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The crystal structure of sucrose.

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There has been an interest in the structure of sucrose in this laboratory for several years. Intensity data were collected in 1944 (using a crystal kindly supplied by Messrs Tate and Lyle) and sections of the three-dimensional Patterson function were computed by W. Cochran and C. A. Beevers. An application of the Harker method was not successful, owing to the absence of heavy atoms in the structure, and it was decided first to proceed with an examination of the sucrose NaBr complex (Beevers & Cochran, 1947). When a more complete three-dimensional Patterson function became available—computed by one of us (C.A.B.) on X-R.A.C. by courtesy of Prof R. Pepinsky—fresh impetus was given to the work, and with the help of these more extensive Patterson maps and the results of the sucrose NaBr investigation, we were able to obtain a structure for the crystal. The preliminary results presented here are not yet sufficiently accurate for any detailed discussion. Adequate refinement would necessitate a complete re-determination of the intensity data, and it is not possible for us to carry on with this work at present.

Sucrose, $C_{12}H_{22}O_{11}$, crystallizes anhydrous from aqueous solution in monoclinic tablets with predominant development of the (100) faces. The space group is $P2_1$, and cell dimensions are

$$a=10\cdot89,\ b=8\cdot69,\ c=7\cdot77\ \text{Å},\ \beta=103^\circ\ .$$

There is cleavage parallel to (100). Intensities were measured for all observable planes, using copper radiation. Inspection of the three-dimensional Patterson function near the origin, especially at 2·5 Å radius, revealed a vector distribution characteristic of the pyranose ring and strikingly resembling the c-axis Patterson projection of glucose (McDonald & Beevers, 1950). The orientation of the pyranose ring obtained in this way was used as a starting point for a photographic application of the vector convergence method (Beevers & Robertson, 1950) which gave the orientation of the furanose ring. The position of the molecule in the unit cell was determined by comparison of the degree of coincidence of the theoretical b-axis Patterson projection for different positions of the molecule and the observed Patterson projection. Refinement was carried out by Fourier and least-square methods, and has so far led to the atomic parameters shown in Table 1.

Table 1. *Atomic parameters*

	x (360ths)	z (360ths)	y (120ths)
C_1	109	177	43
C_2	108	224	57
C_3	102	199	78
C_4	133	152	78
C_5	131	103	63
C_6	165	65	73
C'_1	35	196	17
C'_2	47	134	20
C'_3	3	77	19
C'_4	25	20	17
C'_5	61	47	1
C'_6	102	20	119
O_1	65	141	40
O_2	82	273	51
O_3	111	252	86
O_4	124	122	95
O_5	138	133	48
O_6	207	100	68
O'_1	15	227	34
O'_2	76	115	6
O'_3	335	74	36
O'_4	352	330	10
O'_6	117	14	16

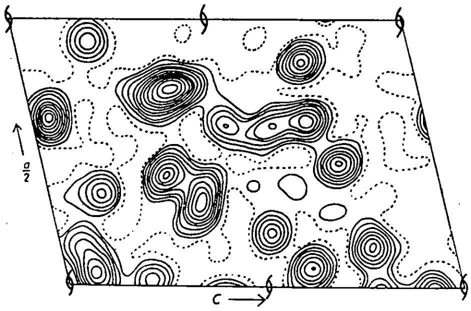

Fig. 1. b-axis Fourier projection.

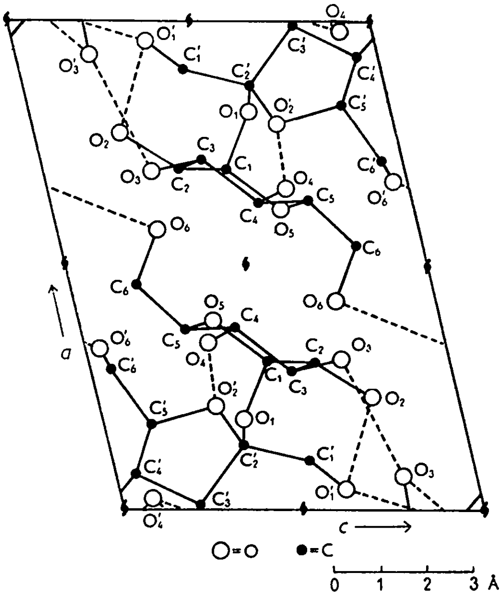

Fig. 2. b-axis projection of the structure.

