parallel to the plane mentioned, making probably an angle near the tetrahedral with the first bond mentioned. For the molecule to be accommodated in the unit cell, the last mentioned bond must be the one occupied by the substituted phenyl group. A conclusion of these considerations is thus that the phenyl groups must be in *cis* position to the hydrogen atoms at the bridge carbons. The same conclusion is reached by Beroza [5], taking stability and intramolecular steric factors into consideration.

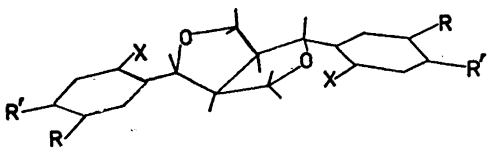

Fig. 1. A probable model of halogen derivatives of pinoresinoldimethylether. X = Br or I.

Fig. 1 shows a drawing in perspective of a probable model based on the arguments given.

A detailed structure determination of diiodopinoresinoldimethylether is in progress.

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1. Erdtman, H. and Gripenberg, J. *Acta Chem. Scand.* **1** (1947) 71.
2. Haworth, R. D. and Woodcock, D. *J. Chem. Soc.* **1939** 1054.
3. Erdtman, H. *Svensk Kem. Tidskr.* **48** (1936) 236.
4. Gripenberg, J. *Suomen Kemistilehti* **19 B** (1946) 138.
5. Beroza, M. *J. Am. Chem. Soc.* **78** (1956) 5082.

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The Structure and Conformation of 1,2,3-Tribromo*cyclohexane* (m.p. 51° C) in the Gas Phase

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Bornubert, Rio and Senechal [1] synthesized a 1,2,3-tribromo*cyclo*hexane (m. p. 51°C) to which they assigned the *eee* conformation on grounds of the compounds reaction used. A sample of their compound was investigated by gas phase electron diffraction in Oslo in order to test the validity of the asigned conformation. The diagrams were taken using distances of 48 cm and 19 cm between the diffraction point and the photographic plate. The data was treated in our usual manner [2], using a damping factor of 0.0036. The $\sigma(r)/r$ radial distribution curve obtained is shown in Fig. 1 (a).

The peak at r = 5.72 Å can only be due to a Br (1*e*)—Br (3*e*) distance. Of the six conformations of 1,2,3-tribromo*cyclo*hexane that can be distinguished with electron diffraction, only those corresponding to *eee* and *eae* contain this distance. Theoretical radial distribution curves were therefore calculated for each of these conformations. It was found that the theoretical *eee* curve gave better agreement with the experimental curve than did the theoretical *eae* curve. However, the agreement was still not particularly good. The peaks at r = 5.72 Å and 4.27 Å in the theoretical *eee* curve were too high, and that at r = 4.63 Å too low. Since the substance is a well defined isomer, these anomalies could only be explained by assuming that in the gas phase it contains either a mixture of the *eee* and *aaa* forms, or else a mixture of the *eae* and *aea* forms. Only the *aaa* conformation would give rise to a substantial peak in the neighbourhood of r = 4.63 Å (due to the Br (1*a*)—Br (2*a*) and Br (2*a*)—Br (3*a*) distances), so it was concluded that the substance must be a mixture of the *eee* and *aaa* forms in the gas phase.

Further theoretical calculations were made using structural models based on the latest parameters for the *cyclo*-hexane ring obtained in our department: C—H=1.103 Å,

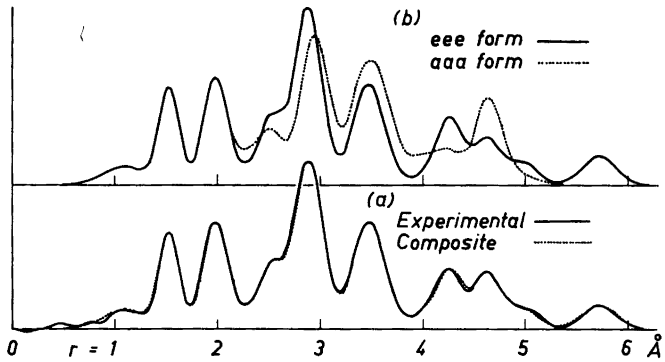

Fig. 1. Theoretical and experimental $\sigma(r)/r$ curves for the 1,2,3-tribromo*cyclo*hexane.

C–C = 1.529 Å, <CCC = 111.5°, <CCH = 110.0°, <HCH = 108.7°.

The C–Br bond distance used was 1.974 Å obtained from the experimental radial distribution curve. In order to get reasonable agreement between the experimental and theoretical curves, some distortion of the models was necessary. The well-defined peak at r = 3.48 Å suggested that this distance represented the closest approach of two non-bonded bromine atoms. This corresponds to a van der Waals radius of 1.74 Å for bromine (*cf.* Pauling's value [3] of 1.95 ± 0.1 Å). Using this value for the Br(1*e*)–Br(2*e*) and Br(1*a*)–Br(3*a*) distances, we calculated the parameters of models with the C–Br bonds distorted from the usual *cyclo*hexane positions. In the case of the *eee* model the distortion was slight; the C(1)–Br and C(3)–Br bonds were out of position by 2°, moved away from the Br(2) atom. As might be expected, the distortion of the *aaa* model was greater; the C(1)–Br and C(3)–Br bonds deviated 20° from the axial position, while the C(2)–Br bond was 9° from the axial position.

Fig. 1(b) shows the theoretical radial distribution curves for these *eee* and *aaa* conformations. Least squares procedure showed that the composite theoretical radial distribution curve giving best agreement with the experimental curve should be constructed on a basis of 19 % of the *aaa* form and 81 % of the *eee* form. In Fig. 1(a) this composite radial distribution curve is compared with the experimental curve. The dispersion of the standard deviation is 4 %.

The accuracy of the ratio between the two forms that we have derived clearly depends on the models we have used for the calculation of the theoretical radial distribution curves. It seems quite probable that small changes in the models would have given slightly different theoretical curves, which might have combined in slightly different proportions to give a composite curve agreeing as well or better with the experimental curve. For this reason we assess our possible error in the distribution ratio as high as ±5 %. The presence of 19 ± 5 % of the *aaa* form corresponds to an energy difference of 1.2 ± 0.3 kcal/mole between the two conformations.

Preliminary X-ray studies of the 1,2,3-tribromo*cyclo*hexane crystals have established a monoclinic structure, with space group $P2_1$, containing two molecules in a unit cell of dimensions: a = 6.44 Å, b = 9.22 Å, c = 7.52 Å and β = 106°.

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1. Cornubert, R., Rio, A. and Senechal, P. *Bull. soc. chim. France* **1955** 46.
2. Almenningen, A. and Bastiansen, O. *Acta Chem. Scand.* **9** (1955) 815.
3. Pauling, L. *The Nature of the Chemical Bond.* Cornell University Press, Ithaca, New York, 1939.

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