Acta Cryst. (1954). **7**, 117

The Crystal Structure of 1.3.5-Triphenylbenzene

BY M. SHEHATA FARAG

Department of Crystallography, University College, London W.C. 1, England

(*Received* 15 *August* 1953 *and in revised form* 25 *September* 1953)

1.3.5-Triphenylbenzene crystals are orthorhombic hemihedral, space group $Pna2_1$, $7{\cdot}47 \times 19{\cdot}66 \times 11{\cdot}19$ Å^3, $M = 306{\cdot}14$, $\varrho = 1{\cdot}221$ g.cm.$^{-3}$, $N = 4$. The structure was solved by trial-and-error methods and then by two- and three-dimensional Fourier syntheses. The molecules, which form an approximately layer arrangement, are not planar, the substituted phenyl groups being twisted about the formal single bonds by (+34°, −27°, +24°) ±2° respectively, out of the plane of the central ring. The average C–C bond length in the rings is 1·39±0·03 Å and between rings it is 1·50±0·03 Å. The physical properties of the crystal may be explained in terms of the structure.

Introduction

1.3.5-Triphenylbenzene crystals, melting at 169°–170° C. can be grown to almost any desired size by slow evaporation of a solution in ether or ether+alcohol. Groth (1919) reports Knopp & Arzruni as finding that the class is orthorhombic holohedral, with $a:b:c = 0{\cdot}5662:1:07666$, and an imperfect (001) cleavage. Orelkin & Lonsdale (1934), however, showed that the crystals are pyro-electric, the original a axis being the polar direction. By X-ray measurements they also showed that the original c axis should be halved. They therefore re-orientated the unit cell to make the polar axis the c direction and their measurements ($a = 7{\cdot}55$, $b = 19{\cdot}76$, $c = 11{\cdot}22$ Å) gave axial ratios $a:b:c = 0{\cdot}382:1:0{\cdot}568$. The true class is orthorhombic hemihedral ($mm2$) and the space group, as determined by systematic absences, is $Pna2_1$. The structure is approximately a layer one, with four molecules lying in or near to the (200) planes.

Krishnan & Banerjee (1934) found the following values for the diamagnetic susceptibilities of the crystal:

$$\chi_a = -313\times10^{-6},\ \chi_b = -155\times10^{-6},\ \chi_c = -140\times10^{-6}\ \text{c.g.s.e.m.u.},$$

using the new axes. It was clear from these measurements that the molecules, if plane, could not be exactly parallel to the (200) planes, but Lonsdale (1937), on the basis of both X-ray and magnetic measurements, suggested that the three phenyl groups must be twisted out of the mean molecular plane by angles of about 25°, and that the molecules as a whole must also be inclined to the (200) planes, one of the benzene–phenyl bonds lying along the [001] direction (Fig. 1).

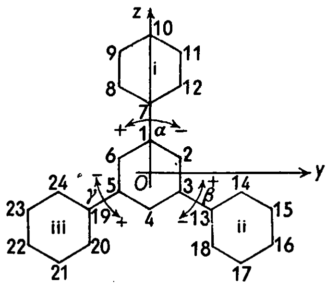


Fig. 1. Formal method of numbering the atoms of 1.3.5-triphenylbenzene used in this paper.

Present investigation

The preliminary X-ray measurements, using Cu $K\alpha$ radiation and very small undistorted crystals, chosen by examination in polarized light and by Laue photographs, confirmed Lonsdale's choice of axes and gave

$$a = 7{\cdot}47\pm0{\cdot}02,\quad b = 19{\cdot}66\pm0{\cdot}05,\quad c = 11{\cdot}19\pm0{\cdot}03\ \text{Å}\,.$$

The crystals gave a small, but positive, piezo-electric effect as well as a pyro-electric effect (about 20 times the spurious effect found for NaCl) and the space group was confirmed as $Pna2_1$. The density was measured by suspension in a solution of NaCl and found to be 1·221 g.cm.$^{-3}$, which, with the molecular weight 306·14, gives 3·95 (4) molecules per unit cell. An attempt to confirm the hemihedry by statistical intensity-distribution tests on various zones failed; probably because, although the crystal is non-centrosymmetric, the phenyl groups are themselves centrosymmetrical and exercise a compensating effect, both individually and in their general grouping.

