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Molecular structures and conformational compositions of 2-chlorobutane and 2-bromobutane; an investigation using gas-phase electron-diffraction data and ab initio molecular orbital calculations[☆]

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Abstract

The structure and conformational composition of 2-chlorobutane and 2-bromobutane have been studied by gas-phase electron diffraction (GED) at 25°C, together with ab initio molecular orbital calculations (HF/6-311+G(d,p)). These molecules may exist as three distinguishable conformers (G+, A, and G−). The symbols refer to anti (A) with a torsion angle $\Phi_2(X_8-C_2-C_3-C_4)$ of about 180° and gauche (G+ and G−) with torsion angles $\Phi_2(X_8-C_2-C_3-C_4)$ of about +60° and 300°(−60°), respectively. It was not possible; from our GED-data alone, to accurately determine the conformational composition because the distance distributions for two of the conformers (G+ and G−) are very similar. The conformational composition for 2-chlorobutane obtained from the ab initio calculations (G+ 62%, A 25% G− 13%) was found to fit the experimental data quite well. For 2-bromobutane the ab initio calculated conformational composition (G+ 58%, A 28% G− 14%) did not, however, fit the experimental data. Here a much better fit was obtained by using only 10% of the A conformer and using the relative energy for the two gauche conformers, as obtained in the ab initio molecular orbital calculations, to calculate the relative amounts of the two gauche forms (G+ 73%, A 10% G− 17%). The results for the principal distances (r_g) and angles \angle_α for the G+ conformer of 2-chlorobutane, with estimated 2σ uncertainties, obtained from the combined GED/ab initio study are: $r(C_1-C_2) = 1.524(3)$ Å, $r(C_2-C_3) = 1.528(3)$ Å, $r(C_3-C_4) = 1.539(3)$ Å, $r(C-Cl) = 1.812(3)$ Å, $r(C-H)_{ave} = 1.098(4)$ Å, $\angle C_1C_2C_3 = 111.5(16)^\circ$, $\angle C_2C_3C_4 = 113.3(5)^\circ$, $\angle C_1C_2Cl = 110.4(9)^\circ$. The results for the G+ conformer of 2-bromobutane are: $r(C_1-C_2) = 1.526(4)$ Å, $r(C_2-C_3) = 1.530(4)$ Å, $r(C_3-C_4) = 1.540(4)$ Å, $r(C-Br) = 1.982(5)$ Å, $r(C-H)_{ave} = 1.111(8)$ Å, $\angle C_1C_2C_3 = 112.5(16)^\circ$, $\angle C_2C_3C_4 = 114.6(15)^\circ$, $\angle C_1C_2Br = 110.1(16)^\circ$. Only average values for $r(C-C)$, $r(C-H)$, $\angle CCC$, and $\angle CCH$ could be determined in the least-squares refinements, the differences between these parameters in the same conformer, and between the different conformers, were kept constant at the values obtained in the ab initio molecular orbital calculations. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

We have earlier investigated the structures and conformational composition of several halogen substituted butanes [1–4] using gas-phase electron diffraction data together with ab initio molecular

[☆] Dedicated to Professor Marit Trøetteberg on the occasion of her 70th birthday.

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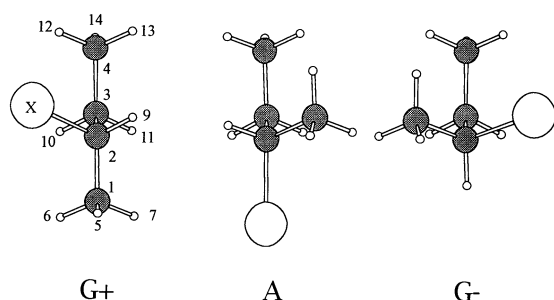


Fig. 1. Diagrams for the three different conformers of 2-halobutane (Cl, Br).

orbital calculations. 2-chlorobutane and 2-bromobutane are other interesting molecules in this series. 2-chlorobutane has been studied by electron diffraction [5–6] earlier, but we found it worthwhile to reinvestigate it since we now can combine the GED-data with results from *ab initio* calculations. We can also now use the same model for both molecules and get a good comparison of the structural parameters in these two molecules. The previous investigation [5–6] of 2-chlorobutane indicated that the G+ conformer was the low-energy form. The symbols A, G+ and G– are used for $X_8-C_2-C_3-C_4$ torsion angles of $\Phi = 180, +60$, and $300^\circ (-60^\circ)$, respectively. The molecule is depicted in Fig. 1, which contains the different possible conformers and a numbering scheme for the atoms.

