

Structure of the Crystalline Compound Benzene-Bromine (1:1)

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Several models have been suggested for the complexes between benzene and halogen molecules known to exist in solutions, one of which, the "axial" model, has the halogen atoms situated on the six-fold axis of the benzene molecule, the symmetry being C_{6v} .

In order to gain some direct experience regarding the structure of complexes containing aromatic hydrocarbons and halogens we have tried to prepare solid compounds and to investigate the crystals by X-rays. In the case of benzene we obtained single crystals of a 1:1 compound with bromine (m.p. -14°C) which were studied at temperatures between -40° and -50°C . Crystals having one of their chief crystallographic axes approximately parallel to the capillary tube in which they were grown were chosen for exposure in a Weissenberg camera. The (monoclinic) axes are $a = 7.75$; $b = 8.83$; $c = 5.94$; $\beta = 99.3^{\circ}$. From observed extinctions all space groups but $C2/m$, $C2$ and Cm could be excluded. Assuming a reasonable value of the density it follows that two molecules of either kind are contained in the unit cell. Suggesting the most symmetrical group $C2/m$ to be the correct one, the parameters of the bromine atoms were worked out from Patterson projections and trial and error computations.

A very satisfactory agreement between observed and calculated intensities was thus obtained. From the coordinates of the bromine atoms alone Fourier maps giving projections of the structure along the a and c axes were computed. Although all structure factor signs were computed neglecting the lighter atoms, the resultant charts turned out to contain, besides the heavy peaks corresponding to the bromine atoms, lower peaks allowing the localisation of the carbon atoms also with some degree of accuracy. The final maps are reproduced in Fig. 1 (a) and (c). No spurious peaks are

observed and termination of series effects are small due to strong thermal vibrations resulting in an unusually marked fall in intensities for larger θ values.

The bromine-bromine distance found is 2.28 \AA and appears therefore to be very nearly the same as observed in the free molecule. The line joining the two bromine atoms is parallel to $[101]$ and passes through the symmetry centre of the benzene ring. The angle between this direction and the benzene plane is at least very nearly 90° . The distance from each bromine atom to the adjacent benzene plane is 3.36 \AA . It is interesting to note that the π electrons of all six C—C bonds must be equally involved in formation of the electron transfer bond. This is not necessarily so, of course, in the case of the 1:1 complex present in solutions. Here a somewhat stronger binding may possibly result if the axis of the bromine molecule is parallel to the benzene plane. The symmetrical chains of alternating benzene and bromine molecules and the fact that both atoms of a bromine molecule take part in bond formation provide an interesting analogy to the structure of the dioxan-bromine compound.

The very marked drop in X-ray intensities for increasing reflexion angles, in fact more marked than in any addition compound so far examined, indicates the weakness of the binding forces between the two components. The amplitudes of vibration appear to be particularly large in directions perpendicular to the direction of the molecule chains — $[101]$. This may indicate either that the potential energy of the bromine atom has only one very flat minimum for a position on the chief axis of the benzene ring or perhaps six minima outside this axis.

The computed "reliability factor" R (taking into account the anisotropic vibrations) is found equal to 0.12 for both projections reproduced in Fig. 1 (a) and (c). We think that the structure derived from our present material is certainly essentially correct, but hope to be able to supplement the investigation with material obtained at lower temperatures. Such investigations might contribute towards clearing up the question (mentioned above) regarding the potential energy curve of the bromine atom.

Received May 6, 1958.