The Molecular Structures and Conformations of Chlorocyclohexane and Bromocyclohexane as Determined by Gas-Phase Electron Diffraction

Quang Shen and Jeffrey M. Peloquin

Department of Chemistry, Colgate University, Hamilton, NY 13346, USA

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The molecular structures of chloro- and bromocyclohexane have been studied at room temperature in the gas phase by electron diffraction. Both molecules exist as a mixture of two conformations with the halogen atoms located at the equatorial and axial positions. The equatorial form is found to be more abundant in both molecules. The conformational analyses incorporated known microwave rotational constants for both the axial and equatorial forms. The major geometrical parameter values (subject to the assumption that the two conformers differ only in the parameters indicated) obtained by least-squares refinement for the equatorial/axial forms are: (chlorocyclohexane) r(C-H) = 1.112(5), r(C-C) = 1.530(2), r(C-Cl) = 1.809(5)Å, ∠CCH = 109.9(6), ∠CCC = 111.3(5), ∠ClCC = 109.3(4)°, Flap-1 = 128(1)/-134, Flap-2 = 131(1)°/-131° and % equatorial = 75(6) %; (bromocyclohexane) r(C-H) = 1.112(16), r(C-C) = 1.530(4), r(C-Br) = 1.967(17)Å/1.975Å, ∠CCH = 107.7(19), ∠CCC = 113.1(16), ∠BrCC = 110.5 (112)°/112.6°, Flap-1 = 127(3)/-127, Flap-2 = 131(3)°/-131° and % equatorial = 70(13) %.

Dedicated to Professor Otto Bastiansen on his 70th birthday

The conformational equilibrium of cyclohexane has been a cornerstone in the understanding of many organic reactions. The equilibrium conversion of chair to chair conformations converts the equatorial protons to the axial positions and *vice versa*. In terms of mono-substituted cyclohexanes, the equilibrium mixtures contain conformers with the substituents in the axial and equatorial positions. Many studies have been carried out on halocyclohexanes using NMR and vibrational spectroscopy.[1–3] Most of these were carried out in the liquid or solution phases, which are poor media for accurate determination of conformational energy differences because of possible interactions between solute and solvent.

Gas-phase electron diffraction structures of chloro-[4] and fluorocyclohexanes[5] have been reported, and the axial populations were estimated to be 45 % and 43 %, respectively. More recently, high resolution microwave studies on all the halocyclohexanes[6–9] have been reported, and the rotational constants for both the axial and equatorial forms, and some of their isotopic species, were obtained. Estimates of the population of the axial and equatorial forms were also obtained. The number of rotational constants did not allow for the complete structure determination of any of the four halocyclohexanes.

The structures and the conformational compositions of halocyclohexanes in the gas phase are important because many semi-empirical and *ab initio* calculations use them as standard compounds to further the understanding of steric and electronic effects in conformational stability. The availability of the rotational constants for both the axial and equatorial forms of halocyclohexanes provides a rare opportunity for them all to be incorporated into the analyses of the ED data, which could result in the determination of the structures of both the major and minor forms.

The conformational composition can perhaps also be determined more accurately as a result of the incorporation of the rotational constants. We therefore decided to investigate the structures and the conformational compositions of chloro- and bromocyclohexane using gas-phase electron diffraction, and our results are reported here.

Experimental

The purities of the commercial samples of chlorocyclohexane (Aldrich Co.) and bromocyclohexane (Kodak Laboratory Chemicals) were checked by gas chromatography, revealing no significant amounts of impurities. These samples were used for the diffraction experiments without further purification. Electron diffraction data were collected at Colgate University using the Colgate/NDSU apparatus on 4×5 inch Kodak Electron Image plates. The nozzle was kept at room temperature. The ambient pressure was maintained below 2×10^{-5} torr during exposures and an accelerating voltage of 40 keV was used. Benzene calibration plates were recorded under conditions identical to those for the samples. Exposure times were about 5 s for the long and 120 s for the short camera distances. The camera distances measured were: 250.81 mm and 97.69 mm for chlorocyclohexane, and 250.81 mm and 92.14 mm for bromocyclohexane. For each molecule, four plates for each camera distance were selected for analysis. They were traced on the photodensitometer at intervals of 0.20 mm for the long and 0.15 mm for the short camera distances. These data were corrected for emulsion saturation, plate flatness and sector imperfections, and were interpolated to integral q $[(40/\pi)\sin(\theta/2)]$ units. Least-squares analysis of the data were carried out following the procedure outlined by Gundersen and Hedberg.[10] The elastic scattering and phase shift factors used in all the calculations were the ones reported by Schäfer *et al.*[11]