Patterson projections, based on oscillation and Weissenberg photographs, with visual estimation of intensities, showed clearly that the structure is of a layer type. The ($hk0$) Patterson projection showed strong peaks which clearly corresponded to intermolecular vectors and which limited the y co-ordinates of the 'centres' of the molecules to certain possible values. The ($0kl$) projection, which was the nearest to the mean molecular planes, showed that some of the intramolecular bonds are parallel to the polar axis [001] and others at approximately 30° and 60° to it. There are, however, other peaks at 7°, 18°, 23°, 43°, 52°, ...

Table 1. *Atomic co-ordinates*

Carbon atom number	x (Å)	y (Å)	z (Å)	x/a	y/b	z/c
1	1·61	3·32	1·22	0·216	0·169	0·109
2	1·63	4·51	0·52	0·218	0·229	0·046
3	1·87	4·51	−0·85	0·250	0·229	−0·076
4	2·13	3·32	−1·51	0·285	0·169	−0·135
5	2·09	2·12	−0·80	0·280	0·108	−0·071
6	1·89	2·15	0·56	0·253	0·109	0·050
7	1·34	3·32	2·71	0·179	0·169	0·242
8	0·65	2·23	3·29	0·087	0·113	0·294
9	0·36	2·23	4·66	0·048	0·113	0·416
10	0·83	3·32	5·42	0·111	0·169	0·484
11	1·61	4·35	4·86	0·216	0·221	0·434
12	1·80	4·35	3·49	0·241	0·221	0·312
13	1·87	5·80	−1·61	0·250	0·295	−0·144
14	2·25	6·99	−0·96	0·301	0·356	−0·086
15	2·19	8·18	−1·66	0·293	0·416	−0·148
16	1·90	8·19	−3·02	0·254	0·417	−0·270
17	1·62	7·00	−3·67	0·217	0·356	−0·328
18	1·58	5·81	−2·96	0·212	0·296	−0·265
19	2·39	0·85	−1·50	0·320	0·043	−0·134
20	2·16	0·75	−2·87	0·289	0·038	−0·256
21	2·37	−0·45	−3·53	0·317	−0·023	−0·315
22	2·89	−1·54	−2·82	0·387	−0·078	−0·252
23	3·10	−1·44	−1·43	0·415	−0·073	−0·128
24	2·83	−0·24	−0·79	0·379	−0·012	−0·071

showing either that the molecule is not planar or that it is tilted to (200) or both.

Although the Patterson projections did give valuable information about the structure, they were not adequate for the immediate suggestion of a structure accurate enough for refinement. A near approximation to the atomic positions was therefore obtained by trials based on the Patterson projections and on considerations of packing.

In the systematic trials CH groups were assumed to be atoms of atomic number 7 and the atomic scattering curve given for anthracene by Robertson, Mathieson & Sinclair (1950) was used. When reasonable values of the parameters were found, these were used in calculating the phase angles and the latter were combined with the observed $|F|$ values to obtain Fourier projections, which were then refined by repeated approximations.

The trials were carried out mainly on the ($0kl$) projection, but this alone could not fix the x_0 co-ordinate, nor the senses of the angles of twist of the phenyl groups. There was a great deal of overlapping in the ($hk0$) and ($h0l$) projections, but the higher orders in these zones and some of the general reflexions (hkl) were found to be very sensitive to variations in certain of the parameters. When a satisfactory agreement had been obtained for the two-dimensional projections, three-dimensional line syntheses were made through 14 of the carbon atoms to check the x co-ordinates of the atoms and, in particular, to confirm the senses of the angles of twist, trials having already indicated that packing considerations must rule out a propeller-shaped molecule having α, β, γ all in the same sense. The co-ordinates of the centre x_0, y_0, z_0 of one molecule as determined by trial and after refinement are as follows:

	x_0	y_0	z_0
By trial	1·87 Å	3·22 Å	−0·14 Å
After refinement	1·87 Å	3·32 Å	−0·12 Å
In fractional co-ordinates	0·250	0·169	−0·011