2. Experimental

The samples of 2-chlorobutane and 2-bromobutane were obtained from Aldrich Chem. Co. (98–99% purity) and were used without any further purification. The diffraction experiments were made with the Oregon State University apparatus using an r^3 sector and Kodak Electron Image plates. The acceleration voltage was about 60 kV (nominal electron wavelength 0.04871 Å and 0.04876 Å for 2-chlorobutane and 2-bromobutane, respectively). Nozzle-to-plate distances of 747.3 and 746.7 mm (long camera, LC) and 298.7 and 299.5 mm (middle camera, MC) were used for 2-chlorobutane and 2-bromobutane, respectively. The voltage/distance calibration was carried out with CS₂ as reference. The analytical procedures for the data reduction have been described elsewhere

[7–9]. Ranges of data for 2-chlorobutane were $2.00 \leq s/\text{\AA}^{-1} \leq 6.50$ and $8.00 \leq s/\text{\AA}^{-1} \leq 32.00$ and for 2-bromobutane $2.00 \leq s/\text{\AA}^{-1} \leq 16.50$ and $8.00 \leq s/\text{\AA}^{-1} \leq 35.75$. The data interval was $\Delta s = 0.25 \text{\AA}^{-1}$. A calculated background [9] was subtracted from the data for each plate to yield experimental molecular intensity curves in the form $sI_m(s)$. The experimental intensity curves are shown in Fig. 2. The data are available as supplementary material. Radial distribution (RD) curves (see Figs. 3 and 4) were calculated in the usual way by Fourier transformation of functions $I'_m(s) = Z_C Z_X (A_C A_X)^{-1} s I_m(s) \exp(-Bs^2)$ with $X = \text{Cl}$ or Br and $B = 0.0020 \text{\AA}^{-2}$, and where $A = s^2 F$ and F are the absolute values of the complex scattering amplitudes. The scattering amplitudes and phases were taken from tables [10].

3. Structure analysis

From results obtained in earlier investigations of halogenated alkanes it was reasonable to assume threefold barriers against torsion about each of the three carbon–carbon bonds. Only torsion about the C_2-C_3 bond will give distinguishable conformers, however, because of symmetry. There are therefore only three distinguishable conformers; G+, A, G– (see Fig. 1).

In the theoretical model used to analyze the electron diffraction data, all the three different conformers were included. Each conformer was defined by the following geometrical parameters ($X = \text{Cl}$ or Br): $r(C_2-C_3)$, $\Delta r_1(C-C) = r(C_2-C_3) - r(C_1-C_2)$, $\Delta r_2(C-C) = r(C_2-C_3) - r(C_3-C_4)$, $r(C-X)$, $r(C_1-H)$, $\Delta r_1(C-H) = r(C_1-H) - r(C_2-H)$, $\Delta r_2(C-H) = r(C_1-H) - r(C_3-H)$, $\Delta r_3(C-H) = r(C_1-H) - r(C_4-H)$, $\angle CCC = (\angle C_1 C_2 C_3 + \angle C_2 C_3 C_4)0.5$, $\Delta \angle(CCC) = (\angle C_1 C_2 C_3 - \angle C_2 C_3 C_4)$, $\angle C_3 C_2 X$, $\angle CC_1 H$, $\Delta \angle_1(CCH) = \angle CC_1 H - \angle C_3 C_2 H$, $\Delta \angle_2(CCH) = \angle CC_1 H - \angle CC_4 H$, $\angle HC_3 H$, $\angle HC_2 X$, $\Phi_1(H_5-C_1-C_2-C_3$ torsion angle), $\Phi_2(X_8-C_2-C_3-C_4$ torsion angle) and $\Phi_3(C_2-C_3-C_4-H_{14}$ torsion angle). For the $r(C-H)$ distances, the $\angle HCH$ and the $\angle CCH$ angles on the same carbon atom average values were used.

To get more information about the structure and conformational composition, *ab initio* molecular

