

to an incorrect solution. It makes use of the available data in a single step solution, rather than following a procedure of successive approximations or depending upon an assumed value of  $c/a$ .

For hexagonal crystals the direct graphical method may be applied by using the appropriate quadratic forms of the Bragg equation:

$$(a/c)^2 = [4 \sin^2 \theta / (\lambda^2 l^2)] a^2 - 4(h^2 + hk + k^2) / (3l^2)$$

(general form)

and

$$a^2 = \lambda^2 (h^2 + hk + k^2) / 3 \sin^2 \theta \quad (\text{for } hk0 \text{ planes}).$$

We wish to thank the Materials Laboratory, Wright Air Development Division, Air Research and Develop-

ment Command, for preparation of alloys and Prof. Lars Thomassen, University of Michigan, for a valuable discussion of the method herein described.

### References

- AZAROFF, L. V. & BUEGGER, M. J. (1958). *The Powder Method in X-ray Crystallography*. New York: McGraw-Hill.
- BARRETT, C. S. (1952). *Structure of Metals*. New York: Mc Graw-Hill.
- DUWEZ, P. & TAYLOR, J. L. (1952). *J. Met.* **4**, 70.
- KLUG, H. P. & ALEXANDER, L. E. (1954). *X-ray Diffraction Procedures*. New York: Wiley.
- TAYLOR, A. & FLOYD, R. W. (1950). *Acta Cryst.* **3**, 285.

## Short Communications

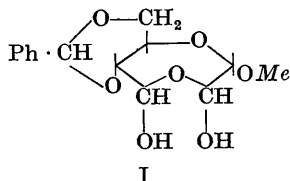
*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors.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

*Acta Cryst.* (1961). **14**, 197

**Crystal data of periodate-oxidised methyl 4,6-O-benzylidene- $\alpha$ -D-glucoside and some of its derivatives.** By J. O. WARWICKER, *The British Cotton Industry Research Association, Shirley Institute, Manchester 20, England*

(Received 17 May 1960)

Interest in the periodate-oxidation of methyl 4,6-O-benzylidene- $\alpha$ -D-glucoside arises because of the possible analogy with similar reactions occurring in the oxidation of cellulose. The oxidised product I



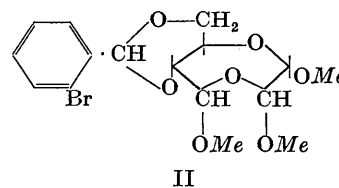
(7,9-dihydroxy-6 $\alpha$ -methoxy-2-phenyl-*trans*-*m*-dioxano[5,4-*e*][1:4]-dioxepan) can be obtained with or without water of hydration by crystallizing from water or from dimethyl sulphoxide respectively (Guthrie & Honeyman, 1959). Needle crystals were obtained from dimethyl sulphoxide. The unit cell dimensions derived from rotation and zero-layer Weissenberg photographs were:

$$a = 24.06, \quad b = 13.18, \quad c = 4.50 \text{ \AA};$$

the space group was  $P2_12_12_1$ . Consideration of the short  $c$ -axis dimension and the space group  $P2_12_12_1$  showed that it was improbable that dimers are formed, and that the correct value of  $Z$  is 4. The measured value of density by flotation was  $1.401 \text{ g.cm.}^{-3}$ . The calculated molecular weight was 301 in good agreement with 298.3, that calculated from the postulated formula I. This provided evidence additional to that of Guthrie & Honeyman (1959) for the correctness of the formula I proposed by them.

Compound I is of interest because it contains a seven-membered ring whose exact conformation and disposition of attached groups are unknown. Some preliminary structural studies to try to elucidate these features were unsuccessful.

An analogue of I, compound II (2-*o*-bromophenyl-6 $\alpha$ ,7,9-trimethoxy-*trans*-*m*-dioxano[5,4-*e*][1:4]-dioxepan) gave needle crystals from ethanol (Colbran, Guthrie & Parsons, 1960).



The unit-cell dimensions were:

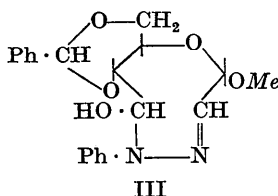
$$a = 12.69, \quad b = 30.12, \quad c = 4.43 \text{ \AA};$$

the space group was  $P2_12_12_1$ . The observed density found from a density-gradient column was  $1.582 \text{ g.cm.}^{-3}$ , and for  $Z=4$  the calculated molecular weight was 403.3 in agreement with 405.2 calculated for II.

The conformation of the seven-membered ring and the disposition of the methoxy groups are again unknown. The presence of the bromine atom in this molecule should help in the elucidation of the structure, but no further work is contemplated at the moment.

The phenylhydrazine derivative of I, thought to be III,

(Guthrie & Honeyman, 1959) gave yellow needle crystals from *n*-butanol.