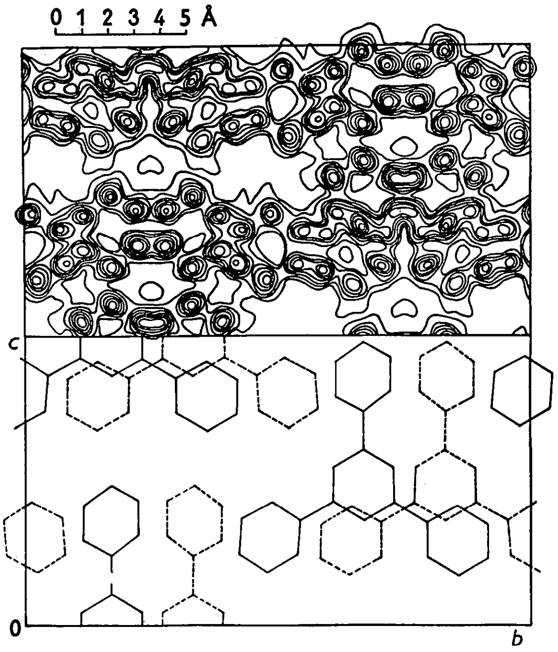
The centres of the remaining three molecules in the unit cell are at

$$(\bar{x}_0, \bar{y}_0, \tfrac{1}{2}+z_0), \quad (\tfrac{1}{2}+x_0, \tfrac{1}{2}-y_0, z_0), \quad (\tfrac{1}{2}-x_0, \tfrac{1}{2}+y_0, \tfrac{1}{2}+z_0)\,.$$

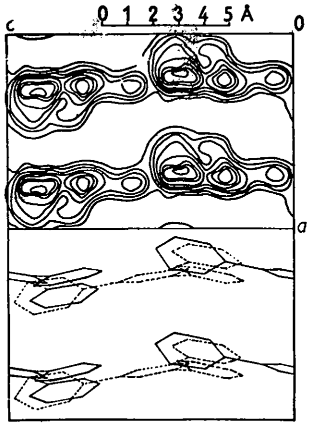
The three-dimensional line syntheses did confirm that the sense of the angle of twist β was opposite to that of α and γ (Fig. 1).

The primary error in the three-dimensional syntheses is the finiteness of summation since, owing to the laboriousness of the phase calculations, only 42% of all observed reflexions were used. The final co-ordinates of the atoms of one molecule are given in Table 1 and the three axial Fourier projections are shown in Fig. 2. The final x co-ordinates are adjusted to correspond, as nearly as possible, to plane, hexagonal phenyl groups, within the limits of experimental error.

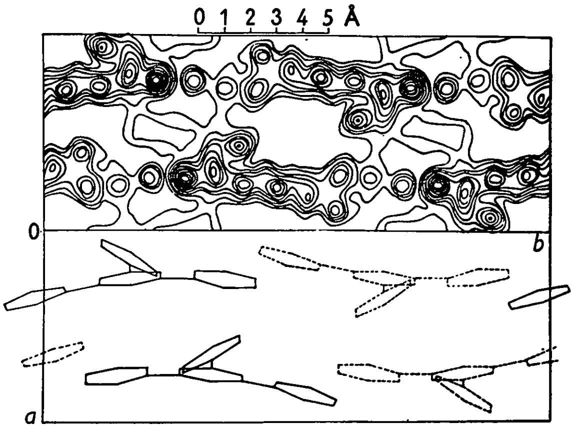
An estimation of the temperature factor for each zone by a comparison of $\Sigma|F_c|$ and $\Sigma|F_o|$ for various $\sin\theta$ groups showed that Robertson's experimental f curve for anthracene (which already included a temperature factor) suited the ($0kl$) zone reasonably well if a small extra temperature correction were made, but that the ($hk0$) and ($h0l$) zones needed a larger temperature correction. After allowing for this extra temperature correction in the ($hk0$) and ($h0l$) zones the reliability factors were: $R(0kl) = 0{\cdot}20$, $R(h0l) = 0{\cdot}23$, $R(hk0) = 0{\cdot}25$, $R(hkl) = 0{\cdot}23$.



(a)



(b)



(c)

Fig. 2. (a) Electron density projected along [100]. The contours are drawn at equal intervals of 1 e.Å^{-2}, the first contour being omitted. The molecules shown in full lines in the key diagram form one layer at $x = \frac{1}{4}$ and those in broken lines form another layer at $x = \frac{3}{4}$. (b) Electron density projected along [010]. The contours are drawn at equal intervals of 3 e.Å^{-2}, the first being omitted. There is a separation of $\frac{1}{2}b$ between the centres of the molecules shown in full and broken lines. (c) Electron density projected along [001]. The contours in this centrosymmetrical projection are drawn at equal intervals of 2 e.Å^{-2}, the first two contours being omitted. There is a separation of $\frac{1}{2}c$ between the centres of the molecules shown in full and broken lines.

