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# Molecular Structure and Conformational Composition of 1-Chlorobutane, 1-Bromobutane, and 1-Iodobutane as Determined by Gas-Phase Electron Diffraction and *ab Initio* Calculations

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Gas-phase electron diffraction (ED), together with *ab initio* molecular orbital calculations, have been used to determine the structure and conformational composition of 1-chlorobutane, 1-bromobutane, and 1-iodobutane. These molecules may in principle exist as mixtures of five different conformers, but only three or four of these were observed in gas phase at temperatures of the ED experiments, 18°C, 18°C, and 23°C, respectively. The observed conformational compositions (1-chlorobutane, 1-bromobutane, and 1-iodobutane) were AA ( $13 \pm 12\%$ ,  $21 \pm 14\%$ ,  $19 \pm 17\%$ ), GA ( $60 \pm 13\%$ ,  $33 \pm 32\%$ ,  $17 \pm 31\%$ ), AG ( $12 \pm 16\%$ ,  $8 \pm 12\%$ ,  $<1\%$ ), and GG ( $12 \pm 16\%$ ,  $38 \pm 34\%$ ,  $64 \pm 31\%$ ). A and G denotes *anti* and *gauche* positions for the  $X-C_1-C_2-C_3$  ( $X = Cl, Br, I$ ), and the  $C_1-C_2-C_3-C_4$  torsion angles. The results for the most important distances ( $r_g$ ) and angles ( $\angle_a$ ) from the combined ED/*ab initio* study for the GA conformer of 1-chlorobutane, with estimated  $2\sigma$  uncertainties, are  $r(C_1-C_2) = 1.519(3)$  Å,  $r(C_2-C_3) = 1.530(3)$  Å,  $r(C_3-C_4) = 1.543(3)$  Å,  $r(C_1-Cl) = 1.800(4)$  Å,  $\angle C_1C_2C_3 = 114.3(6)^\circ$ ,  $\angle C_2C_3C_4 = 112.0(6)^\circ$ ,  $\angle CCl = 112.3(5)^\circ$ . The results for the GA conformer of 1-bromobutane are  $r(C_1-C_2) = 1.513(4)$  Å,  $r(C_2-C_3) = 1.526(4)$  Å,  $r(C_3-C_4) = 1.540(4)$  Å,  $r(C_1-Br) = 1.959(8)$  Å,  $\angle C_1C_2C_3 = 115.3(11)^\circ$ ,  $\angle C_2C_3C_4 = 112.8(11)^\circ$ ,  $\angle CBr = 112.1(14)^\circ$ . The results for 1-chlorobutane and 1-bromobutane are compared with those from earlier electron diffraction investigations. The results for the GA conformer of 1-iodobutane are  $r(C_1-C_2) = 1.506(5)$  Å,  $r(C_2-C_3) = 1.518(5)$  Å,  $r(C_3-C_4) = 1.535(5)$  Å,  $r(C_1-I) = 2.133(11)$  Å,  $\angle C_1C_2C_3 = 116.8(15)^\circ$ ,  $\angle C_2C_3C_4 = 115.3(15)^\circ$ ,  $\angle CCI = 110.2(14)^\circ$ . Differences in length between the different C—H bonds in each molecule, between the different C—C bonds, between the different CCH angles, and between the different CCC angles were kept constant at the values obtained from the *ab initio* calculations.

**KEY WORDS:** Structure; conformation; electron diffraction; *ab initio*; 1-halobutane.

## INTRODUCTION

The 1-halogen-substituted butanes all have been the subject of a number of structure studies carried out using

IR, Raman [1–20], and microwave spectroscopy [21]. In a paper by Ogawa *et al.* [1] all previous spectroscopy investigations are reviewed. These molecules may in principle exist as mixtures of five different conformers. Ogawa *et al.* found that AA, GA, AG, and GG forms of the 1-halobutanes (except 1-fluorobutane) are present in the gas phase. A and G denote *anti* and *gauche* positions for the  $X-C_1-C_2-C_3$ ,  $X = F, Cl, Br, I$ , and the  $C_1-C_2-C_3-C_4$  torsion angles. 1-Bromobutane and 1-chlorobutane have also both earlier been investi-

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gated by electron diffraction [22–24] and four or five different conformers were reported to be present in gas phase. In the present work electron-diffraction studies, together with *ab initio* molecular orbital calculations, have been made for 1-chloro-, 1-bromo-, and 1-iodobutane. It is difficult in molecules like these to determine the structures and conformational compositions from ED data alone without additional structure information. However, by combining the ED data with results from *ab initio* calculations, more accurate and reliable information about the structures and conformational compositions of these molecules can hopefully be obtained. This is the main reason for reinvestigating the chloro and bromo compounds. By studying all three molecules at the same time, using the same model, it was also hoped that information about the conformational effects of the different halogen atoms better could be obtained. Our results will be compared with the results from the earlier ED studies.