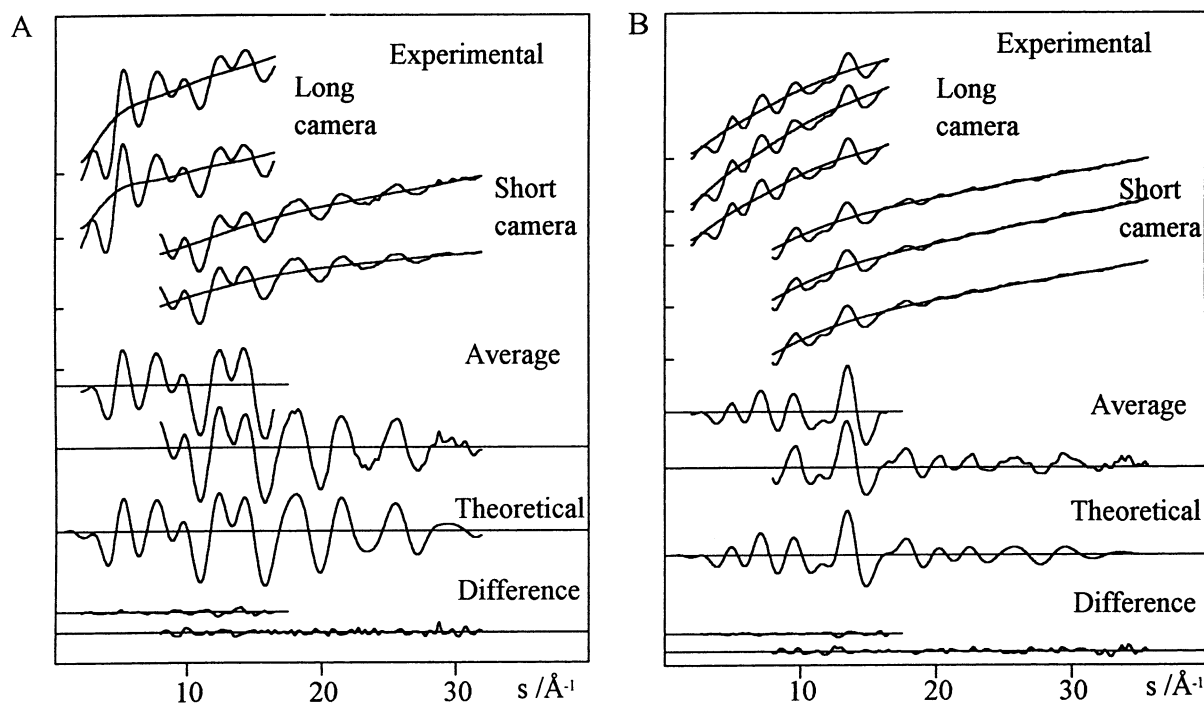


Fig. 2. Experimental intensity curves ($s^4 I(s)$) for (A) 2-chlorobutane and (B) 2-bromobutane from each plate shown magnified 7 times with respect to the final backgrounds on which they are superimposed. The average curves are $sI_m(s) = s(s^4 I_t - \text{background})$. The theoretical curve is for the model in Table 2.

orbital calculations were performed. The calculations were performed using the program GAUSSIAN94 [11]. The geometries were fully optimized at the Hartree–Fock level of theory and with the 6-311G+(d,p) basis set (see Table 1 for the ab initio results). The results from these calculations were used to modify our theoretical model used in the electron diffraction analysis. It is very difficult to determine small differences in distances (Δr) and angles ($\Delta \angle$) from electron-diffraction data alone. These differences were therefore constrained at the values obtained in the ab initio calculations (as were also the differences in the corresponding parameters in the different conformers e.g. C_1-C_2 in G+ and C_1-C_2 in A). These values (Δr and $\Delta \angle$) are believed to be determined fairly accurately by ab initio calculations, even with relatively small basis sets [12]. In an earlier study [13] it has been shown that increasing the level of theory and/or basis set has little or no effect on the structural parameters in halogenated butanes. It should be

mentioned that by using the results from the ab initio calculations, Δr_e is assumed to be equal to Δr_a , assuming that the vibrational corrections are negligible.

In order to correct for shrinkage effects in the experimental distance measurements, appropriate distance conversions are needed. These are given by: $r_a = r_g - l^2/r = r_a + K - l^2/r$, where the perpendicular amplitude corrections, K , and root-mean-square amplitudes of vibration, l , were calculated using the program ASYM40 [14]. The force fields used in these calculations were obtained from ab initio calculations at the Hartree–Fock level of theory and with the 6-311G+(d,p) basis set. The force constants were scaled by a factor of 0.9, except for the torsion angle force constants where a factor of 1.0 was used.

Refinements of the structures were carried out by the least-squares method, adjusting a theoretical $sI_m(s)$ curve simultaneously to the two average experimental intensity curves (one from each camera distance), [15]

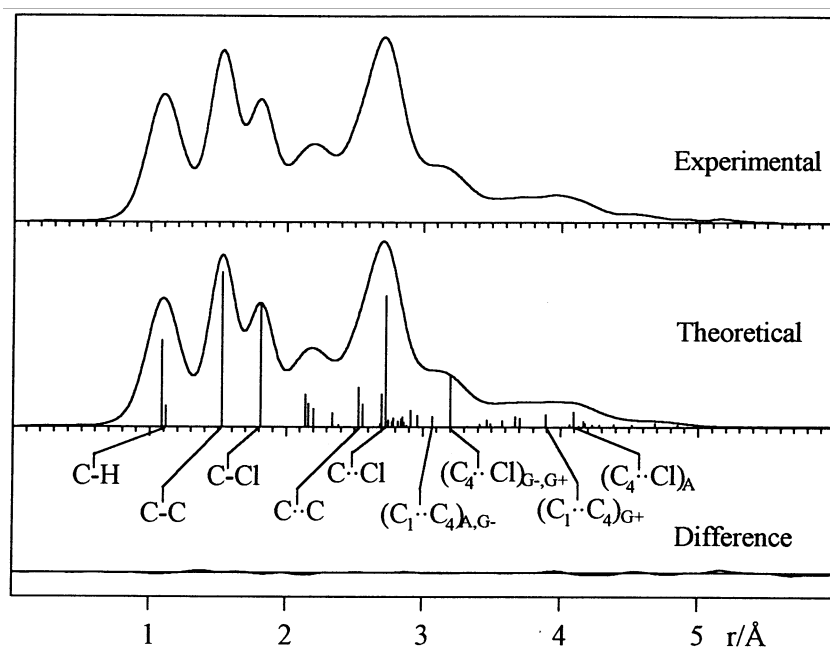


Fig. 3. Radial distribution curves for 2-chlorobutane. The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region $0 \leq s/\text{\AA}^{-1} \leq 1.75$ and $B/\text{\AA}^2 = 0.0020$. Difference curve is experimental minus theoretical. The vertical lines indicate important interatomic distances and the lines have lengths proportional to the distance weights.

