X-Ray Data and Configuration of some Alcohols Derived from *Cyclo*hexane

S. FURBERG and O. HASSEL

Universitetets Kjemiske Institutt, Blindern — Oslo, Norway

A great deal of work has been done in later years in order to elucidate the structure of *cyclo*hexane and its derivatives, especially by Hassel and co-workers[1]. Both electron diffraction and X-ray methods have been employed. In all the compounds hitherto examined it is found that the *cyclo*hexane ring has the staggered "chair" form, with a C—C distance of 1.54 A. and bond angles near the tetrahedral angle. In some cases deviation from tetrahedral angles have been observed[2,3], presumeably due mainly to repulsive forces between atoms in the positions $1\varepsilon\ 3\varepsilon$. However, no complete X-ray structure analysis leading to accurate values of the individual bond lengths and bond angles for this basic carbon skeleton has yet been carried out. Halogen derivatives are not quite suitable for this purpose, as the monosubstituted *cyclo*hexanes are liquids, whereas in compounds with two or more halogen atoms it would probably not be possible to obtain a very accurate determination of the carbon ring. Thus the alcohols of *cyclo*hexane would appear to provide the best point of attack. X-ray data on some of these are given by Patterson and White[4,5], and Hassel and co-workers[6,7], and in one case, α-phloroglucitol dihydrate, the arrangement and configuration of the molecules in the crystal is worked out[7]. The molecules are linked to one another by hydrogen bonds, a feature which we must expect to find in all these compounds.

The results of some of these earlier investigations are given in the table below. We have undertaken a preliminary X-ray investigation of some more alcohols of *cyclo*hexane, with the aim mainly to find a suitable compound for a detailed structure analysis. Space group determinations are, however, also of interest in connection with the possibility of resolving some of these substances into optical antipodes.

Oscillation and Weissenberg photographs were taken, using Fe Kα radiation ($\lambda = 1.934$ A). The cell dimensions obtained are accurate to about 1 %. The densities were determined by the flotation method in mixtures of carbon tetrachloride and benzene.

The following compounds were investigated:

Cis-Resorcitol, m. p. 87°. The crystals have the shape of monoclinic plates, with (010) dominating, and the a and c axes lying along the edges, joining at an angle of 111°. The extinction direction in polarised light lies about 16° from the a axis in the acute angle. The cell dimensions are: $a = 6.74$ A, $b = 19.6$ A, $c = 5.37$ A and $\beta = 111°$. The density is 1.14_4 g/cm³, and there are four molecules (calc. 3.98) in the unit cell.

The only systematic absences occur in the $h0l$-reflexions for odd values of $h + l$, and in the $0k0$-reflexions for odd values of k. The space group is therefore $P2_1/n$.

101 is by far the strongest reflexion, and most atoms are therefore likely to be situated near this plane, a conclusion which is also justified by space considerations.

Trans-(dl)-Resorcitol, m. p. 118°. The crystals are orthorhombic, elongated along the b axis. (100) is a perfect cleavage plane. The following cell dimensions were derived: $a = 15.45$ A, $b = 8.41$ A and $c = 9.96$ A. The density was found to be 1.18_4 g/cm³, and there are eight (calc. 7.97) molecules in the unit cell.

Absent spectra (from Weissenberg photographs) uniquely determine the space group to be *Pbca*.

We had also some *trans-d*-resorcitol at our disposal, but did not succeed in growing single crystals. Only some fibre-like crystalline formations were obtained, which had a repeat unit of 6.35 A along the fibre axis.

Cis-Chinitol, m. p. 106°. The crystals available were needle-shaped, apparently triclinic, but not true single crystals. Only the length of the axis along the needle was determined. It was found to be 6.44 A.

β-Phloroglucitol, m. p. 145°. The crystals are orthorhombic, elongated along the b axis, and bounded by faces (101) and ($\bar{1}$01). The cell dimensions are: $a = 9.00$ A, $b = 10.68$ A and $c = 6.97$ A. The density is 1.30 g/cm³, and the unit cell contains four molecules (calc. 3.98).

Reflexions $h00$, $0k0$ and $00l$ are absent for odd values of h, k and l respectively, and as no other systematic absences occur, the space group is $P2_12_12_1$.

In Table 1 X-ray data are given on all *cyclo*hexane-diols (except for the optically active forms), as well as on the two 1,3,5-*cyclo*hexane-triols. The molecular structures are also included, using the nomenclature introduced by Hassel, where $\varkappa$ stands for a nearly horizontal, ε for a vertical, orientation of the C—O bond with respect to the rough plane of the carbon ring.

