

An Electron Diffraction Analysis of the Conformational Ratio in Monofluorocyclohexane

PER ANDERSEN

Universitetets Kjemiske Institutt, Blindern-Oslo, Norway

Monofluorocyclohexane has been investigated using electron diffraction methods in the gas phase in order to determine the ratio between the axial and equatorial conformations. The best agreement with the experimental distribution curve is obtained when the theoretical curve contains 57 % of the conformation with fluorine in the equatorial position corresponding to an energy difference between the two conformations of approximately 170 cal/mole.

During the last five years attempts have been made using spectroscopic methods, NMR and electron diffraction to determine the ratio of the two conformations in halogenated cyclohexanes. Klæboe, Lothe and Lunde^{1,2} investigated the vibrational spectra of the monohalogenated cyclohexanes in the liquid and solid state and concluded that the *e*-conformation dominates in monochloro- and monobromocyclohexane in the liquid state with 78 % and 85 %, respectively. In the case of monofluorocyclohexane identical spectra were obtained for the liquid, the cubic and the anisotropic solid states. The spectra were investigated down to -150°C and the transition from the cubic to the anisotropic modification was studied in polarized light. It was concluded that one conformation only is present in the liquid state, and it was suggested that an intramolecular hydrogen bond C-H---F might stabilize one of the conformations. Reeves and Strømme³ made an investigation using NMR on monochloro- and monobromocyclohexane and found that the *e*-conformation dominates in both cases with 77 % and 81 %, respectively, in good agreement with the infrared work mentioned above. However, an electron diffraction investigation of monochlorocyclohexane by Atkinson⁴ shows that 55 % of the *e*-conformation is present in the gaseous state. Moreover, an electron diffraction analysis of 1,4-dichloro- and 1,4-dibromocyclohexane by Atkinson and Hassel⁵ led to the conclusion that the *e* and *a* positions are equally populated in both the chloro- and bromo compound. In these substances one should expect to find approximately the same interaction between halogen and the nearest neighbouring carbon and hydrogen atoms as in the monoderivative.

Unless the presence of an intramolecular hydrogen bond should favour one of the conformations of the monofluorocyclohexane molecule there appears to be no reasons for believing that a steric interaction may result in a difference in energy large enough to make one conformation dominate completely. It might be expected that an electron diffraction investigation of the vapour should make it possible to decide at least qualitatively if both axial and equatorial forms are present. An interpretation of the infrared investigation according to which the solid compound contains both forms is not to be excluded but does not appear very satisfactory in view of previously established facts regarding cyclohexane derivatives.

The sample used in the present investigation was kindly placed at the author's disposal by K. Lunde. The diffraction pictures were taken with a distance of 19 resp. 48 cm between the photographic plate and the point of scattering; the intensity curve extended from $s = 1.25$ to $s = 49.5$ ($s = 4 \pi \sin \vartheta/\lambda$). The intensity curve was treated as described elsewhere⁶ and employing three different values of the constant k in the damping expression, viz. 0.009, 0.0015 and 0.0036. The radial distribution curve obtained with $k = 0.0036$ is shown in Fig. 1.

THE RADIAL DISTRIBUTION CURVE

An analysis of the radial distribution curves (Fig. 1) shows that both conformations must be present in the gaseous state. In order to determine the distances associated with the fluorine atom alone it was assumed that the sixmembered ring was undistorted and had the same angles and bond lengths as in cyclohexane itself. The following unpublished cyclohexane values determined in this institute were used; C—C = 1.53 Å, the C—C—C angle 111.5°. A theoretical radial distribution curve built up from Gaussian curves for all the carbon-carbon and carbon-hydrogen distances was subtracted from the experimental $\sigma(r)/r$ curve. The experimental distribution curve and the difference curve containing only the F—C distances are shown in Fig. 1. A theoretical intensity curve was calculated on the basis of all distances and assuming both the *e* and the *a* conformation to be present each with 50 %

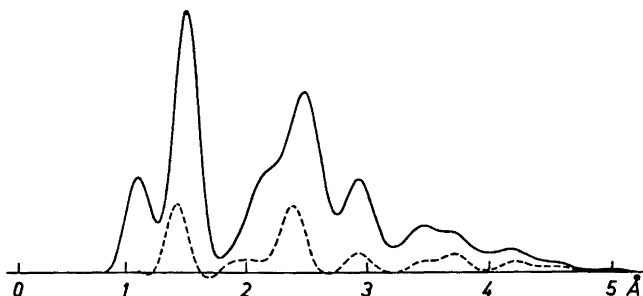


Fig. 1. Radial distribution curve of monofluorocyclohexane (full line) and the distribution curve after subtraction of the contribution from the cyclohexane ring (broken line).

contribution. The experimental intensity curve was extended from $s = 1.25$ to $s = 0$ by adding the theoretical curve and the envelope of the distribution curve was corrected according to the intensity curve.