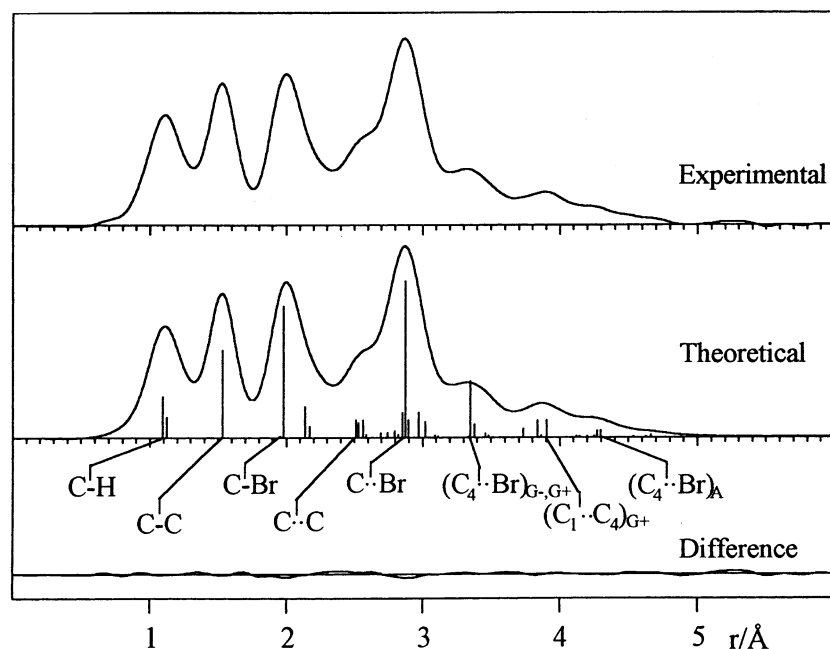


Fig. 4. Radial distribution curves for 2-bromobutane. The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region $0 \leq s/\text{\AA}^{-1} \leq 1.75$ and $B/\text{\AA}^2 = 0.0020$. Difference curve is experimental minus theoretical. The vertical lines indicate important interatomic distances and have lengths proportional to the distance weights.

Table 1

Results from theoretical calculations for 2-chlorobutane and 2-bromobutane using HF/6-311+G(d,p).

Parameters ^a	2-chlorobutane			2-bromobutane		
	G+	A	G–	G+	A	G–
$r(\text{C}_1\text{--C}_2)$	1.5192	1.5196	1.5196	1.5192	1.5198	1.5197
$r(\text{C}_2\text{--C}_3)$	1.5240	1.5259	1.5271	1.5239	1.5263	1.5272
$r(\text{C}_3\text{--C}_4)$	1.5264	1.5303	1.5277	1.5258	1.5215	1.5274
$r(\text{C--X})$	1.8230	1.8219	1.8242	1.9879	1.9871	1.9898
$r(\text{C}_1\text{--H})$	1.0850	1.0845	1.0846	1.0851	1.0845	1.0846
$r(\text{C}_2\text{--H})$	1.0811	1.0811	1.0801	1.0803	1.0803	1.0792
$r(\text{C}_3\text{--H})$	1.0877	1.0856	1.0873	1.0879	1.0852	1.0875
$r(\text{C}_4\text{--H})$	1.0854	1.0858	1.0850	1.0855	1.0857	1.0849
$\angle \text{C}_1\text{C}_2\text{C}_3$	113.19	114.97	115.26	113.25	115.11	115.36
$\angle \text{C}_2\text{C}_3\text{C}_4$	114.94	113.23	116.31	115.35	112.96	116.59
$\angle \text{C}_1\text{C}_2\text{X}$	108.67	108.65	109.08	108.60	108.71	109.17
$\angle \text{C}_3\text{C}_2\text{X}$	110.26	108.58	110.29	110.60	108.68	110.60
$\angle \text{CC}_1\text{H}_{\text{ave}}$	110.44	110.51	110.51	110.49	110.56	110.55
$\angle \text{C}_3\text{C}_2\text{H}$	110.17	109.95	108.53	110.48	110.27	108.82
$\angle \text{C}_4\text{C}_3\text{H}_{10}$	110.29	109.17	109.37	110.35	109.07	109.17
$\angle \text{C}_4\text{C}_3\text{H}_{11}$	109.12	110.10	109.63	108.92	110.00	109.69
$\angle \text{CC}_4\text{H}_{\text{ave}}$	110.96	111.18	111.02	110.97	111.15	111.02
$\angle \text{HC}_2\text{X}$	103.93	103.92	103.40	102.93	102.86	102.18
$\angle \text{H}_{10}\text{C}_3\text{H}_{11}$	106.74	106.81	106.55	106.61	106.84	106.48
$\angle \text{HC}_1\text{H}_{\text{ave}}$	108.48	108.41	108.41	108.43	108.36	108.37
$\angle \text{HC}_4\text{H}_{\text{ave}}$	107.95	107.70	107.87	1107.93	107.73	107.87
$\Phi(\text{C}_4\text{C}_3\text{C}_2\text{X})$	65.26	173.16	–67.32	65.84	172.96	–68.34
$\Phi(\text{C}_3\text{C}_2\text{C}_1\text{H}_5)$	–180.75	–183.01	175.07	–179.65	–177.22	174.55
$\Phi(\text{C}_2\text{C}_3\text{C}_4\text{H}_{14})$	–63.11	–55.30	–62.94	–64.36	–55.35	–62.13
Energy ^b	–616.27131972	–616.27045603	–616.26989040	–2729.13189274	–2729.13121929	–2729.13055202