Table 1. Force field for chloro- and bromocyclohexanes.[a]

Force constant	Value	Force constant	Value
K_{CC}	2.32	F_{CC}	0.260
K_{CH}	4.10	F_{HH}	0.046
K_{CH}	2.24	F_{CH}	0.566
H_{CCC}	0.554	F_{CX}	0.498
H_{CCH}	0.317	F_{HX}	0.681
H_{CCX}	0.511	k_{CH2}	−0.012
H_{HCX}	0.100	k_{CHX}	0.078
H_{HCH}	0.513	H_{tors}	0.101

[a]Stretching force constants have units of mdyn Å^{-1}, bending and torsional force constants have units of mdyn Å, non-bonded Urey-Bradley force constants have units of mdyn Å^{-1}, and intermolecular tension constants have units of mdyn Å.

Data analysis

The amplitudes of vibration for both molecules were calculated using the Urey-Bradley force field obtained for chlorocyclopentane,[12] and the values are shown in Table 1. This force field was used to calculate all the B_Z to B_0 corrections[13] needed in the combined ED and MW analysis.

Fig. 1 shows the axial form and the atomic numbering scheme used for the molecule. The geometrical parameters chosen are as follows: (1) the C-H bond length; (2) an average C-C bond length; (3) the C-Cl bond length; (4) the $C_2C_1C_6$ angle, which is equivalent to the $C_1\cdots C_6$ non-bonded distance; (5) the HCC angle; (6) a ClCC angle; (7) Flap-1, the angle between the planes

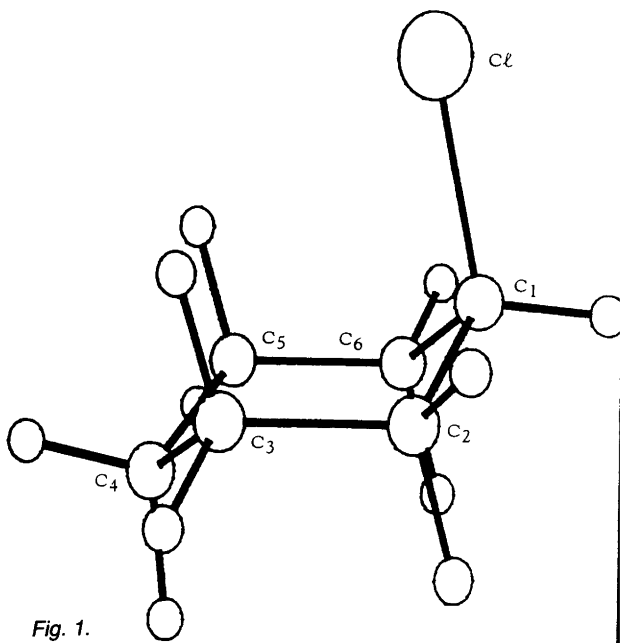

Fig. 1.

Table 2. Structural parameters for chloro- and bromocyclohexanes as determined by least-squares analysis.[a]

Parameter	Chloro	Bromo
r(C–H)	1.112(5)	1.112(16)
<C–C>[b]	1.530(2)	1.530(4)
r(C–X)	1.809(5)	1.967(17)/1.977(50)
∠CCC	111.3(4)	113.1(16)
∠HCC	109.9(6)	107.7(19)
∠XCC	109.3(4)/109.3	110.5(12)/112.5
Flap-1[c]	128.2(7)/–134.4	127(3)/–127
Flap-2[d]	131(1)/–131	131(3)/–131
% E[e]	75(6)	70(13)
Dependent valence and torsional angles for the equatorial form		
∠234=∠456	110.4(4)	109.5(17)
∠345=∠612	111.3(4)	113.1(16)
∠561=∠321	111.8(4)	111.3(12)
T3216=T5612	57.0(7)	57.5(27)
T1654=T1234	55.5(7)	54.1(20)
T3456=T2345	54.4(11)	53.8(33)

