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The Conformational Analysis of *cis*-1,4-Chlorobromo*cyclo*hexane

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Cis-1,4-chlorobromo*cyclo*hexane has been studied in the gaseous state by electron diffraction, and in the liquid and solid states by infra-red spectroscopy. The results show that the compound is all, or nearly all, in the *e*-chloro *a*-bromo conformation.

Some years ago it was found that when crystals of 1*e*,2*e*-dichloro-4*e*,5*e*-dibromo*cyclo*hexane were heated to the melting point they isomerized, and that when the melt cooled it consisted mainly of the 1*e*,2*e*-dichloro-4*a*,5*a*-dibromo isomer [1]. More surprising was the fact that neither infra-red [2] nor electron diffraction [3] investigations were able to establish the expected conformational equilibrium ($ee\mathrm{Cl}_2$-$aa\mathrm{Br}_2 \rightleftharpoons aa\mathrm{Cl}_2$-$ee\mathrm{Br}_2$) between the free molecules of this isomer. The only conformation detectable by both methods was that established by X-ray investigations [4] to exist in the crystal, *viz.* the conformation where the two bromine atoms occupy equatorial positions. These findings were hard to explain by simple steric considerations.

It is true that Kozima and Sakashita [5] did claim to have detected evidence of an equilibrium between the two possible conformations of this compound. However, their infra-red investigation used the KBr-disc method, with high temperatures. These are conditions which are more likely to facilitate an S_N2 reaction (such as the reversal of the isomerization [1]: $ee\mathrm{Cl}_2$—$ee\mathrm{Br}_2 \rightleftharpoons aa\mathrm{Cl}_2$—$ee\mathrm{Br}_2$) than the claimed shift in the conformational equilibrium.

In the circumstances, it seemed worthwhile to investigate another compound which might be expected to have a similar conformational oddity. We chose *cis*-1,4-chlorobromo*cyclo*hexane, which might exist as either of the two conformations shown in Fig. 1, or as a conformational equilibrium between them. To the best of our knowledge this compound has not been described before.

PREPARATION

During the preparation of the *trans*-1,4-chlorobromo*cyclo*-hexane from 4-chloro*cyclo*-hexanol and phosphorus tribromide, an oily fraction boiling between 62°C and 64°C (0.5 mm) was collected [6]. This fraction contains both isomers of 1,4-chlorobromo*cyclo*-hexane. Most of the *trans* isomer was precipitated upon cooling to 5°C. The cooling and

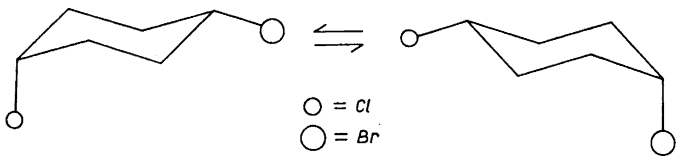

Fig. 1. The possible conformational equilibrium.

filtration was continued until no further crystals formed. Then the filtrate was distilled *in vacuo* in a spinning band column equivalent to 25 theoretical plates. After an appreciable forerun (presumably the remains of the *trans* compound, boiling at about 90°C, 11 mm), a fraction boiling constantly at 97°C (11 mm) was collected. The 97°C fraction solidified on being kept in a refrigerator for some time, and melted again at 21° to 21.5°C. Re-distillation yielded pure *cis*-1,4-chlorobromo*cyclo*hexane with a melting point of 22.0°C.

ELECTRON DIFFRACTION

The electron-diffraction measurements were carried out in the gas phase using the new Oslo apparatus [7] with distances of 19 and 48 cm between the nozzle and the photographic plates. The experimental intensity data, extending from $s = 1.5$ to $s = 45.0$, were treated in the manner described in a series of papers from this institute published after 1955. After appropriate corrections and the inclusion of a damping factor of 0.0024, the experimental intensity curve shown in Fig. 2 was obtained. This was subjected to a Fourier transform to give an initial $\sigma(r)/r$ radial ditribution curve which had substantially the same form as that shown in Fig. 3a.

