GELLER, S. & GILLEO, M. A. (1959). *J. Phys. Chem. Solids*, **9**, 235.

International Tables for the Determination of Crystal Structures (1935). Berlin: Borntraeger.

MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.

MERRITT, L. L. Jr., GUARE, C. & LESSOR, A. E. Jr. (1956). *Acta Cryst.* **9**, 253.

STEWART, J. M. & LINGAFELTER, E. C. (1959). *Acta Cryst.* **12**, 842.

STEWART, J. M. & LINGAFELTER, E. C. (1960). *Rev. Sci. Instrum.* **31**, 399.

STOSICK, A. J. (1945). *J. Amer. Chem. Soc.* **67**, 365.

TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 842.

TYSON, G. N. Jr. & ADAMS, S. C. (1940). *J. Amer. Chem. Soc.* **62**, 1228.

VAN NIEKIRK, J. N. & SCHOENING, F. R. L. (1953). *Acta Cryst.* **6**, 609.

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.

Acta Cryst. (1961). **14**, 891

Low-temperature transitions in methyl ammonium alum.

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(*Received 8 December* 1960)

When Lipson (1935*a*) concluded that the room-temperature structure of methyl ammonium alum was cubic with space group *Pa*3 and unit-cell edge 12·479 kX. units (=12·504 Å), one of his suggestions for the existence of the glide planes was that the methyl ammonium group might have spherical symmetry. Later, in the course of an investigation at microwave frequencies of the variation in dielectric loss with temperature, Griffiths & Powell (1952) observed that a number of compounds, one of which was methyl ammonium alum, exhibited marked anomalous effects and that with methyl ammonium alum the anomaly was of two kinds. Of these, one consisted of a peak in the dielectric loss at a temperature which was frequency-dependent, the peak occurring at temperatures higher than 300 °K. for wave lengths of 1·85 and 0·85 cm. respectively; the other was an abrupt transition in both the real and the imaginary parts of the dielectric constant at 170 °K., the transition temperature being independent of frequency. The present X-ray investigation was undertaken in an attempt to establish whether, on cooling, the abrupt transition at 170 °K. was associated with a cessation of rotation of the methyl ammonium group (as would be shown by disappearance of the glide planes) and, if so, to determine the crystal structure of the new phase.

Weissenberg photographs (Fig. 1) were first obtained at room temperature with the crystal of methyl ammonium alum oscillating about the [100] direction, and after the application of the standard corrections and the insertion of the appropriate scaling and temperature factors the agreement residual was 0·18 for the structural data published by Lipson (1935*a*). The crystal was then cooled progressively from room temperature to 100 °K. by subjecting it to a stream of cold nitrogen gas obtained by controlled boiling of liquid nitrogen in a Dewar vessel. Within this temperature range an abrupt transition to a structure of symmetry lower than cubic was observed optically to occur at 170 °K., and with further cooling the colours of the interference patterns changed gradually until a temperature of 150 °K. was reached after which the pattern remained constant. These observations were repeated with the temperature both increasing and decreasing during several successive temperature cycles until ultimately the 170 °K. transition disappeared and thereafter the sole transition observed was that at 150 °K. between a cubic and a non-cubic phase. The experiment was repeated and the same sequence was again observed.

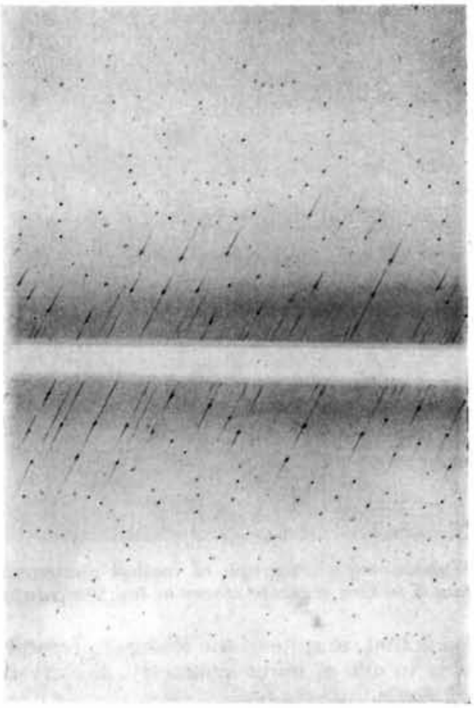

Fig. 1. Weissenberg photograph of methyl ammonium alum.

