

Crystal Structure of the 1,3,5-Triaminocyclohexane Dihydrate and of the Dihydrate and Diammoniate of α Phloroglucitol

PER ANDERSEN and O. HASSEL

Universitetets Kjemiske Institutt, Blindern — Oslo, Norway

The crystal structure of α phloroglucitol dihydrate was determined by the present authors three years ago¹ with the aim of deciding whether the substance contains the *cis* or *trans* form of 1,3,5-cyclohexanetriol. It was found that α phloroglucitol is indeed the *cis* form of the triol and that it has the $\alpha\alpha\alpha$ configuration (Fig. 1) in the solid dihydrate.

As anticipated hydrogen bonds between oxygen atoms play a dominating role in the structure of the crystal. It was found, however, that such bonds are not formed between alcoholic oxygen atoms, but between such oxygen atoms and water oxygens and between oxygen atoms belonging to neighbouring water molecules. In the structure thus obtained the oxygen atom of each water molecule forms four hydrogen bonds: one to a neighbouring water oxygen atom and three additional bonds to hydroxy oxygen atoms belonging to three *different* phloroglucitol molecules. The arrangement of hydrogen bonds around each water oxygen atom, has trigonal symmetry, it is not very different from that observed in the ice structure, and the bond lengths are of the same magnitude (about 2.76 Å). The mutual positions of the two water molecules and the additional six hydroxy groups linking together six molecules of phloroglucitol is shown in Fig. 2.

The subsequent finding² that an isomorphous crystalline diammoniate may be obtained by evaporating the solvent from a solution of α phloroglucitol in liquid anhydrous ammonia made it seem possible that a symmetrical *cis*-1,3,5-triaminocyclohexane might form a dihydrate having the same crystal structure. An attempt to prepare the triamine turned out to be successful³, and X-ray powder photographs indicated that a dihydrate with the expected structure is indeed formed.



Fig. 1. The configuration of a phloroglucitol in crystals of the dihydrate.

When studying this new compound we had a rather limited amount of material at our disposal and all our work had to be carried out in closed vessels in order to protect the substance against the carbon dioxide of the air. We were able to state, however, that the dihydrate gives off its water of crystallisation at 65° C and that the anhydrous amine melts at 148° C. We succeeded also in preparing single crystals of the dihydrate which gave very good rotation and Weissenberg diagrams although the crystals showed poor external development, and had to be kept in sealed capillary tubes, circumstances which made the orientation in the X-ray cameras difficult. We did not succeed in orientating the crystal for rotation about the principal axis, but the diagrams obtained by rotation about the edge of the (face-centered) rhombohedron, the edge of the primitive rhombohedron and the shortest identity period in the basis plane were very satisfactory, the corresponding identity periods being: 12.40 Å, 8.91 Å and 8.62 Å respectively. From these values the identity period along the principal axis could be evaluated and was found equal to 22.23 Å.

The recorded absences of reflexions coincide with those observed for α phloroglucitol dihydrate and the space group is therefore R3c.

The intensities of reflexions are rather similar in both cases indicating that the two substances are indeed isomorphous. The angle φ between the shortest identity period in the basis plane and the projections of the C-O bonds was found to be zero or very nearly zero in the trihydroxy compound, (comp. Fig. 3), a very reasonable finding because in this case only the two sets of O₃-triangles present in the structure (compare Fig. 2) will have the same size. The same argument seems to hold in the case of the triamine structure where a very satisfactory agreement between observed and calculated intensities is obtained with the value $\varphi = 0$ and a model of the triamine molecule having strictly

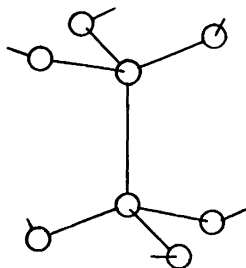


Fig. 2. The assembly of two water oxygens (middle) and six hydroxy oxygens linked together by hydrogen bonds in the α phloroglucitol dihydrate structure.

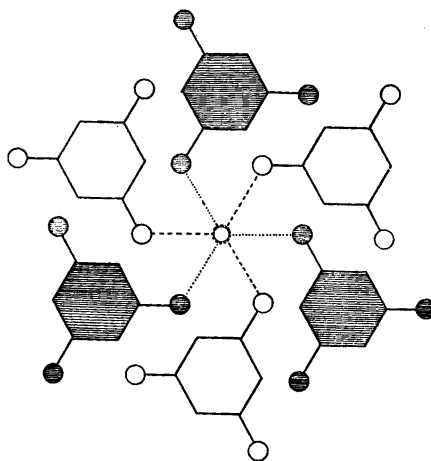


Fig. 3. Projection along the trigonal axis of part of the *a* phloroglucitol dihydrate structure.

tetrahedral valency angles, a C-C-distance of 1.54 Å and a C-N distance of 1.47 Å.