[a]Distances are r_g values in Å, and angles are r_α values in °. Quoted errors are 3 σ values obtained from least-squares analysis. The values given after the slash are the corresponding ones for the axial form; otherwise, axial and equatorial forms are assumed to have the same value. [b]Average value. [c]The angle between planes formed by atoms $C_1C_2C_6$ and $C_2C_6C_3$. [d]The angle between planes formed by atoms $C_4C_3C_5$ and $C_3C_5C_1$. [e]Percentage of equatorial form.

formed by $C_1C_2C_6$ and $C_2C_6C_3$ (a positive value corresponds to a clockwise rotation of the $C_1C_2C_6$ plane about the C_2C_6 axis); and (8) Flap-2, the angle between the planes formed by $C_4C_3C_5$ and $C_3C_5C_2$ (a positive value corresponds to a clockwise rotation of the $C_4C_3C_5$ plane about the C_3C_5 axis). The assumptions made are: (i) all C-H bond lengths are identical, (ii) all C-C bond lengths are identical and (iii) the atoms $C_2C_3C_5C_6$ form a rectangle.

(A) *Chlorocyclohexane.* Models with only the axial form and equatorial form were tested initially, and the equatorial conformation gave by far the better agreement with the ED data. The disagreement between the equatorial-form model and the experimental data in the 4.6 Å region of the radial distribution (RD) curve suggested introduction of a two-conformer model.

Table 3. Observed and calculated rotational constants (in MHz) for chloro- and bromocyclohexanes.[a]

	B_0	B_Z (obs.)	B_Z (calc.)
Equatorial			
^{35}Cl	4292.09	4293.26	4293.29
	1396.98	1396.77	1397.17
	1127.35	1127.20	1126.93
^{37}Cl	4291.6	4292.79	4292.99
	1359.66	1359.45	1359.80
	1102.95	1102.81	1102.51
Axial			
^{35}Cl	3217.79	3217.00	3217.08
	1760.56	1759.97	1760.45
	1508.62	1507.83	1507.24
^{37}Cl	3208.9	3208.10	3208.35
	1719.49	1718.89	1719.44
	1480.17	1479.39	1478.92
Equatorial			
^{79}Br	4280.0	4281.49	4281.21
	894.73	894.55	895.36
	776.00	775.88	775.13
^{81}Br	4279.2	4280.70	4281.07
	885.59	885.41	886.16
	769.13	769.01	768.23
Axial			
^{79}Br	3078.7	3077.87	3077.63
	1169.32	1168.75	1168.55
	1067.86	1067.23	1066.22
^{81}Br	3077.1	3076.23	3076.29
	1158.37	1157.81	1157.51
	1058.89	1058.27	1057.18

[a]B_0 rotational constants taken from Refs. 7 and 8. B_Z–B_0 corrections calculated from the molecular force field given in Table 1.

A model with a mixture of equatorial and axial forms was employed. In addition to the electron diffraction data, six rotational constants[7] for each of the axial (^{35}Cl and ^{37}Cl) and equatorial (^{35}Cl and ^{37}Cl) forms were included in the least-squares analysis. Initially, all the geometrical parameter values for the axial and equatorial forms were assumed to be identical, with the exception of the sign of the parameters Flap-1 and Flap-2. Using