All reflexions were included in the axial zones, but only the strongest 42% of the *hkl* reflexions. According to Wilson (1950) and to Phillips, Rogers & Wilson (1950), it is to be expected that the reliability factor for the centrosymmetrical (*hk*0) zone will have a higher numerical value.

Lists of observed and calculated structure factors have been given by Farag (1953) or may be obtained on application to the author.

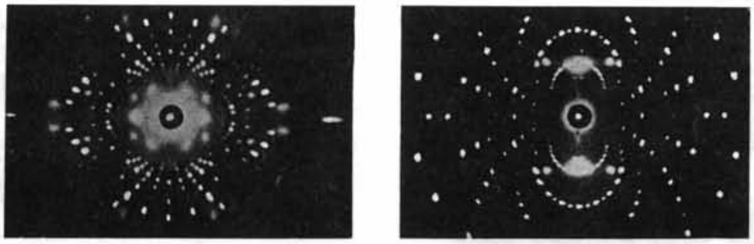
Discussion of the structure

Fedorov (1920) pointed out that 1.3.5-triphenylbenzene, although orthorhombic, is pseudo-hexagonal or pseudo-trigonal, with the present *a* axis as the unique direction, and with $b:c \doteqdot \sqrt{3}:1$. In fact the (200) *layers* are indeed nearly trigonal, the molecules themselves being pseudo-trigonal and the co-ordinates of the centres of the molecules in one layer (at $x = \frac{1}{4}$) being

$$\tfrac{1}{4}, \tfrac{1}{6}, 0;\ \tfrac{1}{4}, \tfrac{4}{6}, \tfrac{1}{2};\ \tfrac{1}{4}, \tfrac{1}{6}, 1\,.$$

The next layer, however, is displaced by $(\frac{1}{2}, \frac{1}{6}, 0)$, which destroys the trigonal symmetry of the whole structure. The thermal diffuse scattering does show pseudo-trigonal symmetry, although the ordinary Laue photograph with the X-rays along [100] does not (Fig. 3(*a*)). It is of particular interest, however, that the strong diffuse spots corresponding to thermal reflexion from the (002) plane, which is parallel to the X-ray beam in Fig. 3(*a*), disappear completely when the crystal is rotated so that the X-rays lie along [010] (Fig. 3(*b*)), even though the (002) plane is still parallel to the X-ray beam. This indicates that the thermal waves affecting the (002) planes are strongly unidirectional; their wave-fronts are parallel to [010] and perpendicular to [100], indicating that the intermolecular bonds parallel to [010] are stronger than those parallel to [100]; this is reasonable, for the latter bridge the layers and are relatively easily broken. (It will be remembered that the imperfect cleavage is normal to [100] in the present unit-cell orientation.)

The diffuse spots corresponding to thermal vibrations affecting the (200) planes are very large and intense in all orientations of those planes, which signifies that all the bonds in the (200) planes are



(a) (b)

Fig. 3. (a) Laue photograph. X-ray beam along [100]; [010] vertical. Note the strong (002) diffuse reflexions on the equatorial layer line. (b) Laue photograph. X-ray beam along [010]; [100] vertical. Note that the strong (002) diffuse reflexions have completely vanished.

stronger than those normal to the (200), and transverse and longitudinal waves are both possible.

The average C–C distance in the rings is 1·39±0·03 Å, and the benzene rings themselves are planar to within ±0·08 Å; the average value for the valency angle is 120±5°.

The C–C bonds between rings in the molecule are of lengths 1·51, 1·50, 1·48 Å respectively for C_1–C_7, C_3–C_{13}, C_5–C_{19}. The corresponding angles of twist are (34°, −27°, +24°) ±2° respectively. It is tempting to relate the lengthening of the benzene–phenyl bonds with the increasing angle of twist, but in fact the differences in bond length are within the limits of experimental error and cannot be regarded as truly significant. The shortening of these bonds from the single-bond length of 1·54 Å *is* significant, however, for there are well-resolved carbon atoms limiting the over-all length of the molecule and it would not be possible to lengthen the benzene–phenyl bonds without unduly shortening the C–C bond lengths within the rings. Fig. 4 shows the intramolecular bond lengths and angles as found. The minimum intermolecular C–C distance is 3·58 Å, nearly along [100]. It will be noted that $\frac{1}{2}a = 3·74$ Å.