## EXPERIMENTAL SECTION AND DATA REDUCTION

The samples of 1-chlorobutane, 1-bromobutane, and 1-iodobutane were obtained from Aldrich Chemical Co. The purity was reported to be 99%, this was checked by gas chromatography before use. Diffraction experiments were made with the Balzers Eldigraph KDG-2 at the University of Oslo [25, 26] on Kodak Electron Image plates with nozzle temperatures of 18°C, 18°C, and 23°C, respectively. The electron wavelength, calibrated with benzene as a reference, was 0.05862 Å for 1-chlorobutane and 1-bromobutane and 0.05872 Å for 1-iodobutane. Data were obtained at two different nozzle-to-plate distances (500.12 and 250.12 mm for 1-chlorobutane and 1-bromobutane, 498.46 and 248.77 mm for 1-iodobutane), and three to six plates were recorded at each distance. The optical densities were measured with a Joyce Loebl double-beam microdensitometer. The data were reduced in the usual way [27–29]. Ranges of data were  $2.00 \leq s/\text{\AA}^{-1} \leq 15.00$  and  $4.00 \leq s/\text{\AA}^{-1} \leq 30.00$  for 1-chlorobutane and  $2.00 \leq s/\text{\AA}^{-1} \leq 15.00$  and  $4.00 < s/\text{\AA}^{-1} \leq 26.00$  for 1-bromobutane and 1-iodobutane. The data interval was  $\Delta s = 0.25 \text{\AA}^{-1}$ . A calculated background [28] was subtracted from the data for each plate to yield experimental molecular intensity curves in the form  $sI_m(s)$ . The average experimental intensity curves for the two camera distances for the three compounds are given in Fig. 1. Radial distribution (RD) curves (Figs. 2, 3, and 4 for 1-chloro-, 1-bromo-, and 1-iodobutane, respectively)

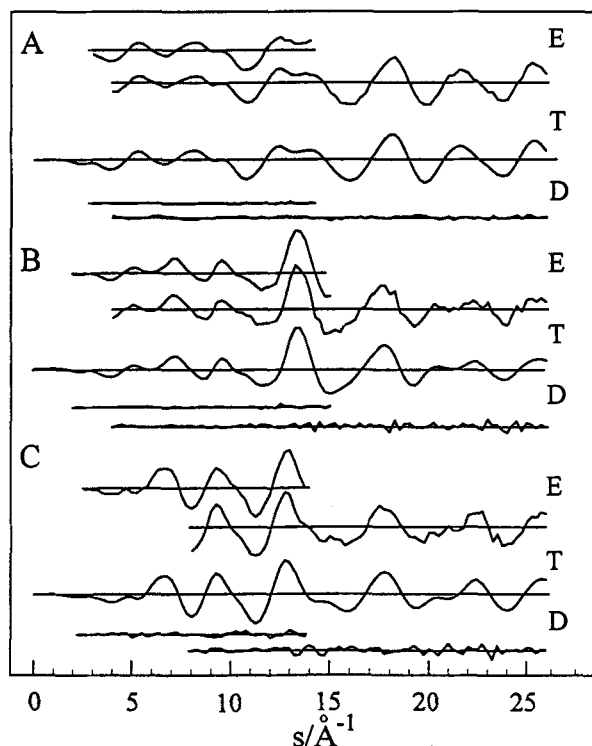


Fig. 1. Intensity curves ( $sI_m(s)$ ) for (A) 1-chlorobutane, (B) 1-bromobutane, and (C) 1-iodobutane. The experimental curves (E) are averages of all plates for the two camera distances. The theoretical curves (T) were calculated from the structural parameters shown in Table II. The difference curves (D) result from subtracting the relevant part of the theoretical curves from the experimental curves.

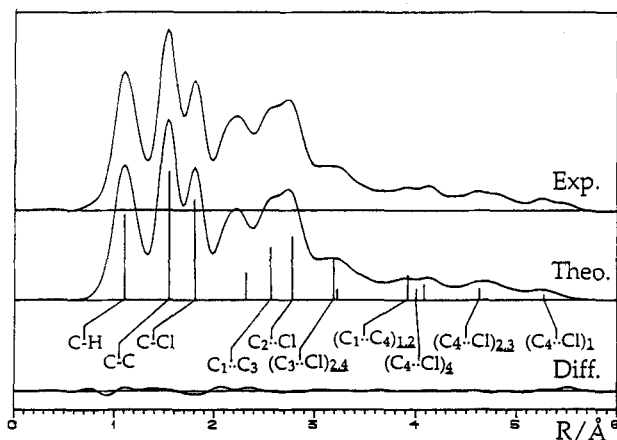


Fig. 2. Radial distribution curves for 1-chlorobutane. The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region  $0 \leq s/\text{\AA}^{-1} \leq 1.75$  and  $B/\text{\AA}^2 = 0.0020$ . Difference curve is experimental minus theoretical. The vertical lines indicate important interatomic distances and have lengths proportional to the distance weights. The subscripts 1, 2, 3, and 4 denote forms AA, GA, AG, and GG, respectively.

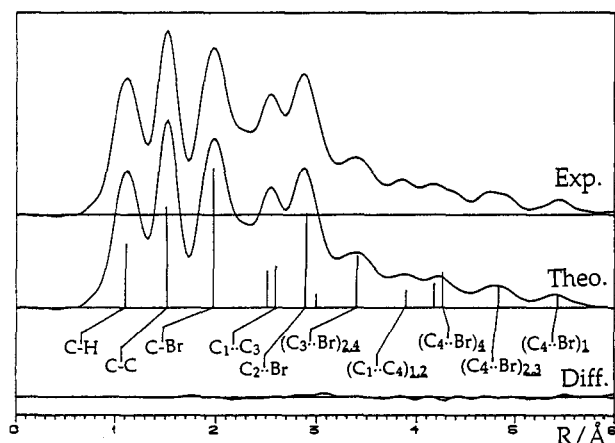


Fig. 3. Radial distribution curves for 1-bromobutane. The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region  $0 \leq s/\text{\AA}^{-1} \leq 1.75$  and  $B/\text{\AA}^2 = 0.0020$ . Difference curve is experimental minus theoretical. The vertical lines indicate important interatomic distances and have lengths proportional to the distance weights. The subscripts 1, 2, 3, and 4 denote the forms AA, GA, AG, and GG, respectively.

were calculated in the usual way by Fourier transformation of  $I'_m(s) = Z_C Z_X (A_C A_X)^{-1} s I_m(s) \exp(-Bs^2)$  with  $B = 0.0020 \text{\AA}^{-2}$  ( $X = \text{Cl}, \text{Br}, \text{or I}$ ) where  $A = s^2 F$ , and  $F$  is the absolute value of the complex scattering amplitudes. The scattering amplitudes and phase were taken from tables [30].