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The final b-axis Fourier projection is shown in Fig. 1, and a diagram of the structure in Fig. 2. The y parameters are somewhat less accurate than the x and z parameters, as is shown by the values of the reliability factor $R=\Sigma||F_o|-|F_c||\div\Sigma|F_o|$ for the different zones: $R_{h0l}=0{\cdot}25$, $R_{0kl}=0{\cdot}33$, $R_{hk0}=0{\cdot}42$. The value of R_{hkl} found for some 200 reflexions lying between $\sin\theta=0{\cdot}15$ and $0{\cdot}80$ is $0{\cdot}33$. The probable error of the atomic positions is considered to be of the order of ±0·08 Å.

The molecule is found to have the same general shape as in the NaBr compound, except that the OH group of the furanose residue attached to C_1' is differently oriented. The packing of the molecules in the crystal appears to be governed by hydrogen-bond formation between the hydroxyl groups mainly of the furanose residues. The contacts between the glucose residues are more of the van der Waals type, and this results in a weakness of the structure across the planes $x=\frac{1}{2}$. To this the cleavage of the crystal must be attributed. The cleavage plane is clearly visible in Fig. 2. The hydrogen bonding, as judged by distances of approach, is not as complete as might have been expected; there are however several O–O contacts only somewhat greater than 3·2 Å, and it is possible that further refinement with much better intensity data might clarify the situation.

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The non-polarity of sodium niobate.

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The conclusion that the space group of $NaNbO_3$ is nonpolar (Vousden, 1951) has been questioned (Pepinsky, 1952) on two grounds: (*a*) that twinning or ambiguities of indexing make the evidence on the space group inconclusive; and (*b*) that it is difficult to reconcile a nonpolar structure with the observed ferroelectric properties, namely dielectric hysteresis (Matthias, 1949) and orientation of crystal axes by an external field (Vousden, 1951). This note is in reply to these criticisms.

Twinning in $NaNbO_3$ is easily detected by the polarizing microscope (except in crystal elongated along b which were not used). Observations of this kind showed that the crystal chosen for rotation about b was untwinned, while that chosen for rotation about a had only two components, one of which was very small and gave reflexions lying on different layer lines from those of the main component.

The space group was determined from 5° oscillation photographs. These were used in preference to Weissenberg photographs for the detection of possible weak reflexions because of their lower background intensity and shorter exposure time. The smallness of the oscillation ensured that the indexing was unambiguous. Since the reflexions were fully resolved and the indexing unambiguous, the only question remaining about the space group is whether the observed absences were accidental; the possibilities resulting from this were discussed in detail in the original paper.

The real difficulty presented by the space group is, however, that the displacements are in antiparallel pairs, rather than that the space group is non-polar. The evidence for the opposite displacements of Nb along a is quite independent of the space group and can be deduced from the powder photographs alone. If the opposite displacements are equal they cannot explain the ferroelectric properties by a spontaneous polarization; if they are unequal (as might be the case with $P2mm$) then only their difference could contribute to the dipole moment, and this again is an unprecendented situation. The analogy with $BaTiO_3$ thus breaks down in either case.

There is, however, a natural solution of the difficulty which can account for the ferroelectric properties, while admitting the antiparallel displacements. It is assumed that the crystal changes from a non-polar to a polar state by the sudden reversal of atomic displacements when the field reaches a certain critical value. The substance must possess two distinct though closely related structures with different space groups but nearly the same free energy.* The non-polar structure having lower energy is normally in equilibrium, but if a sufficiently strong electric field is applied the polar structure can be induced. The substance will then behave as if ferro-electric. If the relaxation time of this metastable structure is comparable with or greater than the period of an applied field, then dielectric hysteresis will occur. The induction of the polar state by the field should be accompanied by quite large changes in the intensities of the weak (superstructure) reflexions; if the Nb displacements are reversed, intensity changes might be visible on powder photographs.

The non-polarity need not, therefore, present any difficulty in principle. A similar effect has been suggested in $PbZrO_3$, because of the shape of the hysteresis loops (Sawaguchi, Shirane & Takagi, 1951). Antiparallel displacements of atoms occur in the structure, although it is not yet certain whether the structure is really non-polar (Sawaguchi, Mamiwa & Hoshino, 1951). It is hoped to discuss this phenomenon more fully in a forthcoming paper on the origin of ferroelectricity, and the name pseudo-ferroelectricity is provisionally proposed for it.

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* The same suggestion has also been made independently by Dr H. D. Megaw (private communication).

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