The radial distribution curve after subtraction of the contribution from the cyclohexane ring itself reproduced in Fig. 1 clearly indicates the presence of all distances both in the equatorial and in the axial conformation. The F—C(1) bond distance at about 1.4 Å and the F—C(2) distance around 2.4 Å should be nearly the same in both conformations, although F_e —C(2) and F_a —C(2) could differ slightly if the C—C—F angle is distorted. The peak at 2.43 Å corresponds to a F_a —C(3) distance and the one around 4.2 Å to the F_e —C(4) distances. The maximum between 3.3 and 3.9 Å contains distances F_a —C(4) around 3.5 Å and F_e —C(3) at about 3.75 Å. The position of the fluorine in the two conformations relative to the cyclohexane ring were determined from these six peaks. Here, an undistorted six-membered ring (C—C: 1.53 Å and C—C—C angle 111.5°) has been assumed. The following distances were determined: F—C: 1.41 Å; F—C(2): 2.35 Å; F_e —C(3): 3.74 Å; F_e —C(4): 4.22 Å; F_a —C(3): 2.93 Å and F_a —C(4): 3.50 Å.

Using these distances theoretical radial distribution curves were constructed from Gaussian curves for both conformations and are reproduced in Fig. 2a.

A least squares procedure on the part of the curve $r > 2.6$ Å was employed in order to determine the ratio of the two conformations from the experimental radial distribution curve. The best agreement with the experimental curve was obtained when the theoretical curve contained 57 % of the *e* form and 43 % of the *a* form leading to a standard deviation ± 2 %. This corresponds to an energy difference of approximately 170 cal/mole between the two conformations. The calculations of the two theoretical radial distribution curves (Fig. 2a) were carried out assuming a cyclohexane ring having the symmetry

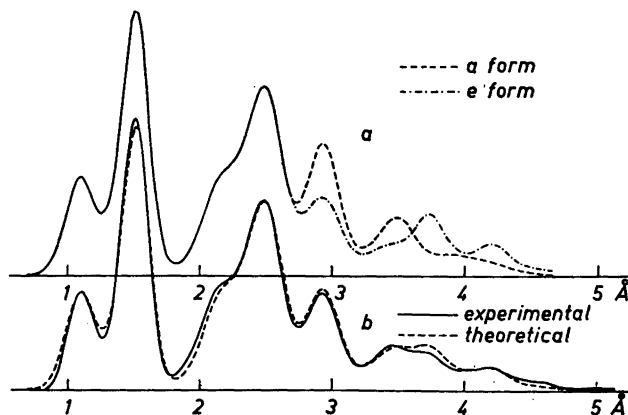


Fig. 2. a: Theoretical radial distribution curves of monofluorocyclohexane for the *e*- and *a*-conformation. b: Experimental and theoretical radial distribution curves. The theoretical curve containing 57 % of the *e*-conformation.

D_{3d} and this makes it difficult to estimate the accuracy of the determined ratio between the two conformations.

The distances determined show that the C—F bond direction is probably not strictly parallel to the chief axis of the ring when fluorine is in the axial position. The tilting is calculated to be 2° away from the axis and could indicate that a slight steric hindrance is present in the axial position. If the hydrogen atoms are assumed to occupy the same positions as in cyclohexane itself the $F_a-H_a(3)$ and $F_e-H_a(2)$ distances will be 2.59 Å and 2.58 Å, respectively, and the fluorine is thus surrounded by hydrogen in the same way in the equatorial and axial positions. There can be no doubt, however, that monofluorocyclohexane is present in both conformations in the gaseous state and the two forms in approximately equal amounts. So far no cases are known where more than one conformation of a cyclohexane derivative has been found in the crystalline state. If the difference in energy of the two conformations is very small, however, one might hope to find cases of polymorphism depending on a transition between different conformations. Transition phenomena in crystals which may be of this kind are now being investigated in this institute.

Acknowledgement. The author wishes to thank Cand.real. Arne Almenningen for taking the electron diffraction pictures and Siv.ing. Liv Fernholt for her assistance with the numerical calculations.

REFERENCES

1. Klæboe, P., Lothe, F. J. and Lunde, K. *Acta Chem. Scand.* **10** (1956) 1465.
2. Klæboe, P., Lothe, F. J. and Lunde, K. *Acta Chem. Scand.* **11** (1957) 1677.
3. Reeves, L. W. and Strömme, K. O. *Can. J. Chem.* **38** (1960) 1241.
4. Atkinson, V. A. *Acta Chem. Scand.* **15** (1961) 599.
5. Atkinson, V. A. and Hassel, O. *Acta Chem. Scand.* **13** (1959) 1737.
6. Bastiansen, O. and Skancke, P. N. *Advan. Chem. Phys.* **3** (1961) 323.

Received June 30, 1962.