

The Conformational Analysis of Chlorocyclohexane by Electron Diffraction

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Chlorocyclohexane has been rigorously re-examined using the latest techniques of gas-phase electron diffraction. A conformational equilibrium containing 45 ± 5 % of the form with chlorine in the axial position gives best agreement with the experimental results. This corresponds to an energy difference of less than 260 cal/mole between the two conformations.

The reliability of electron diffraction conformational assessments, past and present, is discussed.

An early electron diffraction investigation of chlorocyclohexane¹ failed to detect any evidence for the existence of the conformation with chlorine in the axial position. Later Larnaudie² reported infra-red evidence for the co-existence of the axial and equatorial conformations, both in the liquid and in the vapour phase. Since that time there have been several attempts at conformational analysis. Klæboe, Lothe and Lunde³ and Le Fèvre and his colleagues⁴ independently calculate from infra-red data that there is 20 % of the axial form in the liquid phase, but these calculations are based on the assumption that the extinction coefficients of the characteristic equatorial and axial carbon-chlorine bond-stretching bands are equal. The latter group of workers also present alternative calculations, based on the molar Kerr constants, which lead to a value of 30 % for the proportion of the axial conformation present in the liquid phase. Chiurdoglu *et al.*⁵ use a different approach to the infra-red data, and they conclude that there is an energy difference of 300 to 400 cal/mole between the two conformations in the liquid phase, which would correspond to an equilibrium containing 36 ± 2 % of the axial conformation. Kozima and Sakashita⁶ have measured the infra-red spectra of gaseous chlorocyclohexane at 117°C and 200°C and conclude that the energy difference between the two conformations is 340 cal/mole, which corresponds to an equilibrium containing over 40 % of the axial conformation at these temperatures.

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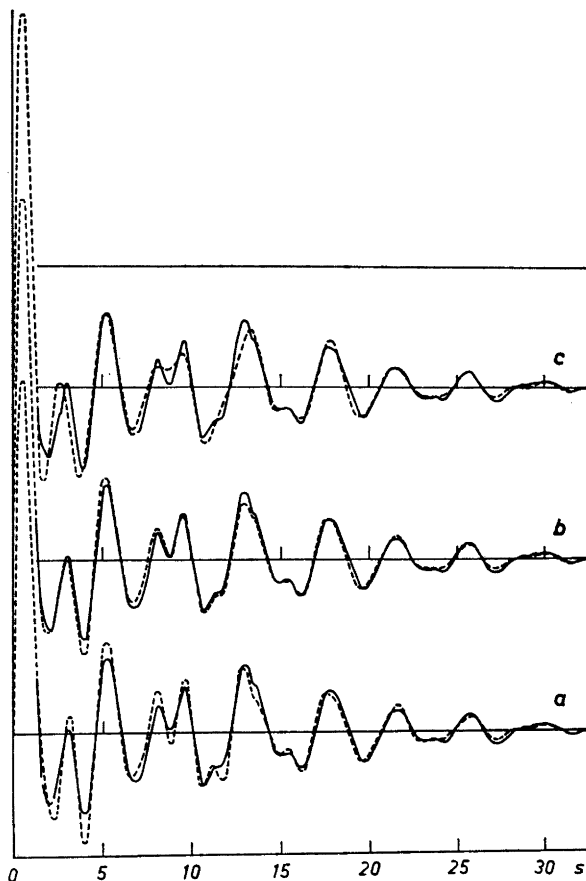


Fig. 1. The experimental intensity curve (full line) compared with the theoretical intensity curves (broken lines) for (a) the *e*-chloro conformation, (b) an equilibrium containing 55 % of the *e*-chloro form and 45 % of the *a*-chloro form, and (c) the *a*-chloro conformation. The heavily damped data for $s > 32.5$ has been omitted.

Since the weight of this evidence seemed to go against the conclusions of the original electron diffraction work, it was decided to re-investigate chloro-*cyclohexane* using the latest electron diffraction procedure, which is very much in advance of the methods in use in 1943.