The only parameters still necessary for the calculation of structure factors are those of the water molecules along the C-axis of the crystal. We have made the assumption that the two water molecules directly connected by hydrogen bonds are symmetrically arranged with respect to the centers of the two nearest cyclohexane rings situated on the same trigonal axis and that the distance of the two oxygen atoms is the same as in the phloroglucitol dihydrate (2.76 Å). This corresponds to a N-H-O bond distance of 2.93 Å which seems reasonable.

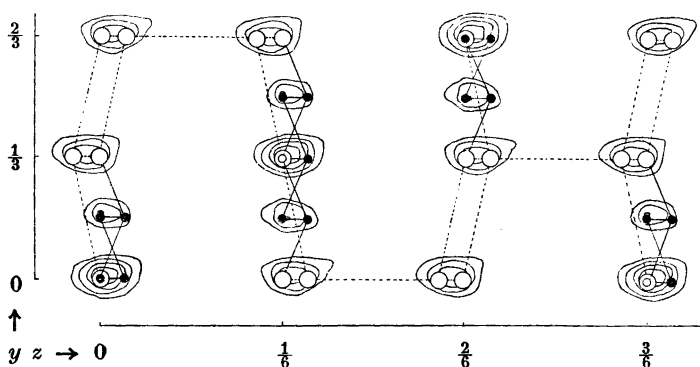


Fig. 4. Map showing the electron density in the triaminocyclohexane dihydrate structure projected along the hexagonal *a*-axis.

Table 1. Observed and calculated F -values for the triaminocyclohexane dihydrate crystals.