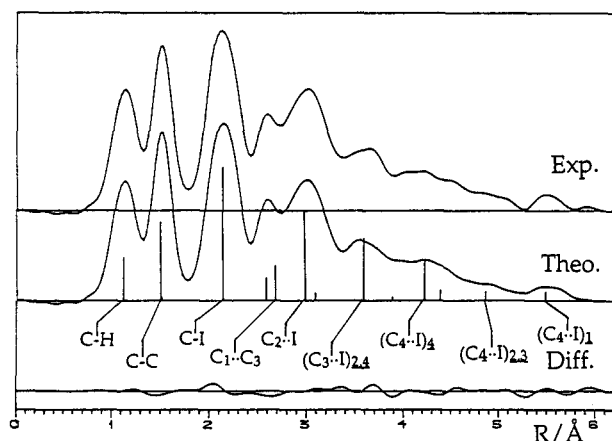


Fig. 4. Radial distribution curves for 1-iodobutane. The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region  $0 \leq s/\text{\AA}^{-1} \leq 1.75$  and  $B/\text{\AA}^2 = 0.0020$ . Difference curve is experimental minus theoretical. The vertical lines indicate important interatomic distances and have lengths proportional to the distance weights. The subscripts 1, 2, 3, and 4 denote the forms AA, GA, AG, and GG, respectively.

## STRUCTURE ANALYSIS

Refinements of the  $r_\alpha$ -type structures were carried out by the least-squares method [31], adjusting theoretical  $sI_m(s)$  curves simultaneously to the two average experimental intensity curves (one from each nozzle-to-plate experiment), using a unit weight matrix. Calculation of vibrational amplitudes ( $l$ ), perpendicular amplitude corrections ( $K$ ), and centrifugal distortion constants ( $\delta r$ ) were carried out by normal coordinate analysis [32], using valence force fields where the force constants were taken from related molecules and from molecular mechanics (MM) calculations [33, 34]. From results obtained in earlier investigations of halogenated alkanes it is reasonable to assume threefold barriers against torsion about each of the three carbon-carbon bonds. 1-Halosubstituted butanes may therefore exist in  $3 \times 3 \times 3 = 27$  different conformations, but many of these are indistinguishable.

The 1-substituted butanes have only five distinguishable conformers: AA, GA, AG, GG, and G+G- (see Figs. 5 and 6), where the first and the second symbol, respectively, refer to torsions about the  $C_1-C_2$  and  $C_2-C_3$  bonds. The symbols refer to *anti* (A) with a torsion angle of  $180^\circ$  and *gauche* (G+ and G-) with torsion angles of  $+60^\circ$  and  $-60^\circ$ , respectively. Calculations of theoretical RD curves for the five possible conformers of 1-chlorobutane, 1-bromobutane, and 1-iodobutane showed that no single conformer gave a good fit to the experimental data (see Fig. 7).

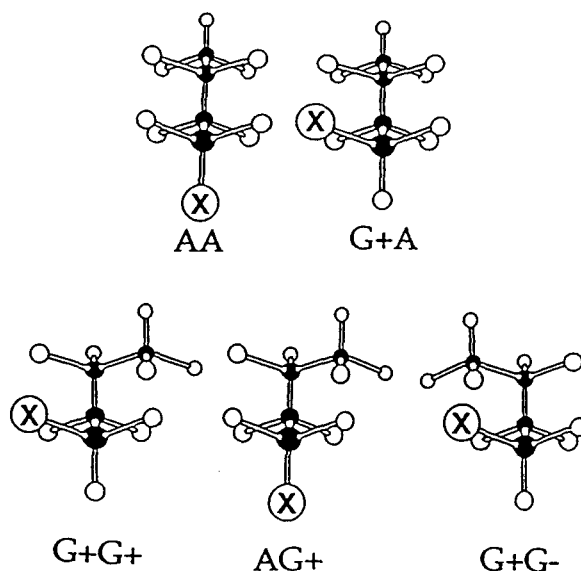


Fig. 5. Diagrams for the five conformers of 1-halobutanes.

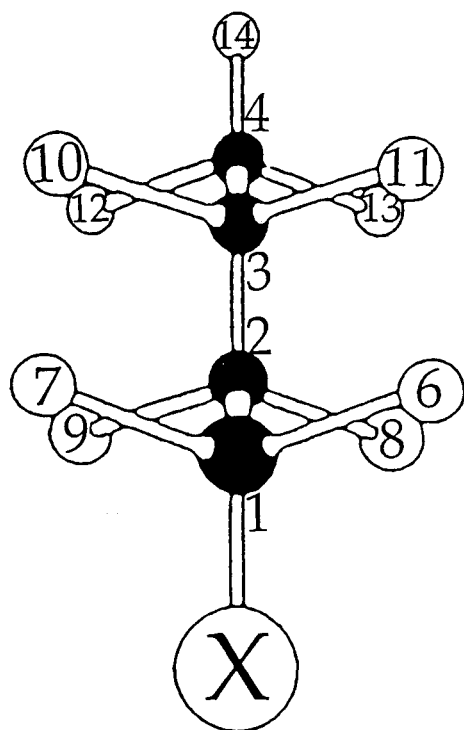


Fig. 6. Diagrams, with atom numbering, of the AA conformer of 1-chloro-, 1-bromo-, and 1-iodobutane.