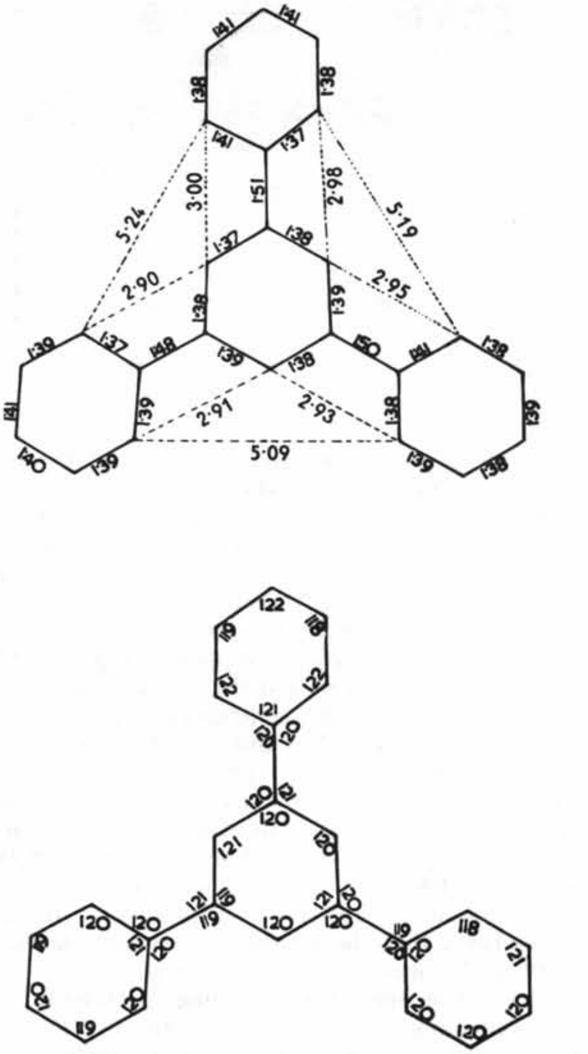


Fig. 4. Intramolecular distances (Å) and valency angles (deg.).

Comparison with electron-diffraction data

Bastiansen & Hassel (1952) have recently examined the vapour of 1.3.5-triphenylbenzene by electron-diffraction methods. They find that the average C–C distance in the ring is 1·42 Å (cf. 1·39 Å in the solid); between rings the C–C length is 1·54 Å (cf. 1·50 Å), and the twist of the phenyl groups about the formal single bonds is 46°±5°, the sense of the twists being most probably statistically + or −. The diminution of lengths and angles observed in the solid state must be related to an increase in the intramolecular forces.

Physical properties of the crystal

The *imperfection of the cleavage* is probably related to the non-planarity of the molecule and its tilt out of the layer plane. Had the molecules been planar and exactly parallel to the (200) planes, a perfect cleavage would have been expected.

The *diamagnetic susceptibilities* of the crystal may be calculated from the structure on the assumption that those of the benzene ring are known. Krishnan & Banerjee (1934) give

$$K_\perp = -37·3\times10^{-6}, \quad K_\parallel = -91·8\times10^{-6} \text{ c.g.s.e.m.u.},$$

and x, the lowering of diamagnetism due to the replacement of one hydrogen atom by half a phenyl bond, may be taken as $2{\cdot}9\times10^{-6}$ (Pascal; cf. Bhatnagar & Mathur, 1936). Then we have

$$\begin{aligned}\chi_a &= \Sigma K_1\cos^2\alpha_1+\Sigma K_2\cos^2\alpha_2+\Sigma K_3\cos^2\alpha_3\,,\\ \chi_b &= \Sigma K_1\cos^2\beta_1+\Sigma K_2\cos^2\beta_2+\Sigma K_3\cos^2\beta_3\,,\\ \chi_c &= \Sigma K_1\cos^2\gamma_1+\Sigma K_2\cos^2\gamma_2+\Sigma K_3\cos^2\gamma_3\,,\end{aligned}$$

where K_1, K_2, K_3 are the principal diamagnetic susceptibilities of any single benzene nucleus having direction cosines $\cos\alpha_1$, $\cos\beta_1$, $\cos\gamma_1$, for K_1 relative to a, b, c, etc. K_1 is taken normal to the plane of each nucleus, K_2 is taken along the direction C_1–C_4, C_7–C_{10}, C_{13}–C_{16}, C_{19}–C_{22} respectively and K_3 is normal to K_1 and K_2 in each case.