$h k l$	$ F_{\text{calc.}} $	$ F_{\text{obs.}} $	$ F_{\text{obs.}} e^{3,33\left(\frac{\sin \theta}{\lambda}\right)^2}$	$h k l$	$ F_{\text{calc.}} $	$ F_{\text{obs.}} $	$ F_{\text{obs.}} e^{3,33\left(\frac{\sin \theta}{\lambda}\right)^2}$
0 0 0 6	225.0	190.8	203.0	0 2 $\bar{2}$ $\bar{10}$	36.7	25.7	32.0
0 0 0 12	126.2	86.4	109.4	0 2 $\bar{2}$ $\bar{16}$	35.6	18.5	30.2
0 0 0 18	27.8	34.4	59.3	0 2 $\bar{2}$ $\bar{22}$	16.9	<11.0	<24.0
0 0 0 24	13.9	10.2	26.7	0 3 $\bar{3}$ 6	82.2	57.2	69.8
0 1 $\bar{1}$ 4	99.3	99.8	104.0	0 3 $\bar{3}$ $\bar{12}$	13.7	17.4	34.0
0 1 $\bar{1}$ 10	84.7	55.9	66.5	0 3 $\bar{3}$ $\bar{24}$	8.7	<9.3	<27.3
0 1 $\bar{1}$ 16	50.9	25.7	40.1	0 4 $\bar{4}$ $\bar{2}$	31.8	26.1	34.4
0 2 $\bar{2}$ 2	58.1	64.3	69.1	0 4 $\bar{4}$ $\bar{8}$	41.2	25.1	35.4
0 2 $\bar{2}$ 8	60.6	52.5	62.5	0 4 $\bar{4}$ $\bar{14}$	21.6	8.1	14.2
0 2 $\bar{2}$ 14	29.1	19.8	29.1	0 5 $\bar{5}$ $\bar{4}$	46.0	38.3	57.1
0 3 $\bar{3}$ 0	102.8	98.5	113.1	0 5 $\bar{5}$ $\bar{10}$	57.2	29.0	50.0
0 3 $\bar{3}$ 6	82.2	57.2	69.8	0 5 $\bar{5}$ $\bar{16}$	36.6	16.1	35.8
0 3 $\bar{3}$ 12	37.7	19.8	28.7	0 6 $\bar{6}$ $\bar{6}$	119.5	61.7	112.2
0 3 $\bar{3}$ 18	13.7	17.4	34.0	0 6 $\bar{6}$ $\bar{12}$	71.4	28.1	61.0
0 4 $\bar{4}$ 4	2.2	<8.6	<11.1	0 6 $\bar{6}$ $\bar{18}$	24.7	9.6	28.3
0 4 $\bar{4}$ 10	28.7	14.0	20.8	0 7 $\bar{7}$ $\bar{2}$	21.1	11.4	23.9
0 4 $\bar{4}$ 16	31.4	8.1	15.8	0 7 $\bar{7}$ $\bar{8}$	18.0	<11.3	<26.2
0 5 $\bar{5}$ 2	18.6	22.9	33.7	0 8 $\bar{8}$ $\bar{4}$	4.0	7.2	20.6
0 5 $\bar{5}$ 8	20.6	19.8	32.0	0 8 $\bar{8}$ $\bar{10}$	13.1	<9.0	<28.2
0 5 $\bar{5}$ 14	20.0	11.4	22.9	0 8 $\bar{8}$ $\bar{16}$	18.0	<5.4	<21.6
0 6 $\bar{6}$ 0	143.5	81.3	140.1	0 9 $\bar{9}$ $\bar{6}$	29.4	<7.5	<26.6
0 6 $\bar{6}$ 6	119.5	61.7	112.2	0 7 $\bar{7}$ $\bar{14}$	14.8	<9.7	<27.8
0 6 $\bar{6}$ 12	71.4	28.1	61.0	0 7 $\bar{7}$ $\bar{20}$	8.9	<4.5	<18.0
0 6 $\bar{6}$ 18	24.7	9.6	28.4	0 5 $\bar{5}$ $\bar{22}$	15.0	<8.4	<27.0
0 7 $\bar{7}$ 4	39.0	16.1	34.3	0 4 $\bar{4}$ $\bar{20}$	2.4	<10.9	<27.2
0 7 $\bar{7}$ 10	46.8	10.9	26.6	0 4 $\bar{4}$ $\bar{26}$	17.3	<5.1	<19.8
0 7 $\bar{7}$ 16	38.8	<8.7	<28.2	0 2 $\bar{2}$ $\bar{28}$	2.3	<5.1	<20.5
0 8 $\bar{8}$ 2	22.0	10.9	28.6	0 1 $\bar{1}$ $\bar{26}$	22.3	<8.6	<26.7
0 8 $\bar{8}$ 8	26.9	7.2	20.6	0 1 $\bar{1}$ $\bar{22}$	17.8	<11.3	<25.6
0 8 $\bar{8}$ 14	16.7	<7.1	<25.4	0 1 $\bar{1}$ $\bar{28}$	13.9	<5.9	<22.0
0 9 $\bar{9}$ 0	32.0	<8.3	<27.6	0 2 $\bar{2}$ $\bar{20}$	1.2	<11.4	<23.3
0 9 $\bar{9}$ 6	29.4	<7.5	<26.6	0 2 $\bar{2}$ $\bar{26}$	15.9	<8.1	<26.1
0 1 $\bar{1}$ $\bar{2}$	57.5	62.7	64.0	0 3 $\bar{3}$ $\bar{24}$	8.7	<9.3	<27.3
0 1 $\bar{1}$ $\bar{8}$	33.2	44.3	49.7	0 4 $\bar{4}$ $\bar{22}$	16.3	<9.7	<27.3
0 1 $\bar{1}$ $\bar{14}$	25.0	29.6	41.7	0 5 $\bar{5}$ $\bar{20}$	2.7	<9.7	<27.8
0 1 $\bar{1}$ $\bar{20}$	6.2	<11.4	<22.4				
0 2 $\bar{2}$ $\bar{4}$	1.3	10.2	11.1				

The intensities were estimated from Weissenberg diagrams using CuK-radiation. Two films were exposed simultaneously inserting a thin aluminium foil between the films. The blackening standard scale was prepared using the

strongest reflexion of the crystal itself as an X-ray source. Varying the exposure time and considering both α and β reflexions the agreement between the results obtained from different pairs of films was very satisfactory.

The agreement between observed intensities of reflexions ($o\ k\ \bar{k}\ l$) and those calculated from the model described above may be judged from Table 1. The calculated values were obtained using Robertsons f -values, thus disregarding the positions of the hydrogen atoms. The value of the reliability factor is 0.19. The structure factors were also calculated with the aid of James and Brindley's f -curves and introducing a temperature factor equal to $e^{3.33(\frac{\sin \theta}{\lambda})^2}$. The reliability factor thus obtained was nearly the same as that obtained in the first case (0.20).