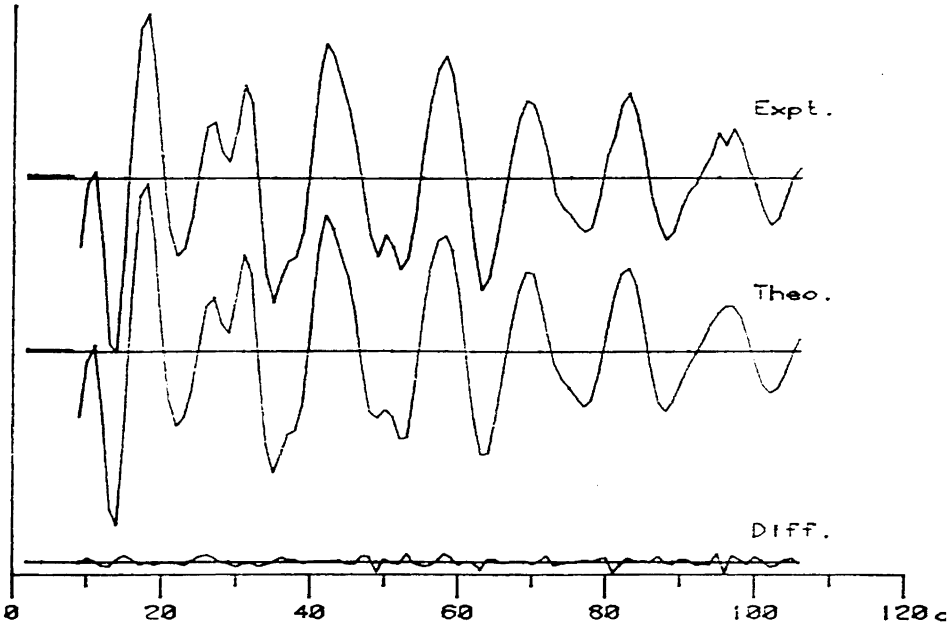

Fig. 2.

this simple model, electron diffraction data were reproduced very satisfactorily. However, the experimental rotational constants for the equatorial and axial forms could not be matched simultaneously, as calculated values for the axial form were too large and those for the equatorial form were too small or *vice versa*. Attempts to introduce differences between the two forms were made (for example, different C-Cl bond lengths or different CCCl angles for the two forms) and we

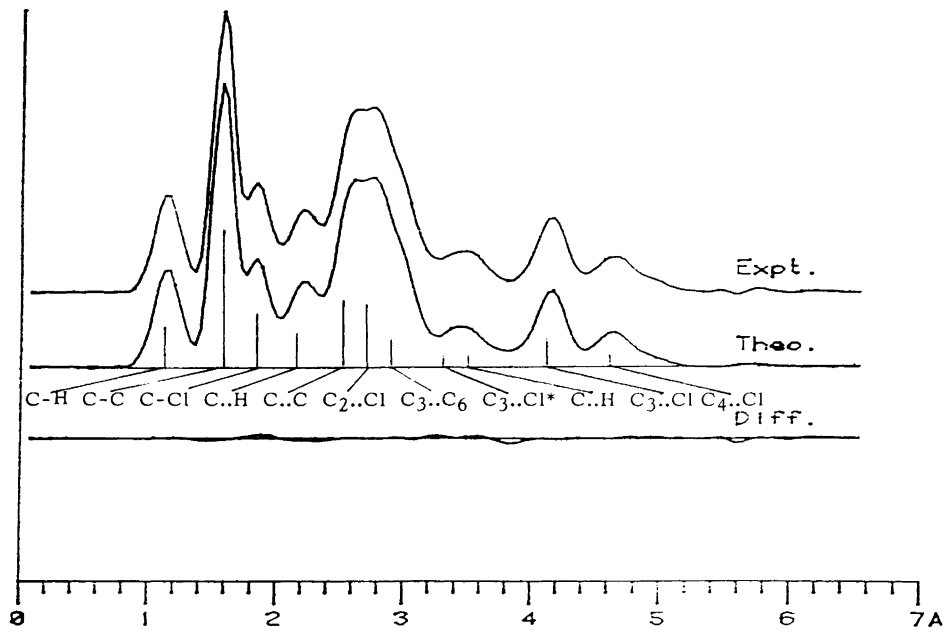

Fig. 3.