It is impossible to determine the structures of molecules with five conformers by electron diffraction without introducing constraints or assumptions. We therefore did *ab initio* molecular orbital calculations for each of the conformers of the three molecules. The geometries were fully optimized at the *ab initio* Hartree-Fock level with use of the program GAUSSIAN 92 [35]. For 1-chlorobutane the 6-31G\* basis set was used. For 1-bromobutane the 6-31G\* basis set was used for C and H, and a compact contracted basis set for third-row atoms [36] was used for Br (HF/6-31G\*/Binning). For 1-iodobutane we first did *ab initio* calculations using the STO-3G\*\* basis set. We did not find these calculations satisfactory, and we therefore also did *ab initio* calculations with the LANL1DZ [37-39] basis set. The results from the calculations for 1-iodobutane (with the LANL1DZ basis set) together with the results for 1-chlorobutane and 1-bromobutane are included in the supplementary material. These *ab initio* results were later used to modify our models for the 1-halobutanes. In Table I the relative energies for the conformers of the three butanes obtained from these calculations are given.

The geometrical parameters chosen to define each of the five conformers are as follows:  $r(C_2-C_3)$ ,  $\Delta r_1(C-C) = r(C_2-C_3) - r(C_3-C_4)$ ,  $\Delta r_2(C-C) = r(C_2-C_3) - r(C_1-C_2)$ ,  $r(C_1-H)$ ,  $\Delta r_1(C-H) =$

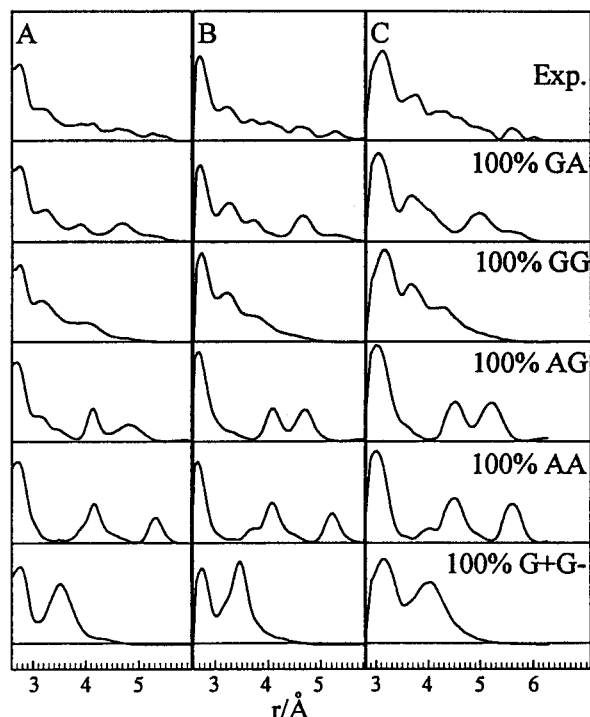


Fig. 7. Theoretical radial distribution curves for 100% GA, 100% GG, 100% AG, 100% AA, and 100% G+G-, for (A) 1-chlorobutane, (B) 1-bromobutane, and (C) 1-iodobutane, together with the experimental curves. Only the conformationally important parts of the curves are shown.

$r(C_1-H) - r(C_2-H)$ ,  $\Delta r_2(C-H) = r(C_1-H) - r(C_3-H)$ ,  $\Delta r_3(C-H) = r(C_1-H) - r(C_4-H)$ ,  $r(C-X)$ ,  $\angle CCC = (\angle C_1C_2C_3 + \angle C_2C_3C_4) \times 0.5$ ,  $\Delta \angle (CCC) = \angle C_1C_2C_3 - \angle C_2C_3C_4$ ,  $\angle CCX$ ,  $\angle CC_1H$ ,  $\Delta \angle (CCCH) = \angle CC_1H - \angle CC_2H$ ,  $\angle HC_{2,3}H = (\angle HC_2H + \angle HC_3H) \times 0.5$ ,  $\Delta \angle HC_{2,3}H = \angle HC_2H - \angle HC_3H$ ,  $\phi_1(X-C_1-C_2-C_3$  torsion angle),  $\phi_2(C_1-C_2-C_3-C_4$  torsion angle), and  $\phi_3(C_2-C_3-C_4-H$  torsion angle).

It is difficult to determine the sign and the magnitude of the differences  $\Delta r$  and  $\Delta \angle$  from the least-squares analysis. These differences were therefore kept constant at the values obtained from the *ab initio* calculations. The  $r(C-H)$  distances and the  $\angle HCH$  angles on the same carbon atom were assumed to be equal. The differences between corresponding parameters in different conformers were kept constant at the calculated values. Not all angles involving hydrogen and not all of the  $C_3-C_4$  torsional angles,  $\phi_3$ , could be determined in the least-squares refinements. They were therefore also given values obtained in the *ab initio* calculations. In addition, some of the parameters had to be refined in separate refinements. Vibrational amplitudes of the same order of

**Table I.** Relative Energies (kJ/mol) for 1-Chlorobutane, 1-Bromobutane, and 1-Iodobutane as Determined from Combined ED/ab Initio Analysis, from ab Initio Calculations, from Molecular Mechanics Calculations (MM) and from a Method Using Empirical Rules (ER).