The usefulness of a further examination of the structure using Fourier methods seemed rather doubtful because the structure does not contain centers of symmetry, but one projection was nevertheless worked out, namely along the hexagonal a -axis. The resulting electron density map is reproduced in Fig. 4 in which the atomic position on which the structure factor calculations were based are indicated by filled and open circles. The general positions of the peaks thus agree very well with the structure described above, but cannot give more detailed informations regarding the value of the parameters. The height of the peaks are not given on an absolute scale.

DISCUSSION OF THE STRUCTURES

According to our findings the structure of the triaminocyclohexane dihydrate corresponds very closely to that of the α phloroglucitol dihydrate and the separation of the two water molecules linked together by a hydrogen bond seems to be nearly the same in both cases (about 2.75 Å). It then follows that the distance between one of those water oxygen atoms and the plane containing the three nitrogen atom linked to it by hydrogen bonds is 0.47 Å and the N-O hydrogen bond distance 2.93 Å. The four hydrogen bonds reaching each water oxygen atom are tetrahedrally distributed in space, but the angles between them are markedly different from the "tetrahedral" angle (109°,5). The angle between the O-O and each of the O-N bonds is only 99°, the angle between two O-N bonds 117°.

Each amino nitrogen atom forms *two* hydrogen bonds to water oxygen atoms. It is obvious, therefore, that the number of hydrogen atoms available for hydrogen bond formation is greater than that necessary in order to establish the number of hydrogen bonds actually present in the structure. It would indeed seem probable that one of the hydrogen atoms of each amino group

Table 2. Lattice constants (hexagonal *a* and *c* axes) and hydrogen bond lengths in the three substances.

Substances	<i>a</i> in Å	<i>c</i> in Å	O-H-O bond in Å	O-H-N bond in Å
<i>α</i> phloroglucitol dihydrate	8.22	21.96	2.76	
1,3,5-triamino cyclohexane dihydrate	8.62	22.23	2.76	2.93
<i>α</i> phloroglucitol diammoniate	8.60	22.00		2.91

does *not* participate in hydrogen bond formation. In this respect the structure differs from that of the *α* phloroglucitol dihydrate in which all available hydrogen atoms are required for hydrogen bond formation. It is easily seen that the fraction of available hydrogen atoms *not* used for the formation of hydrogen bonds is $\frac{3}{10}$ in the triaminocyclohexane dihydrate structure, zero in the structure of *α* phloroglucitol dihydrate and $\frac{2}{9}$ in the *α* phloroglucitol diammoniate structure. The corresponding fraction in a hypothetical triaminocyclohexane diammoniate crystal having a structure of the same type would be $\frac{5}{12}$. Here, however, a serious difficulty would arise: the surplus hydrogen atoms could not remain attached to nitrogen atoms without raising the coordination number of some of the nitrogen atoms above *four*. Without having so far tried to prepare an ammoniate of triaminocyclohexane we therefore think it justified to conclude that a diammoniate having a structure corresponding to those under discussion does *not* exist.

The determination of the structure of the diammoniate of *α* phloroglucitol has proved more difficult than originally expected. The development of the (very unstable) single crystals is rather poor, and it has therefore not been possible to determine the intensities of reflexions with a degree of accuracy comparable to that obtained for the two other substances. However, the lattice constants derived from layer line photographs permit some conclusions to be drawn concerning the hydrogen bond distances in this case also. (Compare Table 2.) The position of the ammonia molecules on the trigonal axis may be varied within rather wide limits without seriously altering the O-H-N bond distance which cannot differ much from 2.91 Å. The N-H-N bond distance, however, could not be determined in a similar way with any degree of accuracy.

SUMMARY

Single crystals of 1 α 3 α 5 α -triaminocyclohexane dihydrate have been prepared and examined by X-ray crystallographic methods. The structure corresponds to that of α phloroglucitol dihydrate previously determined¹. The distance between the two water molecules linked together by a hydrogen bond is the same (2.76 Å) in both crystals and the N-H-O hydrogen bond length is 2.93 Å in the triamino compound. The single crystals obtained of α phloroglucitol diammoniate were too poor to deliver intensity values on which a detailed structure determination could be based. It may safely be concluded, however, that the crystals are isomorphous with those of the two dihydrates mentioned above, and from the lattice constants the O-H-N hydrogen bond distance may then be calculated. The value thus obtained is close to 2.91 Å.

REFERENCES

1. Andersen, Per, and Hassel, O. *Acta Chem. Scand.* **2** (1948) 527.
2. Andersen, Per, and Hassel, O. *Nature* **163** (1949) 721.
3. Hassel, O., and Lunde, K. *Research* **3** (1950) 484.

Received September 25, 1951.