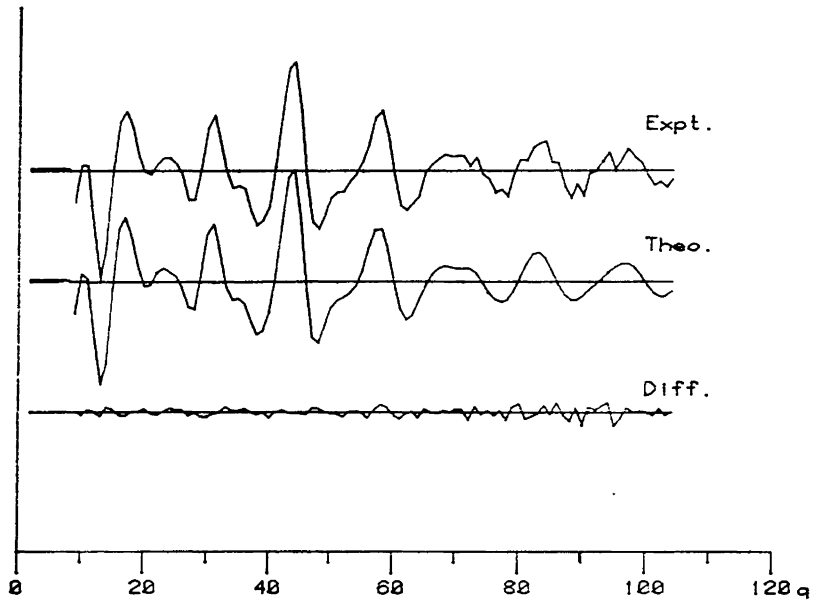

Fig. 4.

found that introduction of a different Flap-1 angle in the axial form made possible simultaneous matching of all twelve rotational constants.

In the combined ED/MW analyses, the equatorial/axial ratio obtained was 75/25(6). In another refinement, where only the ED data were used, the equatorial/axial ratio was found to be 81/19. The final least-squares results obtained

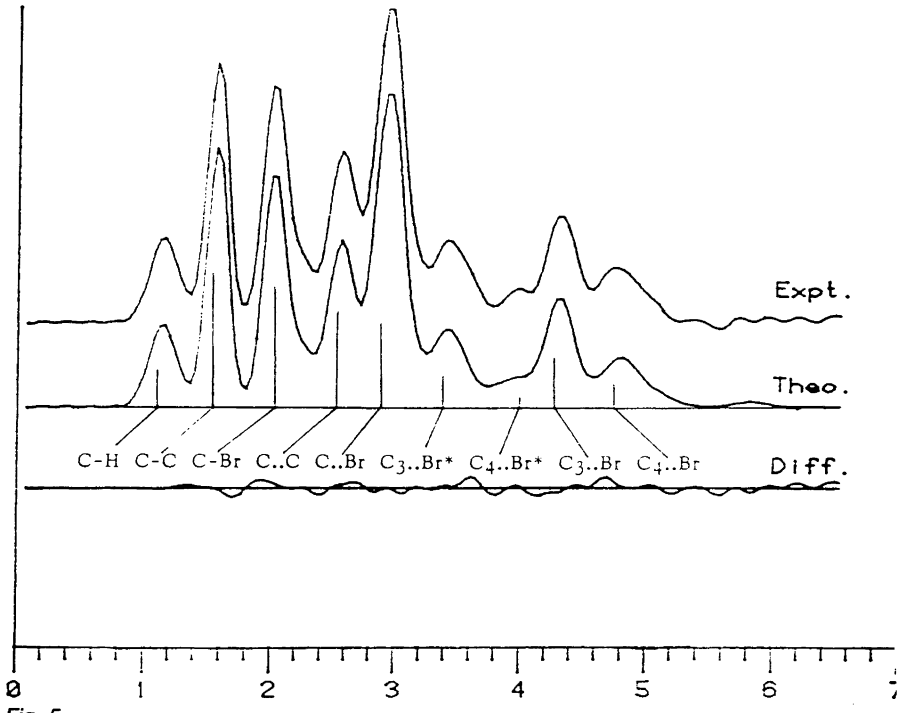

Fig. 5.

from the combined ED/MW analyses for the geometrical parameters and the rotational constants are summarized in Tables 2 and 3, respectively. The corresponding intensity and radial distribution curves are shown in Figs. 2 and 3, respectively.

(B) *Bromocyclohexane.* The geometrical parameters chosen were identical to those used for chlorocyclohexane. A list of the parameters is shown in Table 2. One-conformer models of the axial form and the equatorial form were tested, and the results clearly indicated the presence of a mixture in the vapor at room temperature, with the equatorial form being the major component.

