sugars and small amounts of rhamnose and some other not yet identified compounds could be detected.

1. Gustafsson, Ch., Sundman, J., Pettersson, S., and Lindh, T. *Paper and Timber (Finland)* **33** (1951) 300.
2. Jones, J. K. W., and Schoettler, J. R. *Tappi* **35** (1952) no. 1, 102 A.
3. Björkqvist, K. J., and Jörgensen, L. *Acta Chem. Scand.* **6** (1952) 800.
4. ·Hägglund, E., and Bratt, L. C. *Svensk Kem. Tid.* **48** (1936) 125.
5. Gustafsson, Ch., Sundman, J., and Lindh, T. *Paper and Timber (Finland)* **33** (1951) 1; Saarnio, J., Niskasaari, E., and Gustafsson, Ch. *Suomen Kemistilehti* **B 25** (1952) 25.
6. Sundman, J., Saarnio, J., and Gustafsson, Ch. *Paper and Timber (Finland)* **33** (1951) 115.
7. Wardrop, A. B., and Dadswell, H. E. *Australian J. Sci. Research.* **B 1** (1948) 3.
8. Jayme, G., and Hardess-Steinhäuser, M. *Das Papier* **4** (1950) 104.

The Structure of Dibromocyclohexane of M.P. 49°

S. FURBERG and O. HASSEL

Universitetets Kjemiske Institutt, Blindern — Oslo, Norway

When 1,4- or 1,3-*cyclo*hexanediol is treated with HBr, two solid substances are obtained, one melting at 112°, the other at 49°. It is established beyond doubt that the former is the »trans»-1,4-derivative with both bromine atoms in $\varkappa$ positions. Regarding the structure of the dibromide of m.p. 49°, however, conflicting viewpoints have been put forward. On the basis of rather unconvincing chemical arguments, it has been suggested that the substance is 1,2- or 1,3-dibromo*cyclo*hexane[1], 1-bromomethyl-3-bromo*cyclo*pentane[2] and 1,4-»cis»-dibromo*cyclo*hexane[3]. In 1938 the substance was investigated in this laboratory, using the visual method of electron diffraction. The

diffraction data made it seem probable that the substance was $1\varkappa 3\varkappa$-dibromo*cyclo*hexane[4]. We have recently re-examined the substance, now using the sector method of electron diffraction. Considerable experimental difficulties were encountered and the diagrams obtained were not quite satisfactory. However, they seem to indicate that our earlier suggestion may be incorrect and that the substance probably is $1\varkappa 4$ ε-dibromo*cyclo*hexane. The experimental $\dfrac{\sigma (r)}{r}$ - curve is reproduced in Fig. 1, and appears to exhibit peaks due to both ε- and $\varkappa$-bonded bromine atoms. To account for the position of the maxima IV—VII, it is, however, necessary to assume certain deformations in the ideal $1\varkappa 4\varepsilon$ structure. The dotted curve in Fig. 1 and the interatomic distances given below have been computed from a model in which the carbon ring of the ideal $1\varkappa 4\varepsilon$ structure is flattened by increasing the tetrahedral angles $C_4 - C_3 - C_2$ and $C_4 - C_5 - C_6$ by 5°, the other valency angles being kept unchanged. Deformations are found also in other compounds containing ε-bonded halogen atoms, and are believed to be due to repulsion between these atoms and the nearest ε-bonded hydrogen atoms. The general agreement between experimental and theoretical curves is satisfactory, but maximum VII is much lower than should be expected. In the calculations a $C-C$ distance of 1.54 Å and a $C-Br$ distance of 2.01 Å were used. The maxima are interpreted as follows:

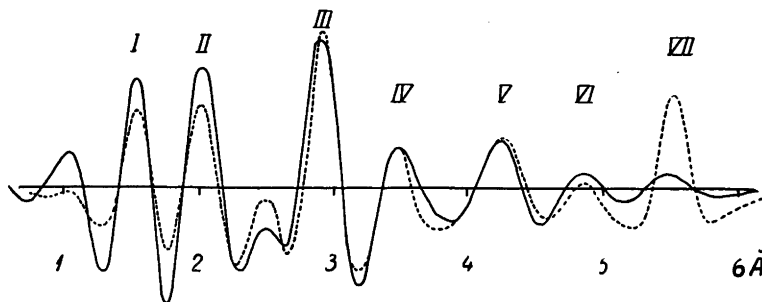| Position of max. (in Å)		Calc. interatomic distances (in Å)	
I	1.53	C_1-C_2	1.54
II	2.02	C_1-Br_1	2.01
III	2.90	$C_1-Br_{2\varkappa\varepsilon}$	2.91
IV	3.48	$C_1-Br_{3\varepsilon}$	3.45
V	4.24	$C_1-Br_{3\varkappa}$	4.30
		$C_1-Br_{4\varepsilon}$	4.11
VI	4.85	$C_1-Br_{4\varkappa}$	4.87
VII	5.47	$Br_{1\varkappa}-Br_{4\varepsilon}$	5.52

Fig. 1. Experimental and theoretical $\dfrac{\sigma\,(r)}{r}$-curves for di-bromo-cyclohexane of m.p. 49°. The theoretical curve (dotted) corresponds to a deformed molecule 1х4ε-dibromo-cyclohexane.

The theoretical curve for 1х3х-dibromo-*cyclo*hexane does not account for the maximum IV, and should have a maximum at 5.78 Å corresponding to the distance $Br_{1х}-Br_{3х}$. The possibility that the molecule is 1-bromomethyl-3-bromo-*cyclo*pentane cannot definitely be ruled out from this experiment, as an orientation of the bromine atom in the methyl group can be found, which gives a theoretical curve similar to that for 1х4ε, although the agreement does not appear to be quite so good.

Preparative work recently carried out in our laboratory using pure isomers of the 1,3- and 1,4-diols and phosphorous tribromide did not give conclusive evidence regarding the positions of the bromine atoms in the molecule.

We have also examined crystals of the substance by X-ray methods. The crystals are monoclinic, with $a = 12.26$ Å, $b = 5.45$ Å, $c = 12.24$ Å, and $\beta = 106.5°$. The higher melting isomer, 1х4х-dibromo*cyclo*hexane, has previously been studied by X-ray methods [5,6], and is also found to be monoclinic, with $a = 12.21$ Å, $b = 5.57$ Å, $c = 6.03$ Å, and $\beta = 107°$. Space group $P2_1/n$. It will be seen that the two substances have nearly the same cell dimen-

sions, apart from the doubling of the c axis. In fact, the two structures must be closely related, as the intensities of the $h0l$ and $0k0$ reflexions are very similar. We have not yet been able to interpret these observations. However, as was to be expected, the Fourier projection along the b axis is very similar for both substances, and seem to indicate that also the isomer melting at 49° is an 1,4-derivative of *cyclo*hexane, in agreement with the conclusions drawn above from electron diffraction measurements.

1. Zelinsky, N. D., and Kozeschkow, K. A. *Ber.* **60** (1927) 1102.
2. Palfray, L., and Rothstein, B. *Compt. rend.* **190** (1930) 189.
3. Rothstein, B. *Ann. Chim.* **14** (1930) 461.
4. Gudmundsen, J. G., and Hassel, O. *Z. phys. Chem.* **B 40** (1938) 326.
5. Halmøy, E., and Hassel, O. *Z. phys. Chem.* **B 16** (1932) 234.
6. Compare Hassel, O., and Lunde, K. *Acta Chem. Scand.* **6** (1952) 1126.