The existence of the non-cubic structures was confirmed by the use of X-ray diffraction techniques whereby

Weissenberg intensity data were obtained with a crystal of methyl ammonium alum maintained respectively at 113 °K. and 162 °K. and oscillating about the [100] direction of the room-temperature cubic structure. Details so far obtained of these and other structural changes are as follows:

1. At 113 °K. the particular orientation of the non-cubic structure about the axis of oscillation appears to be a matter of chance. In one projection there are two two-fold screw axes at right angles to each other, the lengths of the unit-cell edges along these directions being 12·33 and 12·57 Å respectively, and in another projection there are two mutually perpendicular two-fold axes (one of which is a screw) with axial lengths of 12·57 and 12·38 Å; the latter photograph suggests the existence of a set of glide planes perpendicular to the axis of rotation of the crystal. The structure is probably non-centrosymmetric, as the outcome of a pyroelectric test at the temperature of liquid nitrogen was positive, and a feature of this transition is that, in spite of the change in crystal system from cubic to one of lower symmetry, the crystal itself remained single.

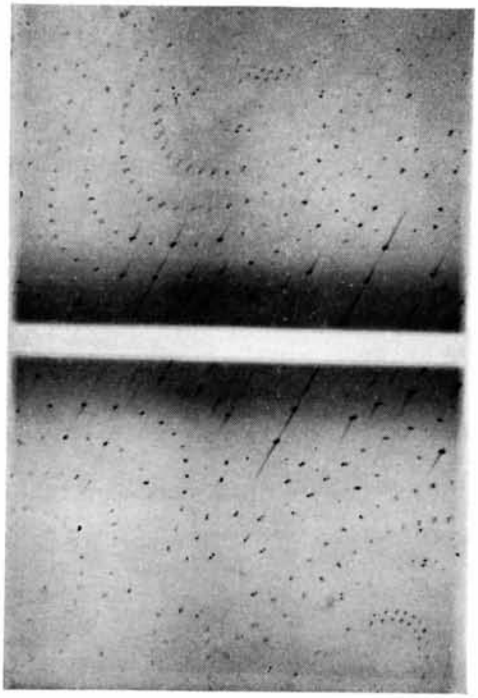

Fig. 2. Weissenberg photograph of methyl ammonium alum obtained in two separate stages at low temperature.

Fig. 2 shows both of the above projections on the same film, the composite photograph having been obtained in two stages in the interval between which the crystal was at room temperature for two days.

2. At 162 °K. there exist simultaneously two non-cubic structures, but in view of the optical evidence it is likely that the nature of these structures will depend upon the previous history of the crystal and upon the temperature between 170 and 150 °K. at which the crystal is maintained. In the actual projection photographed it would appear that the structures have two common axes at 90° to each other, the unit-cell edges in these directions of one structure being 12·46 and 12·44 Å and those of the other being 12·57 and 12·44 Å respectively.

3. After the exposure at 162 °K. the crystal returned, not to its normal room-temperature state, but to one in which there were present two cubic structures both with space group $Pa3$. One of these is that occurring normally at room temperature having $a = 12{\cdot}50$ Å and the other, additional, structure has $a = 12{\cdot}17$ Å (Fig. 3). The fractional coordinates of the sulphur atom in the extra structure (determined from a Patterson synthesis) are (0·31, 0·31, 0·31) and agree with those of the sulphur in the α alums (Lipson, 1935*b*); the sulphur coordinates of the normal methyl ammonium alum are (0·33, 0·33, 0·33).