Conformer <sup>d</sup>	Mult.	1-Chlorobutane				1-Bromobutane				1-Iodobutane			
		$E(\text{ED}/\text{ab})$	$E(\text{ab})^b$	$E(\text{MM})^c$	$E(\text{ED})^d$	$E(\text{ER})^e$	$E(\text{ED}/\text{ab})$	$E(\text{ab})^f$	$E(\text{MM})^g$	$E(\text{ED}/\text{ab})$	$E(\text{ab})^h$	$E(\text{MM})^i$	$E(\text{ER})^j$
AA	1	2.1(21)	0.0	2.5	0.0	0.8	0.0	0.00	2.1	0.0	0.0	1.3(21)	0.4
GA	2	0.0	1.3	0.0	0.0	0.0	0.4(25)	1.3	0.0	3.3(42)	3.3	0.0	0.0
AG	2	3.8(25)	4.2	6.3	5.4	4.2	4.2(33)	4.2	5.0	<i>i</i>	4.2	4.6	3.8
GG	2	3.8(25)	4.6	1.7	4.6	3.3	0.4(25)	4.6	1.7	0.0	6.3	2.1	3.3
G-G+	2	<i>i</i>	13.0	4.2	5.4	3.3	<i>i</i>	14.0	4.6	<i>i</i>	17.2	5.4	3.3

<sup>a</sup>The letters refer to torsion angles  $\text{X}-\text{C}_1-\text{C}_2-\text{C}_3$  and  $\text{C}_1-\text{C}_2-\text{C}_3-\text{C}_4$ , respectively. Energies are in kJ/mol relative to the conformer with the lowest energy.

<sup>b</sup>Ab initio calculations with the HF/6-31G\* basis set.

<sup>c</sup>Earlier molecular-mechanics calculations [12].

<sup>d</sup>Earlier ED investigation [23].

<sup>e</sup>Obtained by using additive scheme for calculating conformational energies [40].

<sup>f</sup>Ab initio calculations with the HF/6-31G\*/Binning basis set.

<sup>g</sup>Earlier ED investigation [22].

<sup>h</sup>Ab initio calculations with the HF/LANL1DZ basis set.

<sup>i</sup>Included in the ED analysis, but present in very small amounts.

<sup>j</sup>Not included in the ED analysis.

magnitude associated with distances of similar length were grouped together as a single parameter, with differences held constant at values determined in the normal coordinate calculations. Those amplitudes which could not be refined were kept constant at the values calculated in the normal coordinate analysis. In the final refinement of 1-chlorobutane three bond distances, three valence angles, nine vibrational amplitudes and two conformational parameters were refined simultaneously. For 1-bromobutane three distances, three angles, six amplitudes, and two conformational parameters were refined simultaneously, while for 1-iodobutane three

distances, two angles, seven amplitudes, and two conformational parameters were refined simultaneously. The results from the final least-squares refinement are given in Table II, where also the values from the ab initio calculations of the GA conformer are given.

In Table III the final values for some selected distances are given, together with calculated and refined values for vibrational amplitudes. The intensity curves for the final models are shown in Fig. 1. Figures 2–4 shows the corresponding RD curves. The correlation matrices for the refined parameters are included in the supplementary material.

Table II. Structural Parameters of 1-Chlorobutane (X = Cl), 1-Bromobutane (X = Br), and 1-Iodobutane (X = I).

	1-Chlorobutane		1-Bromobutane		1-Iodobutane	
	ED/ab Initio	ab Initio <sup>b</sup>	ED/ab Initio	ab Initio <sup>c</sup>	ED/ab Initio	ab Initio <sup>d</sup>
$r(\text{C}_2-\text{C}_3)$	1.522(3)	1.521	1.515(4)	1.529	1.507(5)	1.537
$\Delta r_1(\text{C}-\text{C})$	[0.001]	0.001	[0.001]	0.001	[-0.002]	-0.002
$\Delta r_2(\text{C}-\text{C})$	[0.008]	0.008	[0.008]	0.008	[0.007]	0.007
$r(\text{C}-\text{X})$	1.793(4)	1.802	1.953(8)	1.960	2.127(11)	2.209
$r(\text{C}_1-\text{H})$	1.078(5)	1.079	1.086(8)	1.078	1.100(11)	1.077
$\Delta r_1(\text{C}-\text{H})$	[-0.008]	-0.008	[-0.009]	-0.009	[-0.009]	-0.009
$\Delta r_2(\text{C}-\text{H})$	[-0.007]	-0.007	[-0.008]	-0.008	[-0.008]	-0.008
$\Delta r_3(\text{C}-\text{H})$	[-0.007]	-0.007	[-0.008]	-0.008	[-0.008]	-0.008
$\langle \angle (\text{CCC}) \rangle$	113.1(6)	114.6	114.0(14)	113.6	116.0(15)	114.9
$\Delta \angle (\text{CCC})$	[3.3]	3.3	[2.5]	2.5	[1.6]	1.6
$\angle \text{CCX}$	112.3(5)	112.7	112.1(11)	112.9	110.2(14)	113.7
$\angle \text{CC}_1\text{H}$	111.1(18)	111.5	113.3(43)	112.0	108.3(42)	112.4
$\Delta \angle (\text{CCH})$	[3.7]	3.7	[4.1]	4.1	[4.2]	4.2
$\langle \text{HC}_{2,3}\text{H} \rangle$	[106.6]	106.6	106.6(114)	106.6	107.4(121)	106.7
$\Delta \angle (\text{HC}_{2,3}\text{H})$	[-0.2]	-0.2	[-0.1]	-0.1	[-0.1]	-0.10
Torsional angles for GA, AG, and GG conformers						
$\Phi(\text{X}-\text{C}_1-\text{C}_2-\text{C}_3)_{\text{GA}}$	59(4)	67.3	68(5)	67.6	77(9)	69.8
$\Phi(\text{C}_1-\text{C}_2-\text{C}_3-\text{C}_4)_{\text{GA}}$	168(17)	182.1	170(21)	182.4	176(10)	183.3
$\Phi(\text{C}_2-\text{C}_3-\text{C}_4-\text{H}_{14})_{\text{GA}}$	[179.9]	179.9	182(30)	179.6	185(40)	180.2
$\Phi(\text{X}-\text{C}_1-\text{C}_2-\text{C}_3)_{\text{AG}}$	175(65)	182.9	177(32)	182.7		
$\Phi(\text{C}_1-\text{C}_2-\text{C}_3-\text{C}_4)_{\text{AG}}$	60(23)	66.5	51(31)	66.5		
$\Phi(\text{C}_2-\text{C}_3-\text{C}_4-\text{H}_{14})_{\text{AG}}$	[188.9]	188.9	176(9)	184.7		
$\Phi(\text{X}-\text{C}_1-\text{C}_2-\text{C}_3)_{\text{GG}}$	68(6)	63.6	63(10)	63.5	69(23)	66.1
$\Phi(\text{C}_1-\text{C}_2-\text{C}_3-\text{C}_4)_{\text{GG}}$	64(10)	61.5	51(30)	60.4	50(22)	60.5
$\Phi(\text{C}_2-\text{C}_3-\text{C}_4-\text{H}_{14})_{\text{GG}}$	[185.3]	185.3	[185.7]	185.7	181(13)	185.5
Conformational composition						
$\alpha_{\text{AA}}$	0.13(12)		0.21(14)		0.19(17)	
$\alpha_{\text{GA}}$	0.60(13)		0.33(32)		0.17(31)	
$\alpha_{\text{AG}}$	0.12(16)		0.08(12)		<0.01	
$\alpha_{\text{GG}}$	0.12(13)		0.38(34)		0.64(31)	
$\alpha_{\text{G-G+}}$	0.03(8)		<0.01		<0.01	