^a The Distance are in Ångstroms and the angles are in degrees.^b The energies are given in Hartree.

using a unit weight matrix. In the least-squares refinements amplitudes of the same order of magnitude associated with distances of similar lengths were grouped together as a single parameter, with differences held constant at values determined by the normal coordinate calculations. Those amplitudes, which were not refined, were kept constant at the calculated values. The torsional angle parameters could not be refined and they were therefore constrained at the values obtained in the ab initio calculations. These constraints had little impact on the final results of the other parameters determined in the least-squares refinements. The distance distributions for the G+ and the G– conformers are quite similar, as can be seen from Fig. 5B. It was possible to refine the conformational composition, but the uncertainties on the

obtained values were very large. The conformational composition was therefore kept constant at several different mixtures during the least-squares refinements (see Discussion for more details). In the final refinement for each of the two molecules three distances, four angle, and seven amplitude parameters were refined simultaneously. The results of the final refinements are given in Table 2, together with the results for some selected bond distances, valence angles and amplitudes. The intensity curves calculated for the final models are shown in Fig. 2, together with experimental and difference curves. Figs. 3 and 4 show the corresponding RD-curves, and the correlation matrices for the refined parameters are given in Tables 3 and 4 for 2-chlorobutane and 2-bromobutane, respectively.

Table 2

Structural parameters for the G+ conformer of 2-chlorobutane and 2-bromobutane.

Parameters ^a	2-chlorobutane		2-bromobutane	
	Electron diffraction	Ab initio ^b	Electron diffraction	Ab initio ^b
	r_α/\angle_α		r_α/\angle_α	
$r(\text{C}_2\text{--C}_3)$	1.524(3)	1.524	1.525(4)	1.524
$\Delta r_1(\text{C--C})$	[0.005]	[0.005]	[0.005]	[0.005]
$\Delta r_2(\text{C--C})$	[−0.002]	[−0.002]	[−0.002]	[−0.002]
$r(\text{C--X})$	1.809(3)	1.823	1.979(5)	1.988
$\langle r(\text{C--H}) \rangle$	1.066(4)	1.085	1.074(8)	1.085
$\Delta r_1(\text{C--H})$	[0.004]	[0.004]	[0.005]	[0.005]
$\Delta r_2(\text{C--H})$	[−0.003]	[−0.003]	[−0.003]	[−0.003]
$\Delta r_3(\text{C--H})$	[0.000]	[−0.000]	[−0.000]	[−0.000]
$\langle \angle \text{CCC} \rangle$	112.39(5)	114.07	113.53(15)	114.3
$\Delta \angle \text{CCC}$	[−1.74]	[−1.74]	[−2.10]	[−2.10]
$\angle \text{C}_3\text{C}_2\text{X}$	108.43(7)	110.26	109.30(13)	110.60
$\angle \text{CC}_1\text{H}_{\text{ave}}$	111.14(15)	110.44	107.67(30)	110.49
$\Delta \angle_1\text{CCH}$	[0.27]	[0.27]	[0.88]	[0.88]
$\Delta \angle_2\text{CCH}$	[2.75]	[2.75]	[0.73]	[0.73]
$\Delta \angle_3\text{CCH}$	[−0.52]	[−0.52]	[−0.48]	[−0.48]
$\angle \text{HC}_3\text{H}$	[106.73]	[106.73]	[106.61]	[106.61]
$\angle \text{HC}_2\text{X}$	116.57(19)	103.93	114.65(43)	102.93

