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The Structure of Arsenobenzene

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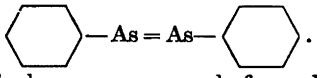
Arsenobenzene is generally formulated as:  . Double bonds, however, are rarely formed between atoms heavier than oxygen.

Lyon and Mann [1] have previously cast some doubt upon the validity of the classical formula on the basis of molecular weight determinations but no satisfactory structure of the molecule has so far been proposed.

In order to obtain a satisfactory molecular formula we are investigating the crystal structure of arsenobenzene. The compound was obtained by the reduction of phenyl arsonic acid. Two different kinds of crystals can be recognised under the polarizing microscope. One kind forms transparent needle shaped crystals which exhibit parallel extinction and are optically biaxial. The other kind of crystals are a little opaque and show oblique extinction. The transparent ones become opaque between 182°C and 192°C and melt at 196°C. The opaque crystals melt at 196°C. We have not yet proved that the transparent crystals are changed to the opaque form by heating but it appears to be likely. Chemical analysis on the mixture give the following results: C 47.60; H 3.37; calc. for $(AsC_6H_5)_n$: C 47.40; H 3.32.

Weissenberg and precession photographs proved the transparent crystals to be monoclinic. Filtered Cu-radiation was employed. The unit cell has the following dimensions, unique axis *b*, the needle axis:

$$a = 24.04 \text{ Å}$$
$$b = 6.20 \text{ Å}$$
$$c = 12.22 \text{ Å}$$
$$\beta = 111.2°$$

The following extinctions were found: $h0l$ for $h = 2n + 1$ and $0k0$ for $k = 2n + 1$. Hence the space group is $P2_1/a$. The density of the crystal is 1.73. Consequently there are 12 $As-C_6H_5$ groups in the unit cell. As the general point is four fold the $As-C_6H_5$ groups must be linked together in groups of three or of six.

The Patterson projection along the *b*-axis indicated very strongly that the molecular unit contains six arsenic atoms forming a non planar ring with a centre of symmetry. A Fourier projection based upon the As-coordinates reveals the whereabouts of the benzene rings.

On this basis we propose that arsenobenzene is $(AsC_6H_5)_6$. Each As-atom forms two single As—As bonds (approximately 2.4 Å) with its neighbours in the ring and a third As—C bond. Isomers of different conformations are possible. The opaque crystals are triclinic. They will be investigated in more detail later.

A refinement of the structure of the monolinic crystals is in progress.

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