Theoretical $\sigma(r)/r$ curves (Fig. 3b) were built up from Gauss curves for each of the two possible conformations. The internuclear distances in the two conformations were calculated from models in which the bond distances were: C—H = 1.074, C—C = 1.529, C—Cl = 1.824 and C—Br = 1.981 Å (obtained from the initial radial distribution curve), and the bond angles were C—C—C = 111.5°, C—C—X = 110.0° and X—C—X = 108.7° (obtained from the latest figures for *cyclo*hexane [8]). The models also included a slight distortion of the axial carbon-halogen bonds, suggested by previous work on related compounds [9]. The carbon-chlorine bond was bent outwards 6.3° from the axial position in the *a*-chloro *e*-bromo model, and the carbon-bromine bond was bent outwards 7.7° from the axial position in the *e*-chloro *a*-bromo model.

The two theoretical radial distribution curves were then Fourier transformed back to give two theoretical intensity curves directly comparable with the experimental intensity curve of Fig. 2. It can be seen at once that the theoretical intensity curve for the *e*-chloro *a*-bromo conformation gives the better agreement with the experimental curve. However, this does not eliminate the possibility that both conformations are present together, so a number of composite theoretical intensity curves were also calculated. The values of the dispersion of the standard error between these curves and the experimental intensity curve are given in Table 1. The steady decrease in the standard error as we proceed from 100 % *a*-chloro *e*-bromo to 100 % *e*-

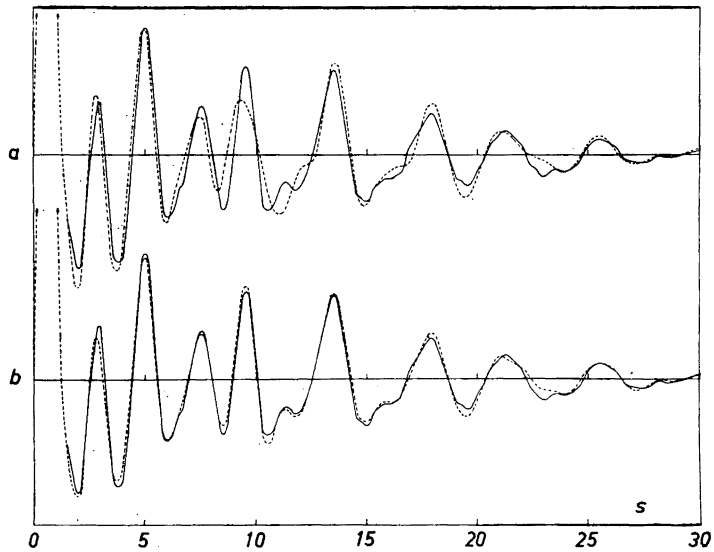

Fig. 2. The experimental intensity curve (full line) compared with the theoretical intensity curves (broken lines) for (a) 1*a*-chloro-4*e*-bromo*cyclo*hexane and (b) 1*e*-chloro-4*a*-bromo*cyclo*hexane. The heavily damped data for $s > 30$ has been omitted so that the figure should still be reasonably distinct after reduction.

chloro *a*-bromo shows that the compound must be all, or nearly all, in the latter conformation.

A final "experimental" radial distribution curve (Fig. 3a) was prepared using the experimental intensity data from $s = 1.5$ to $s = 45.0$, and theoretical intensity data from the *e*-chloro *a*-bromo curve for the experimentally unobtainable inner part from $s = 0$ to $s = 1.5$. It can be seen at once that this final $\sigma(r)/r$ curve agrees well with the theoretical curve for the *e*-chloro *a*-bromo conformation. The dispersion of the standard deviation in that part of the radial distribution curve of relevance for structural assessments ($r > 0.8$ Å) was found to be $\pm$ 8 %.

It is not easy to assess the accuracy of this conformational analysis. While electron diffraction is nowadays very useful in cases where two conformations are present in quantity, it is not very well adapted to the detection of a con-

Table 1. Standard deviation of theoretical intensity curves from the experimental intensity curve, in the range $1.5 < s < 45.0$.