Selected distances and angles

	r_α/\angle_α	r_g	l_{refined}	r_e/\angle_e	$l_{\text{calculated}}$	r_α/\angle_α	r_g	l_{refined}	r_e/\angle_e	$l_{\text{calculated}}$
$r(\text{C}_1\text{--C}_2)$	1.519(3)	1.524	0.065(4)	1.519	0.051	1.521(4)	1.526	0.059(5)	1.519	0.051
$r(\text{C}_2\text{--C}_3)$	1.524(3)	1.528	0.065(4)	1.524	0.051	1.525(4)	1.530	0.059(5)	1.524	0.051
$r(\text{C}_3\text{--C}_4)$	1.526(3)	1.539	0.065(4)	1.526	0.051	1.527(4)	1.540	0.059(5)	1.526	0.051
$r(\text{C--X})$	1.809(3)	1.812	0.063(4)	1.823	0.057	1.979(5)	1.982	0.053(7)	1.988	0.057
$r(\text{C--H})_{\text{av}}$	1.065(4)	1.098	0.087(6)	1.085	0.077	1.074(8)	1.111	0.079(8)	1.085	0.077
$r(\text{C}_1\cdots\text{X})$	2.737(15)	2.740	0.079(5)	2.721	0.075	2.881(28)	2.884	0.078(7)	2.861	0.074
$r(\text{C}_3\cdots\text{X})$	2.709(11)	2.710	0.078(5)	2.751	0.075	2.870(23)	2.873	0.078(7)	2.899	0.074
$r(\text{C}_1\cdots\text{C}_3)$	2.515(8)	2.521	0.078(8)	2.540	0.074	2.533(22)	2.538	0.083(15)	2.541	0.072
$r(\text{C}_2\cdots\text{C}_4)$	2.547(8)	2.552	0.077(8)	2.572	0.073	2.569(22)	2.574	0.083(15)	2.577	0.072
$r(\text{C}_4\cdots\text{X})_{\text{G+}}$	3.186(21)	3.188	0.106(13)	3.270	0.134	3.342(37)	3.346	0.134(25)	3.397	0.130
$r(\text{C}_1\cdots\text{C}_4)_{\text{G+}}$	3.886(11)	3.887	0.089(21)	3.918	0.076	3.910(29)	3.913	0.096(60)	3.921	0.075
$\angle (\text{C}_1\text{C}_2\text{C}_3)$	111.5(5)			113.2		112.5(16)			113.2	
$\angle (\text{C}_2\text{C}_3\text{C}_4)$	113.3(5)			114.9		114.6(15)			115.4	
$\angle (\text{C}_1\text{C}_2\text{X})$	110.4(9)			108.7		110.1(16)			108.6	

^a Distances (r) and amplitudes (l) are in Ångstroms and angles (\angle) are in degrees. Parenthesizes values are 2σ and include estimates of uncertainties in voltage/nozzle height and of correlation in experimental data. Values in square brackets were kept constant at the calculated values.

^b HF level of theory and 6-311 + G(d,p) basis set used.

4. Discussion

The conformational mixture obtained from the ab initio calculated energies, assuming the entropies of the different conformers to be equal (G+ 62%, A 25%, G− 13%) was found to fit the experimental data for 2-chlorobutane quite well ($R = 0.0865$, $R = [\sum w_i(s_i I_i(\text{obs}) - s_i I_i(\text{calc}))/\sum w_i(s_i I_i(\text{obs}))^2]^{1/2}$).

However, it was also possible to obtain a reasonable fit to the experimental data by inclusion of the G+ conformer alone in the model, as can be seen in Fig. 5A ($R = 0.0908$). The similarity in the distance distributions for the G+ and G− conformers results in several different conformational compositions which fit the experimental data. By constraining the conformational composition to different mixtures, it was