RESULTS

The electron diffraction measurements were made with the new Oslo apparatus⁷, using distances of 19 cm and 48 cm between the nozzle and the photographic plates. The experimental data, extending from $s = 1.25$ to

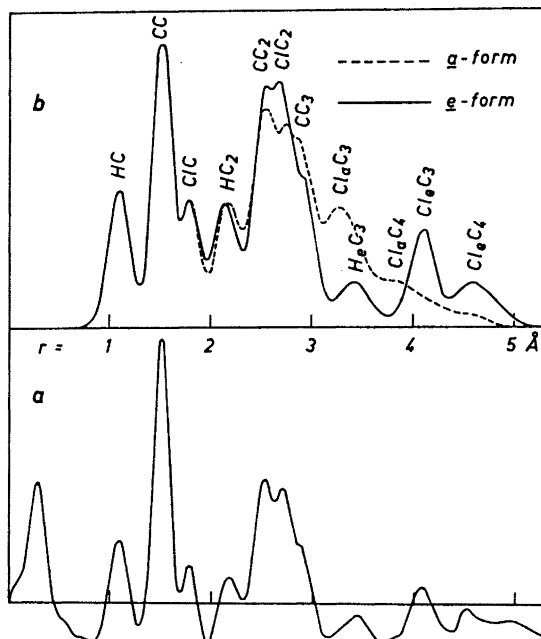


Fig. 2. Radial distribution curves: (a) initial experimental curve, and (b) theoretical curves for the two conformations. The internuclear distances responsible for the principal peaks are indicated.

$s = 45.0$, was subjected to the usual treatment⁸ (including a damping factor of 0.0015), to give the intensity curve shown in Fig. 1. The Fourier transform of this curve is shown in Fig. 2a.

In electron diffraction work it is nowadays our practice to assume a model for the structure of the molecule being investigated, and to construct a theoretical radial distribution curve by summing Gauss curves, one for each internuclear distance r in the model. The area of each Gauss curve has to be proportional to the product of the atomic numbers of the two nuclei divided by the distance between them. Except in the simplest cases it is unrewarding to try and correlate the actual heights and widths of these Gauss curves with molecular vibrations, so the construction of the theoretical radial distribution curve is merely a matter of adjusting (within reasonable limits) the shape (but not the area) of the individual Gauss curves so that the sum curve agrees well with the experimental radial distribution curve. Despite this apparent flexibility in its construction the theoretical radial distribution curve is remarkably sensitive to the r values of the assumed model, and small errors in this model will give a theoretical curve with peaks perceptibly out of position when compared with experimental curve.

Since chlorocyclohexane might exist in two conformations it was necessary to construct a theoretical radial distribution curve for each form (Fig. 2b).

The internuclear distances used were calculated from models in which the bond distances were: C—H = 1.102 Å, C—C = 1.530 Å and C—Cl = 1.810 Å (obtained from the initial experimental 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 the parent compound, *cyclohexane*⁹). The model for the axial conformation included a distortion of the carbon-chlorine 6.3° outwards from the axial position (suggested by previous work on related compounds¹⁰).

Comparison between Figs. 2a and 2b shows good correlation between the positions of the peaks, so it may be taken that the models used are acceptable. It remains to analyse the sizes and shapes of the peaks in order to deduce the conformational equilibrium. This can not be done directly because the true sizes of the peaks in the initial experimental radial distribution curve are uncertain. This uncertainty is due to the omission from the Fourier transform of the inner peak of the intensity curve, which is experimentally unobtainable.

So instead of pursuing the correlation of the radial distribution curves, the two theoretical radial distribution curves were Fourier transformed back to give theoretical intensity curves, one for each conformation. Fig. 1 shows that neither the theoretical intensity curve for the equatorial conformation, nor that for the axial conformation, fits the experimental intensity curve particularly well. A number of composite theoretical intensity curves, representing different mixtures of the two conformations, were drawn and shown to give better agreement with the experimental curve. Table 1 shows that the mixture giving best agreement with the experimental curve would contain about 43 % of the axial conformation.