The unit-cell dimensions were:

$$a = 16.27, b = 12.03, c = 4.95 \text{ \AA}, \gamma = 94.3^\circ;$$

the space group was  $P2_1$ . The density measured with a density-gradient column was  $1.266 \text{ g.cm.}^{-3}$ , and with  $Z=2$  the calculated molecular weight was 368.3 in agreement with 370.4 calculated for III. The correct structure of this molecule is still uncertain.

An ethanolamine derivative of compound I (Colbran, Guthrie & Parsons, 1960) was prepared but difficulty was found in elucidating its structure. X-ray work was undertaken in the hope that the determination of the molecular weight would help. Colourless needles were obtained from aqueous methanol. The unit-cell dimensions were:

$$a = 21.67, b = 16.66, c = 4.63 \text{ \AA};$$

the space group was  $P2_12_12_1$ . The density measured by flotation was  $1.302 \text{ g.cm.}^{-3}$  and assuming  $Z=4$  the calculated molecular weight was found to be 327.7. This value of the molecular weight is consistent with that derived from the elementary analysis of the compound, but despite this agreement, difficulty still exists in giving an exact formula for the compound.

*Acta Cryst.* (1961). **14**, 198

### Accuracy in structure analysis of layer silicates: Some further comments on the structure of prochlorite. By H. STEINFINK,\* *Shell Development Company, Houston, Texas, U. S. A.*

(Received 24 April 1960 and in revised form 21 July 1960)

Mathieson, Radoslovich & Walker (1959), in their criticism of the crystal structure of a monoclinic chlorite (Steinfink, 1958), assert that the data do not support the findings and that '... unwarranted structural features ...' were proposed. The contention is made that 51 positional parameters were derived from 78 reflections, although a  $R(h0l) = 0.148$  is reported in the paper and clearly indicates that additional reflections to those listed in Table 3 were used during the analysis of the structure. The primary interest in these layer silicate structures was the determination of deviations from 'ideal'  $y$  parameters. In general the  $k=3n$  reflections are relatively insensitive to these deviations, as shown below, and the 85 ( $h0l$ ) reflections in particular are not of great interest once they have been used in the refinement of the  $x$

The density-gradient columns used for the estimation of the density of compound II and III were formed from saturated aqueous solutions of inorganic salts.

	Density range
1. Water-lead nitrate	1.0-1.4 $\text{g.cm.}^{-3}$
2. Water-sodium tungstate	1.0-1.55
3. Potassium chloride-sodium iodide	1.2-1.9

Column 3 was used for compound II and columns 1 and 2 for compound III. Columns made with organic liquids were unsuitable because of the solubility of the compounds in the solvents. Details of forming and calibrating these columns are given by Linderstrøm-Lang (1937, 1938) and Preston & Nimkar (1950). The density gradient was found to be linear over small distances only, and it was therefore necessary to draw a calibration graph with values obtained with four or five reference standards placed in the region of the column where preliminary tests had shown that the crystal of unknown density would float.

The author wishes to acknowledge the helpful advice of Dr J. C. Speakman. Thanks are also due to Mr D. M. Cooke in helping to investigate the use of density-gradient columns.

### References

- COLBRAN, R. L., GUTHRIE, R. D. & PARSONS, M. A. (1960). *J. Chem. Soc.* (In the press.)  
 GUTHRIE, R. D. & HONEYMAN, J. (1959). *J. Chem. Soc.* p. 2441.  
 LINDERSTRØM-LANG, K. (1937). *Nature, Lond.* **139**, 713.  
 LINDERSTRØM-LANG, K. (1938). *Mikrochim. Acta*, **3**, 210.  
 PRESTON, J. M. & NIMKAR, M. V. (1950). *J. Text. Inst. Manchr.* **41**, T446.

and  $z$  parameters. The 47 positional parameters (four are fixed by the space group) were therefore determined by a total of 163 reflections.

The authors also claim that the electron-density maps do not support the coordinates of Table 2. Consider the contributions to the ( $0kl$ ) structure factors from the individual atoms when they have 'ideal'  $y$  parameters. When  $k=3n$  the imaginary part of the structure factor is nearly zero, and deviations from 'ideal'  $y$  parameters will not cause large deviations from the phase angle values  $0^\circ$  or  $180^\circ$ . For the  $k \neq 3n$  reflections, the oxygens forming the base of the  $\text{SiO}_4$  tetrahedron and the silicon atom at  $y=1/6$  will cause the phase angle to assume values different from  $0^\circ$  or  $180^\circ$ , and the values of these phase angles will be sensitive to deviations from the 'ideal'  $y$  parameters of the atoms. Thus the ( $0kl$ ) projection will be heavily weighted in favor of 'ideal'  $y$  coordinates because the majority of the strong reflections are

\* Chemist, Shell Development Company (A Division of Shell Oil Company), Houston, Texas, U.S.A.