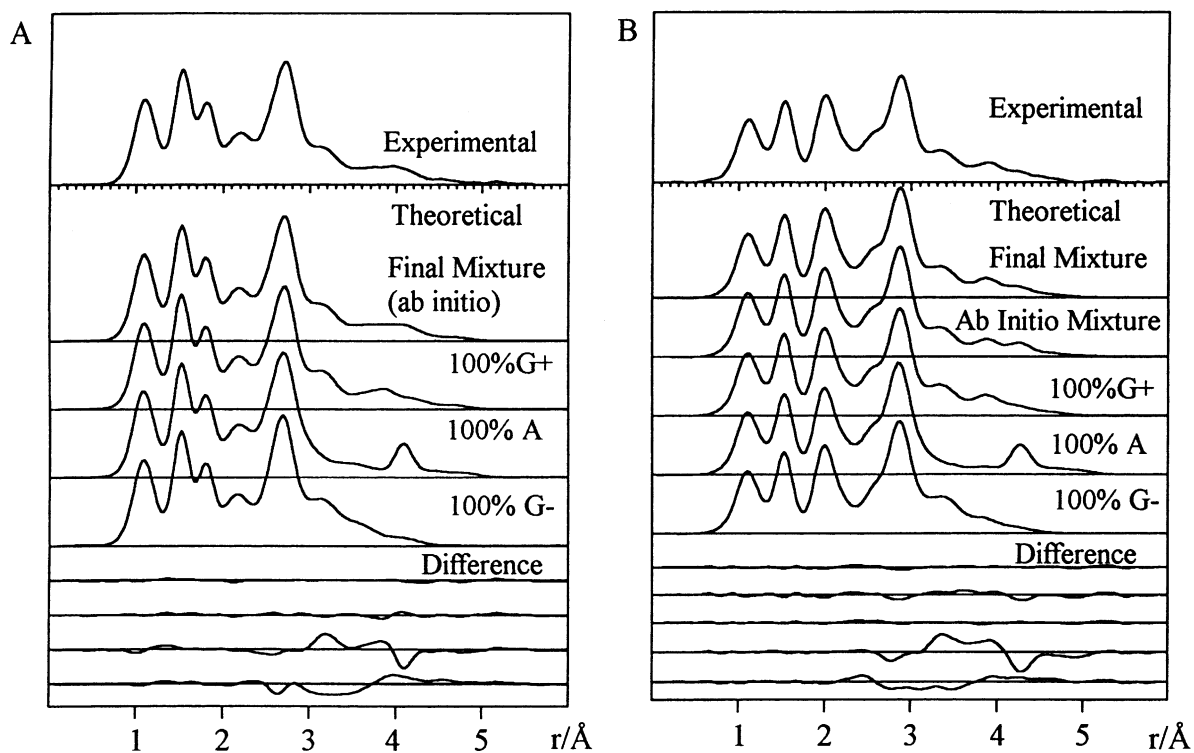


Fig. 5. (A) Theoretical radial distribution curves for 2-chlorobutane for 100% G + , 100% A and 100% G – together with the final theoretical and experimental RD-curves. (B) Theoretical radial distribution curves for 2-bromobutane for 100% G + , 100% A and 100% G – together with the final theoretical and experimental curves.

Table 3

Correlation matrix (X100) for parameters refined in the final least-squares refinements for 2-chlorobutane

		σ_{LS}^a	r_1	r_2	r_3	\angle_4	\angle_5	\angle_6	\angle_7	l_8	l_9	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}
1	$r(C_2-C_3)$	0.0026	100	11	-14	-23	-18	-7	-27	-6	-14	0	-11	-5	8	2
2	$r(C_2-Cl)$	0.0033		100	2	17	-30	12	17	7	-6	-1	-10	-4	1	2
3	$r(C_1-H)$	0.0042		100	1	4	-13	0	13	15	13	13	4	10	1	
4	$\angle(CCC)_{ave}$	0.5401		100	-5	7	-57	-24	-12	24	-25	-16	-15	0		
5	$\angle(CC_2Cl)$	0.6730				100	20	42	4	11	7	37	-19	6	1	
6	$\angle(CCl_1H)$	1.5292					100	24	-4	19	6	0	-29	-21	2	
7	$\angle(HC_2Cl)$	1.8811						100	13	11	17	34	-2	-21	2	
8	$l(C_2-C_2)$	0.0009							100	25	43	41	21	19	0	
9	$l(C_2-Cl)$	0.0010								100	39	28	7	13	1	
10	$l(C_2-H)$	0.0016									100	37	14	20	1	
11	$l(C_{1...}Cl)$	0.0015										100	51	4	-1	
12	$l(C_{1...}C_3)$	0.0027											100	7	-1	
13	$l(C_{4...}Cl)$	0.0045												100	7	
14	$L(C_{1...}C_4)$	0.0110													100	

^a Standard deviation from least-squares refinements. Distances (r) and amplitudes (l) and in Ångströms and angles (\angle) are in degrees.

Table 4

Correlation matrix (X100) for parameters refined in the final least-squares refinements for 2-bromobutane

		$\sigma_{\text{LS}}^{\text{a}}$	R_1	r_2	r_3	\angle_4	\angle_5	\angle_6	\angle_7	l_8	l_9	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}
1	$r(\text{C}_2\text{--C}_3)$	0.0040	100	−17	−11	−29	−5	−12	24	0	3	6	0	9	4	2
2	$r(\text{C}_2\text{--Cl})$	0.0053		100	−1	−8	−12	33	29	−12	−24	−12	−5	6	−5	3
3	$r(\text{C}_1\text{--H})$	0.0076			100	0	−5	−6	−7	11	10	7	12	1	−1	9
4	$\angle(\text{CCC})_{\text{ave}}$	1.5475				100	−44	−14	−85	−5	−5	−5	−30	−13	−15	−7
5	$\angle(\text{CC}_2\text{Cl})$	1.3407					100	3	58	−10	−10	−8	25	4	−1	10
6	$\angle(\text{CC}_1\text{H})$	2.9820						100	33	21	−17	20	38	−33	−18	17
7	$\angle(\text{HC}_2\text{Cl})$								100	−2	−11	−1	30	−3	−18	17
8	$l(\text{C}_2\text{--C}_1)$	0.0015								100	31	30	40	−3	4	8
9	$l(\text{C}_2\text{--Cl})$	0.0023									100	26	22	10	14	−1
10	$l(\text{C}_1\text{--H})$	0.0026										100	35	−4	0	8
11	$l(\text{C}_1\text{--Cl})$	0.0023											100	−9	−18	21
12	$l(\text{C}_1\text{--C}_3)$													100	5	−2
13	$l(\text{C}_4\text{--Cl})$	0.0086													100	−17
14	$l(\text{C}_1\text{--C}_4)$	0.0232														100