Final "experimental" radial distribution curves were then prepared using the experimental intensity data from $s = 1.25$ to $s = 45.0$, and theoretical intensity data for the experimentally unobtainable inner peak over $s = 0$ to $s = 1.25$, in the Fourier transform.

It has been suggested that the inclusion of this theoretical intensity data must affect the final "experimental" radial distribution curve and so invalidate

Table 1. Standard deviation of theoretical intensity curves from experimental intensity curve in the range $1.25 \leq s \leq 45.0$

Percentage of <i>a</i> -form in theoretical intensity curve.	Percentage dispersion of the standard error.
0	32.3
10	27.1
20	23.1
30	20.0
40	18.5
45	18.5
50	19.1
60	21.6
70	25.4
80	30.2
90	34.9
100	40.8

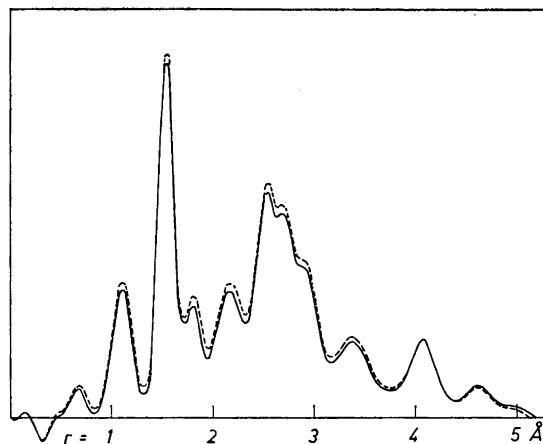


Fig. 3. Radial distribution curves: the full curve was calculated by including theoretical intensity data for the *e*-form, the broken curve by including it for the *a*-form, over the range $0 < s < 1.25$.

the subsequent analysis, but Fig. 3 shows that whichever theoretical intensity curve the additional data is taken from makes very little difference to the final "experimental" radial distribution curve obtained.

A factor having greater effect on the final analysis is the adjusting of the shapes of the individual Gauss curves which make up the theoretical radial distribution curves for the two conformations. It is possible by making some Gauss curves tall and slim, and others short and fat, to shift the apparent position of the equilibrium by up to 10 %.

In order to investigate this more closely a number of different theoretical curves were constructed for each of the two conformations, keeping the same molecular model and the same area for each Gauss curve, but varying the heights and widths of the Gauss curves within reasonable limits. These theoretical radial distribution curves were constructed in pairs, one for each confor-

Table 2. The correlation between some theoretical and experimental radial distribution curves.

Pre-selected equilibrium, <i>a/e</i>	30/70	40/60	45/55	50/50	60/40
Percentage dispersion of standard error for pre-selected equilibrium*	7.6	6.5	6.4	6.5	8.2
Best equilibrium, <i>a/e</i> , by least squares calculation	39/61	44/56	45/55	47/53	50/50
Shift from pre-selected to best equilibrium	+9	+4	0	-3	-10

* The great improvement of these errors over those in Table I is due more to the omission of the non-structural part of the radial distribution curve ($r < 0.8$ Å) than to the slight re-adjustment of the theoretical curves.

mation, so that the composite theoretical curve for a *pre-selected* conformational equilibrium should give *as good a fit as possible* with the final "experimental" radial distribution curve. The standard errors of these fits (Table 2) show that equilibria containing between 40 and 50 % of the axial form still give the best agreement with the experimental results.

A second, and perhaps more instructive, indication of the real position of the conformational equilibrium was obtained by using least squares procedure to calculate the equilibrium giving *the best fit* between the "experimental" curve and *any* composite curve based on each of the above biased pairs of theoretical curves. These calculations showed (Table 2) that the equilibrium containing 45 % of the axial conformation gave the best and most consistent agreement with the experimental results. The size of the shift from the pre-selected equilibrium toward which the theoretical curves were biased, to the best equilibrium seems to give a better indication of the possible error than does the standard deviation.