<sup>a</sup>Distances ( $r_a$ ) are in Ångströms, angles ( $\angle_a$ ) are in degrees. Parenthesized values are estimated  $2\sigma$  and include estimates of uncertainties in voltage/camera heights and of data correlation. Values in brackets were kept constant at the calculated values.

<sup>b</sup>Ab initio calculations with the 6-31G\* basis set.

<sup>c</sup>Ab initio calculations with the 6-31G\*/Binning basis set.

<sup>d</sup>Ab initio calculations with the LANL1DZ basis set.

Table III. Selected Distances, Amplitudes, and Important Valence Angles for 1-Chlorobutane (X = Cl), 1-Bromobutane (X = Br), and 1-Iodobutane (X = I) for the GA Conformer.

Parameter <sup>a</sup>	1-Chlorobutane			1-Bromobutane			1-Iodobutane		
	$r_g/\angle_\alpha$	$l_{\text{refined}}$	$l_{\text{calc}}$	$r_g/\angle_\alpha$	$l_{\text{refined}}$	$l_{\text{calc}}$	$r_g/\angle_\alpha$	$l_{\text{refined}}$	$l_{\text{calc}}$
$r(\text{C}_1-\text{C}_2)$	1.519(3)	0.057(4)	0.048	1.513(4)	0.052(6)	0.048	1.506(5)	0.053(9)	0.048
$r(\text{C}_2-\text{C}_3)$	1.530(3)	0.057(4)	0.048	1.526(4)	0.052(6)	0.048	1.518(5)	0.053(9)	0.048
$r(\text{C}_3-\text{C}_4)$	1.543(3)	0.057(4)	0.048	1.540(4)	0.052(6)	0.048	1.535(5)	0.053(9)	0.048
$r(\text{C}_1-\text{X})$	1.800(4)	0.048(4)	0.048	1.959(8)	0.065(10)	0.051	2.133(11)	0.049(12)	0.053
$r(\text{C}_1-\text{H})$	1.097(5)	[0.078]	0.078	1.104(8)	0.082(8)	0.078	1.118(11)	0.084(12)	0.078
$r(\text{C}_2-\text{H})$	1.107(5)	[0.078]	0.078	1.118(9)	0.082(8)	0.078	1.132(11)	0.084(12)	0.078
$r(\text{C}_3-\text{H})$	1.121(5)	[0.078]	0.078	1.134(9)	0.082(8)	0.078	1.141(11)	0.084(12)	0.078
$r(\text{C}_4-\text{H})$	1.108(5)	[0.078]	0.078	1.110(9)	0.082(8)	0.078	1.135(11)	0.084(12)	0.078
$r(\text{X} \cdots \text{H}_7)$	2.366(14)	0.100(24)	0.111	2.495(28)	0.111(67)	0.113	2.718(15)	0.083(69)	0.116
$r(\text{C}_2 \cdots \text{X})$	2.756(8)	0.070(7)	0.072	2.886(16)	0.071(11)	0.079	3.000(26)	0.079(35)	0.095
$r(\text{C}_1 \cdots \text{C}_3)$	2.556(9)	0.061(7)	0.072	2.559(18)	0.065(11)	0.075	2.568(21)	0.073(19)	0.074
$r(\text{C}_2 \cdots \text{C}_4)$	2.532(9)	0.064(7)	0.076	2.537(18)	0.065(11)	0.075	2.560(21)	0.073(19)	0.074
$\angle \text{C}_1\text{C}_2\text{C}_3$	114.3(6)			115.3(11)			116.8(15)		
$\angle \text{C}_2\text{C}_3\text{C}_4$	112.0(6)			112.8(11)			115.3(15)		
$\angle \text{CC}_1\text{X}$	112.3(5)			112.1(14)			110.2(14)		
$\angle \text{CC}_1\text{H}$	111.1(18)			113.4(43)			108.3(39)		
$\angle \text{CC}_2\text{H}$	108.9(18)			108.7(43)			108.1(39)		
$\angle \text{CC}_3\text{H}$	109.5(18)			109.3(43)			108.4(39)		
$\angle \text{CC}_4\text{H}$	110.7(18)			112.6(43)			107.0(39)		
Dependent distances for different conformers									
$r(\text{C}_3 \cdots \text{X})_{\text{GA}}$	3.202(17)	0.135(58)	0.157	3.412(23)	0.134(33)	0.174	3.614(38)	0.130(46)	0.191
$r(\text{C}_3 \cdots \text{X})_{\text{GG}}$	3.330(16)	0.130(58)	0.152	3.379(24)	0.127(33)	0.167	3.607(41)	0.125(46)	0.186
