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UNIT CELL AND SPACE-GROUP OF DIANISYLACETYLENE

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Dianisylacetylene ($CH_3OC_6H_4C$) is of interest because the substance prepared by Latif and Chowdhury[1] was obtained in two crystalline forms, A (50%) and B (14%), m.p. 145°C and 122°C respectively. These two products were tested analytically and both of them were identified as dianisylacetylene. Final confirmation was made through independent synthesis of dianisylacetylene by oxidising the dihydrozane of anisil[2] with HgO and comparing IR spectra of both A and B. The B type crystals were found to be very fine and thin, while those of A type were needle-shaped and a bit larger than those of B type. The average shape and dimensions of these crystals were as follows:

The section perpendicular to the needle axis was an irregular polygon. For A type crystal, the largest diagonal of the polygon was 0.20 mm and the length perpendicular to this was about 0.12 mm while for B type, these values were roughly 0.12 mm and 0.08 mm respectively. From the diffraction photographs, it was found that most of the A type crystals were either twinned or badly formed, but those of B type were well developed. Both types of crystals were examined under the polarising microscope and they gave straight extinctions suggestive of biaxial crystal.

A few good specimens of crystals of both the type were sorted out and the rotation and Wissenberg photographs about *a*, *b* and *c*—crystallographic axes were obtained to measure the cell dimensions and the space group. The cell is orthorhombic and its dimension came out to be exactly the same for both the types, viz.

$$a = 24.41 \pm .06\text{Å}$$
$$b = 15.72 \pm .05\text{Å}$$
$$c = 7.94 \pm .04\text{Å}$$
$$\alpha = \beta = \gamma = \pi/2$$

The density of the crystal measured by flotation is 1.12 g cm^{-3} and the density calculated for eight molecules in the unit cell is 1.11 g cm^{-3}.

Reflexions hko, hkl, hk2, hk3, hk4 and hk5 recorded in equinclination Wissenberg photographs using Cu$K\alpha$-radiation, provided the data from which the space group and structure are to be determined. The intensities of the reflexions were measured by the multiple-film technique and visual comparison with crystal reflected calibration spots of known relative exposure. The systematic absences in the X-ray reflexions (h01 for l odd, hko for h odd and okl for k odd) show that the space group is *P b c a*.

A Pattarson-map was calculated with hko reflexions, and this was used to obtain the approximate orientations of the phenyl rings and the position of the centre of the molecule. It was estimated that the molecule might not be perfectly flat in this projection and this would lie about 20° with the *a*-axis. Since there are eight molecules in the unit cell and the number of equivalent general positions in the space group *P b c a* is also eight, it was not possible from the above experimental evidence, to draw any conclusion about the symmetry of the molecule. The twinning of A type crystals of dianisylacetylene might have probably increased their melting point (145°C) than those of B type (122°C) which are all fine and well developed.

Further investigations are being carried out and the details will be published later.

References

1. A. Latif and D.N. Chowdhury, Tetrahedron Letters, **14,** 1735 (1968).
2. Org. Synth. Coll. (John Wiley, New York, 1963), vol. IV, p. 377.