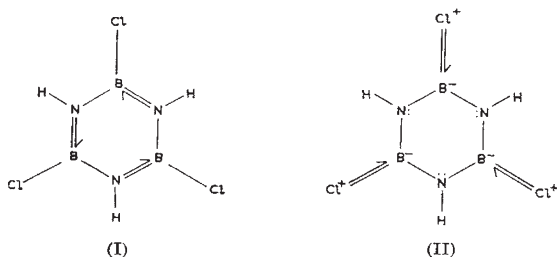
If the intermolecular distances are compared, however, it will be seen that in spite of the close similarity in the structures, there is an unexpected difference in the nearest Cl–Cl′, Cl–H′ and H–H′ distances in the two structures.

$C_6H_3Cl_3$ Cl–Cl′:   3·628, 3·650, 3·749, 4·042 A.
             Cl–H′:   2·963, 2·968, 2·984 A.
             H–H′:   2·647 A.

$B_3N_3H_3Cl_3$ Cl–Cl′:   4·020, 4·054, 4·247, 4·301 A.
             Cl–H′:   2·484, 2·524 A.
             H–H′:   2·810 A.

The implication of this would seem to be that both Cl and H atoms are charged in the trichloroborazole molecule, with a corresponding reduction in the double-bond character of the ring, in spite of the short B–N distance ; that is, that there is a larger contribution from (II) than would be expected on the basis of intramolecular distances only.

That the borazole ring in this structure has considerably less double-bond character than has the benzene ring is also supported by measurements of the

diamagnetic anisotropy, made by Mrs. E. W. Toor[5]. These lead to a molecular anisotropy of $\Delta K = 18 \times 10^{-6}$ as compared with 60×10^{-6} for benzene. The corresponding measurements on $C_6H_3Cl_3$ have not been made, but those on the isomorphous $C_6H_3Br_3$ give $\Delta K = 47 \times 10^{-6}$. From this it would seem that there is some reduction in the aromatic character of benzene also on substitution. The only other partially substituted benzene derivative for which both an accurate structure analysis and diamagnetic susceptibilities are available is $1:4C_6H_4O_2$, for which $\Delta K = 40·5 \times 10^{-6}$. It would be very desirable indeed to have more measurements on such compounds and also to be able to compare intermolecular distances in cases where the packing seems to depend more on Cl–Cl′, H–H′ and Cl–H′ than on C–C′, C–Cl′ or C–H′ distances.

It may even be possible to determine whether substituent atoms are charged positively or negatively, by forming mixed crystals with compounds of known electronic constitution, and observing the resulting intermolecular distances.

<div align="right">KATHLEEN LONSDALE</div>

University College,
London, W.C.1.
Aug. 20.

[1] Milledge, H. J., and Pant, L. M. (in preparation).
[2] Coursen, D. L., and Hoard, J. L., *J. Amer. Chem. Soc.*, **74**, 1742 (1952)
[3] Wiberg, E., unpublished report, referred to by Coursen and Hoard.
[4] Rector, C. W., Schæffer, G. W., and Platt, J. R., *J. Chem. Phys.*, **17**, 460 (1949).
[5] Lonsdale, K., and Toor, E. W. (unpublished work).

Influence of the Size of the Halogen Atom on the Difference between Lattice Constants of Copper dipyridine dichloride and dibromide

IN verifying the validity of Peyron's and Jörgensen's rule in organic halogen complexes of copper, Serátor[1] found that a compound intermediate between $CuPy_2Cl_2$ and $CuPy_2Br_2$ exists. Crystallochemical studies of these compounds were based on the crystal structure of $CuPy_2Cl_2$, which has been solved by Dunitz[2]. We have solved the crystal structure of the bromine derivative[3].

$CuPy_2Br_2$ and $CuPy_2Cl_2$ have very similar structures. Both are monoclinic (space group $P2_1/n$) with octahedral co-ordination of halogens and nitrogens around copper atoms ; the co-ordination octahedra, with shared edges, are oriented in the direction of the growth axis of the needle-formed crystals. The difference between these compounds lies in the position of halogens, the orientation of the symmetry elements with respect to the lattice vectors and, of course, in the values of the lattice constants (Fig. 1).
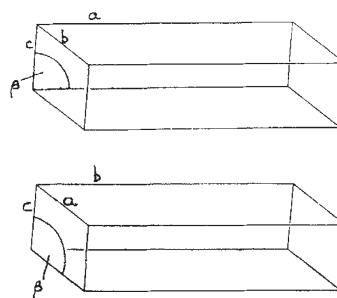

Fig. 1. A comparison of the lattice constants of $CuPy_2Cl_2$ and $CuPy_2Br_2$. Top, $CuPy_2Cl_2$, $P2_1/n$. a, 17·00 kX; b, 8·59 kX; c, 3·87 kX; β, 91°52′. Bottom, $CuPy_2Br_2$, $P2_1/n$. a, 8·30 kX; b, 17·72 kX; c, 4·04 kX; β, 96°.