LETTERS TO THE EDITORS

The Editors do not hold themselves responsible for opinions expressed by their correspondents. No notice is taken of anonymous communications

Crystal Structure of Benzene at − 3° C.

A PRELIMINARY determination[1] of the crystal structure of benzene at − 22° C. showed that the crystals are orthorhombic, space-group *Pbca*, with four centro-symmetrical molecules in the unit cell, and that the normals to the planes of the molecules are roughly perpendicular to the *b*-axis and inclined at about 50° to the *c*-axis. We have now completed the first stage of refinement of the structure at − 3° C. Crystals were grown in Lindemann glass tubes of wall thickness 0·05 mm. and bore 0·36 mm. by the method of Keesom and Taconis[2] as modified by later workers[3]. 288 independent reflexion intensities representing 56 per cent of the total possible with copper radiation were estimated visually from oscillation photographs about all three principal axes. Chromium-*K* radiation was used to obtain accurate values of the unit cell dimensions by the Straumanis method; the revised dimensions are $a = 7·46_0$, $b = 9·66_6$ and $c = 7·03_4$ A.

Adjustments to the carbon atom co-ordinates of the original analysis were first made by a Fourier transform method and by plotting difference projections on (100) and (001). The process was completed by five cycles of three-dimensional refinement on the University of Manchester electronic computor, using programmes for differential syntheses in the space-group *Pbca* prepared by Drs. F. Ahmed, D. W. J. Cruickshank and P. J. Wheatley[4]. The contribution of the hydrogen atoms to the calculated structure factors was included on the assumption that these atoms are situated at a distance of 1·08 A. radially from the carbon atoms. The values of the temperature coefficients B used for the carbon and hydrogen atoms were 6·0 and 9·0 × 10^{-16} cm.^{2} respectively. Corrections for termination of series errors were applied by the method of Booth[5]. The 'disagreement index' now stands at 14 per cent.

As the molecules are centro-symmetrical, three independent values of the C—C bond lengths and of the CCC angles are obtained from the analysis; these are :

Bond-lengths (A.)		Bond-angles	
C_1C_2	= 1·377	$C_2C_1C_2$	= 119° 28′
C_2C_3	= 1·382	$C_1C_2C_3$	= 120° 49′
C_3C_4	= 1·374	$C_2C_3C_4$	= 119° 42′
Mean	= 1·378	Sum	= 359° 59′

The mean standard deviation[6] of the atomic co-ordinates is 0·0057 A.; the standard deviation of the C—C bond-length after allowing for internal correlation is $0·0057/\sqrt{3}$ or 0·0033 A. The small differences between the three independent bond-lengths are thus not significant; but there appears to be a significant difference between our mean value of 1·378 A. and the preliminary value of 1·396–1·401 A. obtained by Stoicheff[7] from his measurements on the Raman spectrum of the vapour at 61° C.

The best plane through the molecule is :

$$0·7109x + 0·2229y + 0·6671z = 0,$$

the origin being at the centre of symmetry and the co-ordinates (x, y, z) in angström units. The per-pendicular distances of the carbon atoms from this plane are :

$$C_1 − 0·0015, \quad C_2 + 0·0015, \quad C_3 − 0·0015 A.,$$

showing that the molecule is accurately planar. The normal to the molecular plane is inclined at 77° to the *b*-axis and 48° to the *c*-axis.

Further work is now in progress to locate the hydrogen atoms, and it is proposed to extend the investigation to lower temperatures.

E. G. COX
J. A. S. SMITH

Department of Inorganic and
Structural Chemistry,
The University, Leeds 2.
Nov. 23.

[1] Cox, E. G., *Proc. Roy. Soc.*, A, **135**, 491 (1932).
[2] Keesom, W. H., and Taconis, K. W., *Physica*, **2**, 463 (1935).
[3] Kaufman, H. S., and Fankuchen, I., *Rev. Sci. Instr.*, **20**, 733 (1949). Abrahams, S. C., Collin, R. L., Lipscomb, W. N., and Reed, T. B., *Rev. Sci. Instr.*, **21**, 396 (1950).
[4] Ahmed, F., and Cruickshank, D. W. J., *Acta Cryst.*, **6**, 765 (1953).
[5] Booth, A. D., *Proc. Roy. Soc.*, A, **188**, 57 (1946).
[6] Cruickshank, D. W. J., *Acta Cryst.*, **2**, 65 (1949).
[7] Stoicheff, B., *J. Chem. Phys.*, **21**, 1410 (1953).

Effect of a Citrate Ion Impurity on the Size and Shape of Calcium Phosphate Crystals

IT is commonly observed that a change in the size and shape of a crystal occurs when an impurity is added to the solution from which the crystal is grown. One such change, or habit modification, is that of crystals of gypsum (calcium sulphate), which in the presence of sodium citrate change from long needles to short stubby rods[1]. The mechanism of such habit modification of crystals is obscure, but the impurity is believed to be adsorbed on the surfaces of the growing crystal, and thus to cause an alteration in their rates of growth which results in the observed change in size and shape. Since the calcium and citrate ions associate in solution to form a complex, it was possible that other calcium compounds than gypsum adsorb the citrate ion, leading to habit modification of their crystals. In fact, the surface of the calcium phosphate crystals in bone has been supposed to be the site of the bone citrate[2]. It is therefore of interest to investigate the effect of citrate on the growth of calcium phosphate crystals.

To prepare calcium phosphate crystals[3], a 0·1 M phosphate solution at pH 7·4 is obtained by mixing 789 ml. of 0·1 M disodium hydrogen phosphate with 211 ml. of 0·1 M dihydrogen sodium phosphate solution. On the addition of this phosphate solution to a 0·1 M solution of calcium chloride, a white precipitate is formed throughout the solution. After approximately an hour, however, the solution clears, the precipitate having fallen down as small tabular crystals of about 1 mm. in length (Fig. 1). The rate at which the precipitate crystallizes out of the solution appears to be dependent on the ratio of dibasic to monobasic sodium phosphate, that is, on the pH of the phosphate solution ; the higher the pH, that is, the higher the concentration of dibasic sodium phosphate, the slower is the rate of crystallization and the greater the amount of precipitate formed. The crystals, however, remain the same in size and shape. The pH selected was 7·4. This is convenient because the crystals are formed in good quantity and fairly rapidly. In addition, this is the pH of the blood.