For the central nucleus

$$\begin{aligned}K_1 &= K_\perp-3x = -83{\cdot}1\times10^{-6}\,,\\ K_2 = K_3 &= K_\parallel-3x = -28{\cdot}6\times10^{-6}\,.\end{aligned}$$

For the three substituted phenyls

$$\begin{aligned}K_1 &= K_\perp-x = -88{\cdot}9\times10^{-6}\,,\\ K_2 = K_3 &= K_\parallel-x = -34{\cdot}4\times10^{-6}\,,\end{aligned}$$

and the appropriate direction cosines are given by Farag (1953) or may be calculated from the atomic co-ordinates.

Table 2 shows the agreement between the calculated and observed crystal susceptibilities.

Table 2. *Crystal susceptibilities*

	Calculated	Observed
χ_a	$-322{\cdot}9\times10^{-6}$	-313×10^{-6} c.g.s.e.m.u.
χ_b	$-151{\cdot}8$	-155
χ_c	$-138{\cdot}5$	-140
$\bar{\chi}$	$-204{\cdot}4$	-203

By consideration of the *molecular refractivities* deduced from the density and the refraction indices of the crystal, Prof. E. G. Cox (private communication) deduced that the three phenyl groups must be rotated about the formal single bonds by about ±30° out of the plane of the central nucleus. Given the structure, the molecular refractivities may be calculated from the known refractivities of the benzene molecule (Hartshorne & Stuart, 1950), if interaction is neglected. Cox has given $r_\perp = 15{\cdot}7$ cm.^{3}, $r_\parallel = 31{\cdot}4$ cm.^{3}. Using a similar procedure as for the diamagnetic susceptibilities, we find:

	Calc.	Obs.
R_a	71·0	77·6
R_b	119·7	115·0
R_c	123·5	115·5

The 'observed' molecular refractivities are obtained from the refractive indices by the formula

$$R = \frac{n^2-1}{n^2+2}\,\frac{M}{\varrho}\,,$$

where

$$M = 306{\cdot}14,\quad \varrho_{\text{calc.}} = 1{\cdot}205\ \text{g.cm.}^{-3}$$

and

$$n_a = 1{\cdot}5241,\quad n_b = 1{\cdot}8670,\quad n_c = 1{\cdot}8725$$

for the sodium D line (Groth (1919) but referred to the new axes). It will be seen that the optics are consistent not only with the layer nature of the structure, but also with the deviations of the molecule from planarity.

The author wishes to express his gratitude to Prof. Kathleen Lonsdale for advice and criticism. Thanks are also due to Prof. E. G. Cox of Leeds University for giving facilities for using the Hollerith equipment in the three-dimensional summation, and for permission to quote from a private communication.

References

Bastiansen, O. & Hassel, O. (1952). *Acta Chem. Scand.* **6**, 205.

Bhatnagar, S. S. & Mathur, K. N. (1936). *Physical Principles and Applications of Magneto-chemistry*, pp. 67–93. London: Macmillan.

Farag, M. S. (1953). Ph.D. Thesis, University of London.

Fedorov, E. S. (1920). *Das Kristallreich. Tabellen zur Kristallochemischen Analyse*. Acad. Sci. USSR.

Groth, P. (1919). *Chemische Krystallographie*, vol. 5, p. 241. Leipzig: Engelmann.

Hartshorne, N. H. & Stuart, A. (1950). *Crystals and the Polarising Microscope*, 2nd ed., p. 154. London: Arnold.

Krishnan, K. S. & Banerjee, S. (1934). *Philos. Trans.* A, **234**, 265.

Lonsdale, K. (1937). *Z. Kristallogr.* **97**, 91.

Orelkin, B. & Lonsdale, K. (1934). *Proc. Roy. Soc.* A, **144**, 630.

Phillips, D. C., Rogers, D. & Wilson, A. J. C. (1950). *Acta Cryst.* **3**, 398.

Robertson, J. M., Mathieson, A. McL. & Sinclair, V. C. (1950). *Acta Cryst.* **3**, 251.

Wilson, A. J. C. (1950). *Acta Cryst.* **3**, 397.