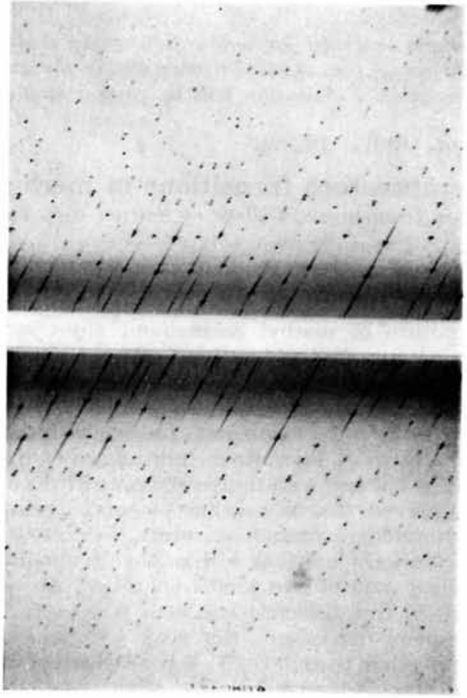

Fig. 3. Weissenberg photograph of methyl ammonium alum obtained at room temperature after the crystal had been maintained at low temperature.

4. To obtain further data the same crystal was oscillated at room temperature about the [010] direction and from the resulting Weissenberg photograph it was evident that, in the meantime, the additional structure had become most obviously twinned but that the normal room-temperature structure had been unaffected. The twinning may have been caused by vibration to which the crystal had been subjected during the re-orientation about the second axis and was apparently not a time effect as no further changes occurred during a waiting period of two weeks. In an attempt to relieve any strains that may have been present the crystal was annealed for two hours at 320 °K. (30·5 °K. below the melting point) after which it was found that the additional structure had persisted but that the normal structure had disappeared. The crystal had now broken into a number of single-crystal fragments and on the single-crystal patterns were superimposed weak powder rings.

Detailed examinations of the structural changes reported here are in progress.

During the course of the preliminary investigation it was noted in a periodical review of the literature that Pepinsky, Jona & Shirane (1956) had observed the appearance at 176 °K. of a peak in the dielectric constant of methyl ammonium alum, the occurrence of the peak being accompanied by a sharp maximum in the loss factor; this effect is presumably similar to that reported by Griffiths & Powell (1952).

References

GRIFFITHS, J. H. E. & POWELL, J. A. (1952). *Proc. Phys. Soc.* A, **65**, 289.
LIPSON, H. (1935*a*). *Phil. Mag.* **19**, 887.
LIPSON, H. (1935*b*). *Proc. Roy. Soc.* A, **151**, 347.
PEPINSKY, R., JONA, F. & SHIRANE, G. (1956). *Phys. Rev.* **102**, 1181.

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An X-ray crystallographic study of 1-(5′-bromo-2′-hydroxy-4′-methoxyphenyl)-3-oxo-isoindolo-1-en.

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(*Received* 3 *January* 1961)

Lamchen (in preparation) has described the synthesis of a red crystalline compound which he has formulated as 1-(2′-hydroxy-4′-methoxyphenyl)-3-oxo-isoindolo-1-en (I*a*). An alternative structure (II), with the same empirical formula ($C_{15}H_{11}NO_3$), could be suggested for this compound and the present study was undertaken to decide between these alternatives. To enable a direct structure determination by the 'heavy-atom method', a bromo-derivative was prepared in which the bromine atom was substituted on to the phenyl group at one of the positions 3′-, 5′- or 6′-; on chemical grounds, the 5′-position (structure I*b*) seemed most probable and has been verified by the X-ray analysis.