A two-conformer model incorporating axial and equatorial forms was introduced to fit both the ED and MW data. Twelve rotational constants,[8] six for each of the axial and equatorial forms (the ^{79}Br and ^{81}Br isotopic species), were incorporated into the ED data analysis. With the assumption that all geometrical parameters for the axial and equatorial forms were identical, except for the signs of Flap-1 and Flap-2, the MW data were not reproduced satisfactorily. Only when some of the parameters were allowed to differ could agreement for all twelve constants be obtained. First, one parameter was allowed to have different values in the two forms. A 2° difference in the BrCC valence angle improved the agreement between the observed and calculated values of the axial and equatorial rotational constants, to within 2 MHz. This difference was reduced when a difference in the C-Br bond lengths was also included. The C-Br bond length difference was refined to be 0.010Å when the CCBr angle in the axial form was assumed to be 2° larger than that in the equatorial form. A larger angle difference was tested but the results were less satisfactory. Unfortunately these two differences could not be refined simultaneously. The final least-squares results and the calculated rotational constants are shown in Tables 2 and 3, respectively. The corresponding intensity and radial distribution curves are shown in Figs. 4 and 5, respectively. The equatorial/axial ratio obtained from the ED/MW analysis was 70/30(13), while the ratio was 67/33 when only the ED data were used in the least-squares analysis.

Table 5. Conformational energies (kJ mol^{-1}) for cyclohexyl halides obtained by different methods.[a]

Method	Fluoro	Chloro	Bromo
ED(ΔG^0)	–	2.7(7)[b]	2.1020)[b]
MW(ΔE)	1.09(12)[c]	2.14(63)[d]	3.02(1.26)[e]
(ΔG^0)	1.25(12)[c]	–	3.4(1.7)[f]
MM2(ΔE)	0.585[g]	1.59[g]	1.84[g]

[a]Energy differences are calculated as axial−equatorial. [b]This work. [c]Ref. 6. [d]Ref. 7. [e]Ref. 8. [f]Ref. 5. [g]Ref. 15.

Conclusions

The major structural parameters for chloro- and bromocyclohexane and related molecules are summarized in Table 4. The average C-C bond lengths in the two halocyclohexanes obtained

Table 4. Comparison of some geometrical parameters of cyclohexane and halo-substituted cyclohexanes determined by gas-phase electron diffraction.[a]

Parameters	Cyclohexane	Chloro	Bromo	Fluoro	Chloro
r(C–H)	1.104(5)	1.112(5)	1.112(16)	–	1.102
r(C–C)	1.531(2)	1.530(2)	1.530(4)	1.53	1.530
r(C–X)	–	1.809(5)	1.967(17)	1.41	1.810
∠CCC	111.5(3)	111.2[b]	111.3[b]	111.5	111.5
τCCCC	54.6(5)	55.6[b]	55.1[b]	–	–
%E	–	75(6)	70(13)	57	55
Ref.	14	This work	This work	5	4

[a]Distances in Å and angles in °. Parenthesized values are the quoted errors. Errors in data from Refs. 4 and 5 are difficult to estimate because the cyclohexane ring structure is assumed. [b]Average values calculated from the values in Table 2.

from this combined ED/MW study are very similar to the values reported for cyclohexane[14] (1.531Å). The average CCC valence angle and the average ring dihedral angles in both chloro- and bromocyclohexane are almost identical to the values reported for cyclohexane.

The conformational compositions of chloro- and bromocyclohexane vapors at room temperature contain 75(6) % and 70(13) % equatorial form, respectively. These values correspond to free energy differences (axial–equatorial) of 2.7 (7) kJ mol^{-1} and 2.1(20) kJ mol^{-1} for the chloro and bromo compounds, respectively. They compare very favorably with the values obtained from microwave measurements (see Table 5). The error in the conformational composition for bromocyclohexane in this study was very large and made any comparison between the chloro and bromo compounds meaningless. The free energy difference obtained for chlorocyclohexane compared extremely well with the energy difference [2.1(6) kJ mol^{-1}] reported for the high-resolution MW investigation.[7] For halocyclohexanes, the energy difference is about 0.2 kJ mol^{-1} smaller than the free energy difference. The microwave free energy difference could be as high as 2.3 kJ mol^{-1} for chlorocyclohexane. The gas-phase MW and our present ED studies showed that the conformational energy differences between axial and equatorial forms calculated by MM2[15] for fluoro-, chloro- and bromocyclohexanes are about 0.5 kJ mol^{-1} too small.

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