Percentage of *e*-chloro *a*-bromo form in theoretical intensity curve	Percentage dispersion of standard error between theoretical and experimental curves.
0	41.7
25	34.5
50	27.8
70	23.4
90	20.3
95	19.7
100	19.4

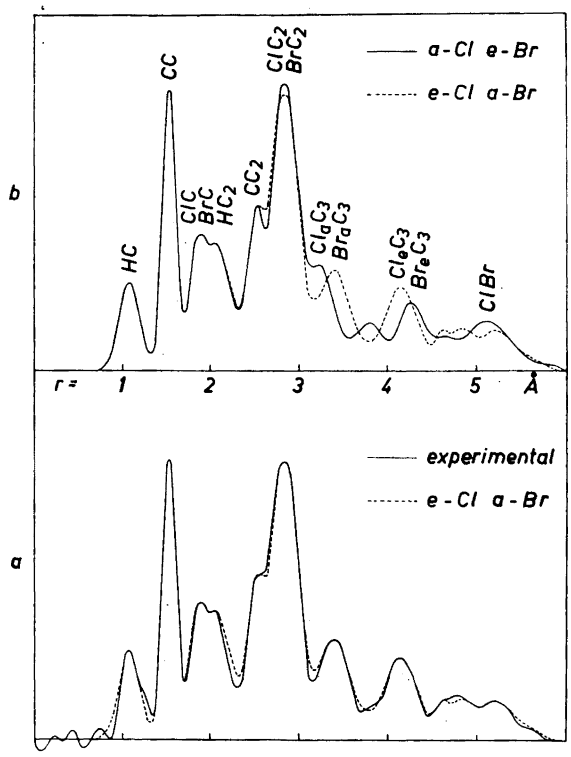

Fig. 3. Theoretical and experimental radial distribution curves for *cis*-1,4-chlorobromo*cyclo*hexane. The internuclear distances responsible for the principal peaks are indicated.

formation present as a trace. A small quantity of the undetected conformation might easily be masked by the major component. However, we feel safe to conclude from this part of the work, that *at least* 90 % of the substance is in the *e*-chloro *a*-bromo form in the gaseous state. This means that the energy difference between the two conformations must exceed 1.2 kcal/mole.

INFRA-RED SPECTRA

The spectra were recorded on a Perkin-Elmer model 21 spectrometer using a sodium chloride cell which permitted work at high and low temperatures. The vapour pressure of *cis*-1,4-chlorobromo*cyclo*hexane is not high enough to give a satisfactory recording of the spectrum of the gas in a 1 m cell, so only the liquid and solid states could be investigated. No solvents were used. The liquid was pure, and crystallisation of the solid was always confirmed by inspection in polarised light.

Typical spectra of the liquid and solid states are reproduced in Fig. 4. It can be seen that the spectra are practically identical, and contain only such minor variations as might be expected as the effect on the vibrations of the changes of state and temperature. Other spectra, taken of samples with

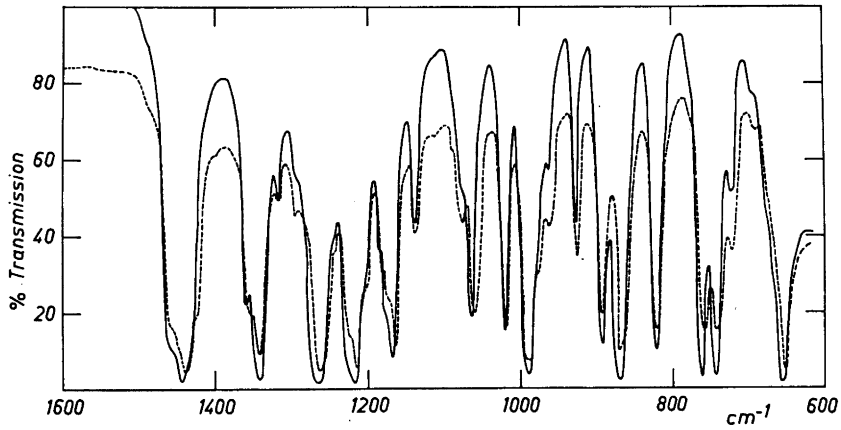

Fig. 4. Infrared spectra of *cis*-1,4-chlorobromo*cyclo*hexane: ———— liquid, at about 30°C; — — — — solid, at about 0°C.