$r(\text{C}_3 \cdots \text{X})_{\text{AA}}$	4.113(9)	0.074(24)	0.074	4.256(12)	0.088(92)	0.078	4.393(22)	0.078(139)	0.070
$r(\text{C}_3 \cdots \text{X})_{\text{AG}}$	4.132(9)	0.073(24)	0.074	4.265(18)	0.088(92)	0.078			
$r(\text{C}_1 \cdots \text{C}_4)_{\text{AG}}$	3.199(21)	0.134(270)	0.160	3.025(41)	0.143(123)	0.163			
$r(\text{C}_1 \cdots \text{C}_4)_{\text{GG}}$	3.170(22)	0.126(270)	0.152	3.075(54)	0.134(123)	0.154	3.144(59)	0.103(100)	0.161
$r(\text{C}_1 \cdots \text{C}_4)_{\text{AA}}$	3.869(12)	0.089(43)	0.075	3.867(24)	0.073(59)	0.077	3.884(29)	0.127(252)	0.076
$r(\text{C}_1 \cdots \text{C}_4)_{\text{GA}}$	3.882(12)	0.090(43)	0.076	3.891(25)	0.073(59)	0.077	3.916(29)	0.127(252)	0.076
$r(\text{C}_4 \cdots \text{X})_{\text{GG}}$	4.083(21)	0.312(364)	0.282	3.886(43)	0.241(176)	0.297	4.214(55)	0.242(197)	0.321
$r(\text{C}_4 \cdots \text{X})_{\text{GA}}$	4.666(19)	0.200(88)	0.169	4.825(25)	0.129(91)	0.195	4.938(46)	0.133(272)	0.217
$r(\text{C}_4 \cdots \text{X})_{\text{AG}}$	4.843(22)	0.194(88)	0.163	4.882(42)	0.102(91)	0.169			
$r(\text{C}_4 \cdots \text{X})_{\text{AA}}$	5.257(14)	0.081(151)	0.098	5.389(18)	0.085(111)	0.076	5.505(33)	0.067(147)	0.119

<sup>a</sup>Distances ( $r_g$ ) and amplitudes ( $l$ ) are in Ångströms, angles ( $\angle_\alpha$ ) are in degrees. Parenthesized values are  $2\sigma$  and include uncertainties in voltage/nozzle height and correlation in experimental data. Values in brackets were kept constant at the calculated values.

## DISCUSSION

If we assume that the different conformers have the same entropies apart from the multiplicities, the observed conformational compositions (see Table II) correspond to the relative energies given in Table I. The variation in the conformational compositions obtained in the present study is shown in Fig. 8. Certain patterns may be recognized. From Fig. 8 it can be seen that when going from 1-chlorobutane to 1-iodobutane the amount of GG form is increasing; i.e., the energy of this form is decreasing as the halogen substituent gets larger. For the GA, AG, and G-G+ forms the opposite trend is observed, these forms are found in decreasing amounts

as we go from 1-chlorobutane to 1-iodobutane. For the AA form no systematic trend is observed. It should be kept in mind, however, that the error limits on the observed mole fractions (and the corresponding energy differences) are large.

The results for the conformational energies, obtained in our electron-diffraction investigations, are in Table I compared with the results obtained by ab initio calculations, with the results from earlier molecular mechanics calculations [34] and with the results obtained using an additive scheme [40]. For all three molecules the agreement between the molecular mechanics results and the ED results is fairly good. Except for the GG conformer of 1-bromobutane and 1-iodobutane where



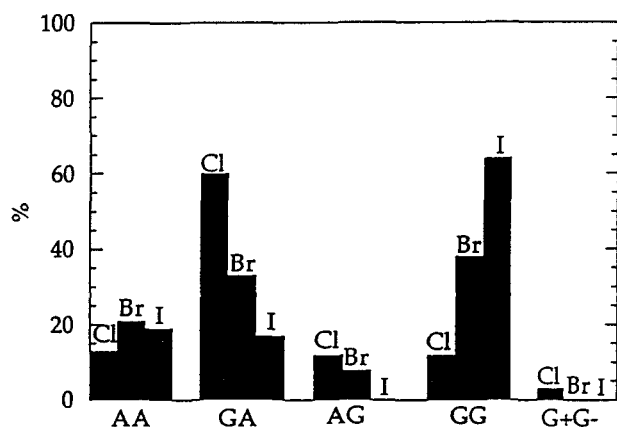


Fig. 8. Conformational compositions of 1-chloro-, 1-bromo-, and 1-iodobutane obtained by electron diffraction.