^a Standard deviation from least-squares refinements. Distances (*r*) are in Ångströms and angles (∠) are in degrees.

found possible to include up to 30% of the G– conformer before the fit to the experimental data deteriorated significantly. In the same way it was possible to include up to 40% of the A conformer before the fit worsened. When the conformational composition was allowed to refine the following mixture was obtained: G+ 72(41)%, A 17(11)%, G– 11(42)%, however the least-squares uncertainties on these values are quite high (*R* = 0.0870). These results agree with the earlier investigation of 2-chlorobutane [6] which showed that at least 50% of the G+ conformer is present in the gas phase.

The situation for 2-bromobutane is not as clear. The conformational mixture obtained ab initio was not in satisfactory agreement with that derived for the experimental data. The radial distribution (RD) curves for different conformational compositions of gaseous 2-bromobutane are shown in Fig. 5B. From the plots it can be seen that the ab initio composition leads to too large a peak at 4.3 Å, corresponding to the C⋯Br_A distance. To improve the fit to the experimental data the percentage of the A conformer in the model had to be reduced from 28 to 10%. The relative energy difference between the two other conformers (G+ and G–) was maintained at the ab initio value when calculating the relative amounts of these two forms resulting in the following composition: G+ 73%, A 10%, G– 17% (*R* = 0.131).

A model composed of 100% G+ conformer also

gave a fairly good fit to the experimental data (Fig. 5B) (*R* = 0.137). The conformational composition was constrained at different mixtures as for 2-chlorobutane and a reasonable fit to the data could be obtained for models containing up to 30–35% of the G– conformer. As a result it was not possible to draw definite conclusions regarding the conformational compositions but for both 2-chloro- and 2-bromobutane the G+ conformer with a planar carbon skeleton was found to be the low-energy conformer which is in agreement with previous studies on other halogenated butanes [1–4]. The structural parameters (bond lengths and angles) obtained from all the refinements were similar, independent of the conformational composition. The results for the G+ conformer from the final refinements on 2-chlorobutane (G+ 62%, A 25%, G– 13%) and 2-bromobutane (G+ 73%, A 10%, G– 17%) are presented in Table 2.

The corresponding bond distances in the two molecules studied are very similar and seem to be mainly independent of the type of halogen substituent (see Table 2). The bond angles in the two molecules are also similar, the largest difference being about 1°.

The values for the structural parameters obtained from the electron diffraction data on both molecules are in reasonable agreement with the parameter values obtained from ab initio calculations (see Table 2). The difference in distance type should be noted when comparing these results. Results from the theoretical

calculations are given as r_g/\angle_c and from the electron diffraction investigation as r_g/\angle_α and r_g/\angle_α .

When the parameter values for 2-chlorobutane obtained in this study are compared with those from the earlier investigation [1,2] some differences are observed. The value for the C–Cl bond ($r_g = 1.812(3)$ Å) was found to be greater than that obtained previously ($r_g = 1.780(4)$ Å). Using average values for structural parameters over all three conformers for 2-halobutane and 2-halopropane [16,17] the bond distances (average C–C and C–Cl) for 2-chlorobutane found here ($r_g(\text{C–C}) = 1.531(3)$ Å, $r_g(\text{C–Cl}) = 1.812(4)$ Å) are almost equal to the corresponding distances in 2-chloropropane [16] ($r_g(\text{C–C}) = 1.527(1)$ Å, $r_g(\text{C–Cl}) = 1.812(1)$ Å). When the average bond angles are compared for the two molecules, the differences are of the order of 1° or less. When an equivalent comparison is made of the bromo compounds (2-bromobutane and 2-bromopropane) more variation is observed between equivalent parameters. Both the C–C and C–Br bond distances in 2-bromobutane ($r_g(\text{C–C}) = 1.532(4)$ Å, $r_g(\text{C–Br}) = 1.982(6)$ Å) are longer than those in 2-bromopropane [17] ($r_g(\text{C–C}) = 1.508(15)$ Å, $r_g(\text{C–Br}) = 1.957(10)$ Å). We can offer no explanation for these differences but it should be noted that in the case of the bromo compounds r_g values are being compared with r_s from microwave measurements.

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Supplementary data

Supplementary data has been deposited with the B.L.L.D. as sup. 26665.

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