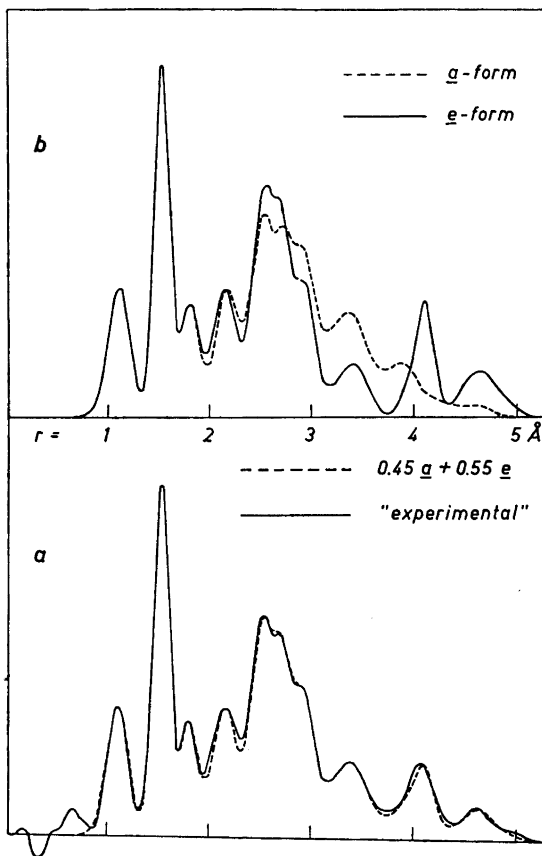


Fig. 4. Final radial distribution curves.

DISCUSSION

Chlorocyclohexane. A conformational equilibrium containing 45 % of the compound in the form with chlorine in the axial position gives best agreement with the final "experimental" radial distribution curve (Fig. 4). The electron diffraction procedure is too complex to permit theoretical limits of error for the conformational analysis to be calculated, but the self-consistency of the results suggests that these might be confidently put at ± 5 %. An equilibrium containing 45 ± 5 % of the axial conformation corresponds to an energy difference of less than 260 cal/mole between the two conformations. This is in fair agreement with that infra-red work which involves no assumptions about extinction coefficients^{5,6}. Moreover it is consistent with the results for *trans*-1,4-dichlorocyclohexane, where both possible conformations were found in about equal proportions¹⁰.

Conformational analysis by electron diffraction. At the time when Hassel and Viervoll¹ investigated chlorocyclohexane the electron diffraction procedure did not give very good resolution of the radial distribution curve, so they made a differential radial distribution curve by subtracting the curve for cyclohexane itself from that for chlorocyclohexane, and then sought for evidence of the carbon-chlorine distances in this differential curve. Unfortunately, they had no accurate figures for the geometry of the cyclohexane ring, so they had to assume that all the bond angles were tetrahedral. This theoretical model gave them values for the Cl_aC_3 and Cl_aC_4 distances which were appreciably smaller than those we now believe to be correct, and which coincided with troughs in their differential curve. If they had better figures for the bond angles they might have detected the presence of the axial conformation, but the method would still have been inadequate for determining the proportions in which the two forms were present.

Since that time the resolution obtainable from electron diffraction measurements has steadily improved, and during the last decade several substituted cyclohexanes have been ascribed to one conformation or another on the basis of qualitative peak assignments made directly in the radial distribution curve. However, this sort of approach can still lead to errors, as can be seen from Fig. 2 where all the peaks of the experimental curve can be accounted for qualitatively by the conformation containing equatorial chlorine alone. It was only when the relative sizes of the peaks were considered that this assignment was found to be inadequate.

Modern electron diffraction procedure gives sufficiently well-resolved peaks in the radial distribution curve for the structures of single substances to be accurately determined. This can be extended to the conformational analysis of cyclic compounds provided (1) the structure of the parent cyclic compound is first accurately determined and (2) the areas under the radial distribution curves are treated quantitatively. A provisional result can be obtained by following the procedure outlined in this paper as far as the comparison of theoretical and experimental intensity curves, but it is probably safer to carry on to the correlation of theoretical and final "experimental" radial distribution curves because these curves are more readily interpreted in structural terms.

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