<p align="center">*Table 1.*</p>

Compound	Structure	Space group	a	b	c	Number of molecules
α-*Cyclo*hexane-diol-(1,2) m. p. 99°	$1\varkappa2\varepsilon$	*Pcab*	7.62	8.55	19.57	8
γ-*Cyclo*hexane-diol-(1,2) m. p. 104°	$1\varkappa2\varkappa$	*I2/a*	19.13	9.92	7.23	8
Cis-Resorcitol	$1\varkappa3\varkappa$	$P2_1/n$	6.74	19.6	5.37	4
Trans-Resorcitol	$1\varkappa3\varepsilon$	*Pbca*	15.45	8.41	9.96	8
Cis-Chinitol	$1\varkappa4\varepsilon$	—	—	—	6.44	—
Trans-Chinitol	$1\varkappa4\varkappa$	$P2_1/n$	6.31	21.23	7.26	6
α-Phloroglucitol	$1\varkappa3\varkappa5\varkappa$	*R3c*	r = 8.71, α = 56°			2
β-Phloroglucitol	$1\varkappa3\varepsilon5\varkappa$	$P2_12_12_1$	9.00	10.68	6.97	4

There are only two possible isomers (optical antipodes not included) of the 1,2, 1,3 and 1,4-diols, and of the 1,3,5-triols. In each case it is therefore essential to know the configuration of one isomer only.

It will be seen that conclusions regarding the symmetry of the molecules can be drawn from the X-ray data above only for two of the compounds, namely *trans*-chinitol and α-phloroglucitol. In the others all molecules occupy general positions in the unit cell. In the case of *trans*-chinitol, two of the six molecules in the cell must possess a centre of symmetry, as pointed out by White [5], and this substance therefore has the configuration $\varkappa\varkappa$ or $\varepsilon\varepsilon$. For the molecules of α-phloroglucitol trigonal symmetry is required, showing that it is a $\varkappa\varkappa\varkappa \rightleftharpoons \varepsilon\varepsilon\varepsilon$ compound. A further analysis proved that the form present in the crystal is the $\varkappa\varkappa\varkappa$ form [7]. The configurations of the 1,2 and 1,3-diols can not be deduced from these preliminary X-ray data. However, optical resolution has been obtained for γ-*cyclo*hexane-diol-(1,2) and for *trans*-resorcitol [8], thus proving the first one to be $\varkappa\varkappa \rightleftharpoons \varepsilon\varepsilon$, whereas the latter is $\varkappa\varepsilon \rightleftharpoons \varepsilon\varkappa$. For the *cyclo*hexane-diols-(1,2) this conclusion is confirmed also by an electron diffraction investigation [9].

The space groups are all consistent with the structures given in the table. In the crystals of *trans*-resorcitol and γ-*cyclo*hexane-diol 1,2 there is an equal number of *d*- and *l*-molecules, in agreement with the possibility of resolving these compounds. The molecules of *cis*-resorcitol, the 1,4-diols and the 1,3,5-triols all have a plane of symmetry, and can therefore not be resolved. Any space group would be permitted for these compounds. The last substance, α-*cyclo*hexane-diol-(1,2), is interesting, as the crystals contain both *d*- and *l*-molecules, but no resolution has nevertheless been obtained. This is due to the transposition of the *cyclo*hexane ring, which transfers $1\varkappa2\varepsilon$ into its optical antipode $1\varepsilon2\varkappa$, thus making it impossible to resolve the compound.

As mentioned before, we were interested in finding a substance suited for a detailed analysis of the carbon skeleton of *cyclo*hexane. The best one would appear to be *cis*-resorcitol, its main advantages being centres of symmetry and two relatively short axes.

SUMMARY

The space groups of the resorcitols and of β-phloroglucitol have been determined, and all X-ray data given in the literature on diols and triols of *cyclo*hexane are collected. It is shown that the chemical and physical information available at this stage suffices to deduce the configurations of these compounds, and that the space groups found are all compatible with the assigned structures.

REFERENCES

1. Hassel, O. *Research*. A review of articles dating from the beginning of the thirties is under publication.
2. Hassel, O., and Wang Lund, E. *Acta Cryst.* 2 (1949) 309.
3. Bastiansen, O., Ellefsen, Ø., and Hassel, O. *Acta Chem. Scand.* 3 (1949) 918.
4. Patterson, A. L., and White, T. N. *Z. Krist.* 78 (1931) 76.
5. White, T. N. *Z. Krist.* 80 (1931) 6.
6. Halmøy, E., and Hassel, O. *Z. physikal. Ch.* B 17 (1932) 258.
7. Andersen, P., and Hassel, O. *Acta Chem. Scand.* 2 (1948) 527.
8. Rigby, W. *J. Chem. Soc.* (1949) 1588.
9. Ottar, B. *Acta Chem. Scand.* 1 (1947) 521.