different solidification times and recorded at temperatures down to —170°C, also show little or no variation in the relative intensities and positions of the spectral bands.

The probability of a simultaneous crystallisation of the two conformations, or an unchanging ratio between these conformations under various conditions of temperature and state, must be very low, for this would require not only similar melting points for the two conformations, but also identical lattice packing forces and even identical energy contents for the free molecules.

We therefore conclude that there is only one detectable conformation present in *cis*-1,4-chlorobromo*cyclo*hexane in both the liquid and solid states. This view is supported by our spectral assignments in the carbon-halogen stretching region.

In this region there are strong bands at 743 and 654 cm^{-1}, a weak band at 722 cm^{-1} and an inflection at about 690 cm^{-1}.

Previous work with monohalogeno-*cyclo*hexanes [10], *trans*-1,2-dihalogeno-*cyclo*hexanes [11], *cis*-1,4-dihalogeno-*cyclo*hexanes and the mono-conformational [12] crystals of *trans*-1,4-dihalogeno*cyclo*hexanes, has shown that the different carbon-halogen stretching vibrations are represented by bands which are always found within a few cm^{-1} of the following average frequencies:

C—Cl_e	740 cm^{-1}
C—Cl_a	685 cm^{-1}
C—Br_e	685 cm^{-1}
C—Br_a	655 cm^{-1}

The main bands of the *cis*-1,4-chlorobromo*cyclo*hexane in this region must therefor be assigned to the C—Cl_e and C—Br_a stretching vibrations, and it must be concluded that the compound exists mainly in the *e*-chloro *a*-bromo conformation in the solid and liquid states.

The inflection at 690 cm^{-1} could be assigned to the C—Cl_a and/or C—Br_e vibrations. However, it persists unchanged under all recording conditions,

and must therefore be regarded as doubtful evidence of a possible conformational equilibrium. Even if this inflection is taken as evidence of the existence of an *a*-chloro *e*-bromo form, it could hardly represent more than about 2 % of an equilibrium mixture. This would put the energy difference between the two forms up to at least 2.3 kcal/mole.

DISCUSSION

Only the *e*-chloro *a*-bromo conformation of *cis*-1,4-chlorobromo-*cyclo*hexane has been detected in the gas, liquid and solid states. The infra-red part of this investigation, which is better suited to the detection of traces of the other possible conformation, shows that if this form is present it must be less than 2 % of the whole.

The conclusion must therefore be either (a) there is a conformational equilibrium, but the *e*-chloro *a*-bromo form predominates overwhelmingly and the energy difference between the two forms exceeds 2.3 kcal/mole, or (b) there is no conformational equilibrium, no ring inversion, and the only form produced by our preparative route is the *e*-chloro *a*-bromo conformation. If the latter case is true, it may be that of the disubstituted *cyclo*hexanes only the *ee* forms can invert their rings. In this connection it is interesting to note that a systematic difference has recently been discovered between the proton magnetic resonance spectra of *ee* and *ea* disubstituted *cyclo*hexanes [13].

The preference for the *e*-chloro *a*-bromo conformation, rather than the other possibility, can not be explained on steric grounds. If steric forces were the only ones concerned, we would expect the bulkier bromine atom to prefer the more open equatorial position, as it seems to do in 1,2-dichloro-4,5 dibromo-*cyclo*hexane [2-4]. However, *cis*-1,4-bromomethyl*cyclo*hexane [14] provides another case where bromine is reported to be mainly in the sterically less-favoured axial position.

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