the *ab initio* calculations gave much higher energies than that suggested by the experiment, the *ab initio* and the ED results are also in fairly good agreement. The results obtained using an additive scheme developed for chloro- and bromoalkanes [40] are not far from the experimental values for most conformers in 1-chlorobutane and 1-bromobutane, but for 1-iodobutane the agreement between the results from these two methods is not good at all. Our experimental results for the conformational compositions are in Table I also compared with the earlier ED results for 1-chlorobutane [23] and 1-bromobutane [22]. For 1-chlorobutane the earlier investigation concluded that the AA and the GA conformers both were low-energy forms with approximately equal energy. In the present study we find that the GA form has the lowest relative energy with the AA conformer 2.1 kJ/mol higher in energy. It should be noted, however, that in

the earlier investigation both the structural parameters and the conformational compositions were determined by analysis of the area and the positions of the peaks in the RD curves only, no least-squares refinements of the intensity curves were attempted. With this in mind, the agreement between the earlier ED investigations and our study must be considered satisfactory.

Several spectroscopic studies of halogenated butanes have been carried out and in a work by Ogawa *et al.* [1] all these results are compared. The conclusion in their work was that all possible conformers, except G+G-, are present in both gas phase and liquid phase for all 1-halogenated butanes. This is in agreement with our results, except that we find a small amount of the G+G- conformer in 1-chlorobutane, and we did not observe the AG conformer in 1-iodobutane. A small amount of this conformer could, however, be present in 1-iodobutane, and a model for 1-chlorobutane with no G+G- conformer present gave almost as good a fit to the experimental data as our final model did.

The results for the geometrical parameters from the *ab initio* calculations for the three 1-halobutanes are in reasonable agreement with the experimental results (see Table II), except for  $r(\text{C}-\text{C})$  and  $r(\text{C}-\text{X})$  in 1-iodobutane where, due to the basis set we had to use, the calculated distances are too long. When comparing the results obtained by the different *ab initio* calculations we find that (see Table II)  $\Delta r(\text{C}-\text{C})$ ,  $\Delta r(\text{C}-\text{H})$ ,  $\Delta \angle(\text{CCC})$ , and  $\Delta \angle(\text{CCH})$  have the same sign and magnitude for all three compounds. In general, when comparing results from theoretical calculations with results obtained by ED analysis, the *differences* in the distances and angles probably are much more reliable parameters than the absolute value of these parameters.

Table IV. Structure Parameters of 1-Halogen-Substituted Propanes (X = Cl, I) and 1-Halogen-Substituted Butanes (X = Cl, Br, I).

Parameter <sup>a</sup>	1-Chloropropane <sup>c</sup>	1-Chlorobutane <sup>d</sup>	1-Bromobutane <sup>d</sup>	1-Iodopropane <sup>c</sup>	1-Iodobutane <sup>d</sup>
C—X	1.796(2)	1.800(4)	1.959(8)	2.164(8)	2.133(11)
C <sub>1</sub> —C <sub>2</sub>	1.525(2) <sup>b</sup>	1.519(3)	1.513(4)	1.521(5)	1.506(5)
C <sub>2</sub> —C <sub>3</sub>		1.530(3)	1.526(4)	1.537(5)	1.518(5)
C <sub>3</sub> —C <sub>4</sub>		1.543(3)	1.540(4)		1.535(5)
CCX	112.2(6)	112.3(5)	112.1(14)	113.0(4)	110.2(14)
C <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	113.9(5)	114.3(6)	115.3(11)	113.9(9)	116.8(15)
C <sub>2</sub> C <sub>3</sub> C <sub>4</sub>		112.0(6)	112.8(11)		115.3(15)
$\Phi_1$	63.9(12)	58.9(41)	67.7(52)	66.1(5)	77(9)
References	43	This work	This work	44	This work

<sup>a</sup>Distances ( $r_g$ ) and amplitudes ( $l$ ) are in Ångströms, angles ( $\angle_\omega$ ) are in degrees. Parenthesized values are  $2\sigma$  and include uncertainties in voltage/nozzle height and correlation in experimental data.

<sup>b</sup>Average values.

<sup>c</sup>Results for the G conformer.

<sup>d</sup>Results for the GA conformer.

This is also why we have used these differences as constraints in our least-squares refinements. The distance parameters obtained from ab initio calculations are in principal  $r_e$  values and those derived from electron diffraction are either  $r_a$  or  $r_g$ . The following approximate expression is obtained for these distances:  $r_a = r_e + \langle \Delta z \rangle_T$ . The term  $\Delta z$  is increasing with temperature and depends on vibrational quantities. For relative rigid molecules,  $\langle \Delta z \rangle_T$  are usually smaller than the experimental uncertainties [41].

If the CCX angles in 1-chloro-, 1-bromo-, and 1-iodobutane are compared (see Table IV), one finds that there are only small differences. The corresponding C—C distances decrease slightly when going from *n*-butane [42] ( $r(\text{C—C}) = 1.531(2)$  Å in *n*-butane) to 1-iodobutane. Going from *n*-butane ( $\angle \text{CCC} = 113.8^\circ$  in *n*-butane) to 1-iodobutane the CCC angles show an increasing value. In Table IV some of the important parameter values for the three 1-halobutanes are also compared with corresponding parameter values in 1-chloropropane [43] and 1-iodopropane [44]. When comparing 1-chloropropane with 1-chlorobutane we see that there are little or no differences between the corresponding structure parameters. For the iodo compounds there are larger differences between the corresponding structure parameter values. The experimental C—I bond length in 1-iodobutane is significantly shorter than the value in 1-iodopropane. We have no good explanation for this observed difference.

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**Registry No.**  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{Cl}$ , 109-65-9,  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{Br}$ , 109-69-3,  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{I}$ , 543-69-8.

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