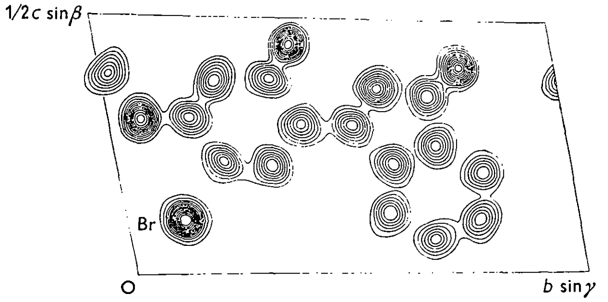
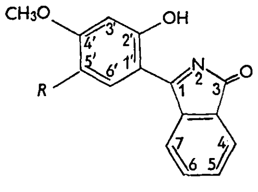
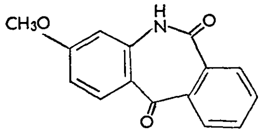


Fig. 1. The electron-density projection normal to the *a*-axis. The first contour is at 2 e.Å^{-2} and the contour interval is 1 e.Å^{-2}, except over the bromine atom where the interval is 5 e.Å^{-2}.



(I*a*): *R* = H
(I*b*): *R* = Br



(II)

The crystals grow from a chloroform–petroleum–ether solution in the form of very fine, deep-red needles which are frequently twinned. X-ray oscillation and Weissenberg photographs showed them to be triclinic, with one very short unit-cell dimension parallel to the needle axis.

Crystal data

$C_{15}H_{10}NO_3Br$, $M = 332{\cdot}2$,
$a = 3{\cdot}96 \pm 0{\cdot}01$, $b = 11{\cdot}91 \pm 0{\cdot}03$, $c = 13{\cdot}53 \pm 0{\cdot}04$ Å ,
(λ(Cu $K\alpha$) = 1·5418 Å)
$\alpha = 100° \; 46' \pm 20'$, $\beta = 91° \; 40' \pm 20'$, $\gamma = 91° \; 20' \pm 20'$,
$U = 625{\cdot}6$ Å^3, $D_m = 1{\cdot}76$ g.cm.$^{-3}$, $Z = 2$, $D_c = 1{\cdot}763$ g.cm.$^{-3}$,
$F(000) = 332$.

The 0*kl* intensity data were measured by visual estimation, from a series of multiple-film Weissenberg photographs. Of the 417 non-equivalent reflections within the Cu $K\alpha$ limit, 339 were recorded. A statistical survey of the intensity data gave an $N(z)$ distribution approximating more closely to the theoretical curve for a non-centrosymmetric projection (Howells, Phillips & Rogers, 1950), suggesting the space group $P1$. However, when allowance is made for the predominant heavy bromine atoms, as suggested by Sim (1958), the results seem to favour the centrosymmetric space group $P\bar{1}$.

(y, z) parameters for all the atoms in the molecule were derived from an electron-density projection calculated with the phases of the bromine contributions to the structure factors. A set of 0*kl* structure factors based on these atomic positions showed satisfactory agreement with the observed structure amplitudes (the reliability factor $R = \Sigma|F_o - F_c| / \Sigma|F_o| = 0{\cdot}17$). The final electron-density distribution is shown in Fig. 1 where a clearly resolved projection of the atomic maxima corresponding to a molecule of structure I*b* can be seen. The average peak height over the carbon atoms is 8·8 e.Å^{-2} and over the oxygen atoms is 12·3 e.Å^{-2}, while the peak height of the one nitrogen atom is 11·0 e.Å^{-2}.

The present two-dimensional analysis confirms the proposed structure (I*b*). Packing considerations suggest that the molecules are linked by a system of O–H ··· N bonds approximately 2·8 Å in length; a complete analysis is required to investigate this hydrogen bonding and to provide details of the molecular geometry.

The author wishes to thank Prof. R. W. James, F.R.S., for his interest in this work. Financial assistance from the South African Council for Scientific and Industrial Research is gratefully acknowledged.

References

HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
SIM, G. A. (1958). *Acta Cryst.* **11**, 123.