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Molecular structure and conformational composition of 1,1-dichlorobutane: a gas-phase electron diffraction and ab initio investigation¹

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Abstract

Gas-phase electron diffraction data obtained at 23°C, together with results from ab initio molecular orbital calculations (HF/6-31G(d)), were used to determine the structure and conformational composition of 1,1-dichlorobutane. Of the five distinguishable conformers (AA, G + A, AG +, G + G + and G + G –), the G + A conformer was found to be the low-energy form, and the investigation also indicated that certain amounts of the AA and G + G – conformers might be present. The symbols describing the conformers refer to torsion about the C₁–C₂ and C₂–C₃ bonds, anti (A) with H₅–C₁–C₂–C₃ and C₁–C₂–C₃–C₄ torsion angles of 180° and gauche (G + or G –) with torsion angles of +60° or 300° (–60°) respectively. The results for the principal distances (r_e) and angles (\angle_e) from the combined electron diffraction/ab initio study for the G + A conformer, with estimated 2 σ uncertainties, were as follows: $r(C_1-C_2) = 1.521(4)$ Å, $r(C_2-C_3) = 1.539(4)$ Å, $r(C_3-C_4) = 1.546(4)$ Å, $r(C-Cl_6) = 1.782(3)$ Å, $r(C-Cl_7) = 1.782(3)$ Å, $\langle r(C-H) \rangle = 1.106(6)$ Å, $\angle C_1C_2C_3 = 114.4(13)^\circ$, $\angle C_2C_3C_4 = 112.5(13)^\circ$, $\angle CCl_6Cl_7 = 110.4(7)^\circ$, $\angle CCl_6Cl_7 = 111.9(7)^\circ$, $\langle \angle CCH \rangle = 108.9(47)^\circ$. Only average values for $r(C-C)$, $r(C-Cl)$, $r(C-H)$, $\angle CCC$, $\angle CCX$ and $\angle CCH$ were determined in the least-square refinements; the differences between the values for these parameters in the same conformer and between the different conformers were kept constant at the values obtained from the ab initio molecular orbital calculations. © 1997 Elsevier Science B.V.

Keywords: Ab initio; 1,1-Dichlorobutane; Electron diffraction; Structure

1. Introduction

As part of a project studying the structures and conformational compositions of halogen-substituted butanes, we have previously investigated the following molecules: 1-chlorobutane, 1-bromobutane, 1-iodobutane [1], 1,3-dichlorobutane, 1,3-dibromobu-

tane [2], 1,4-dichlorobutane and 1,4-dibromobutane [3]. For most of these molecules, one of the low-energy conformers is that in which the carbon framework is planar and the C–X (X = halogen) bond(s) is gauche to a C–C bond. All of these molecules have, at most, one halogen atom bonded to a carbon atom. As a continuation of this work, we also wished to study 1,1-dichlorobutane, in which two halogen atoms are bonded to the same carbon atom. 1,1-Dichlorobutane may exist as five distinguishable conformers (AA, G + A, AG +, G + G + and G + G –, see also

¹ Dedicated to Professor Kozo Kuchitsu on the occasion of his 70th birthday.

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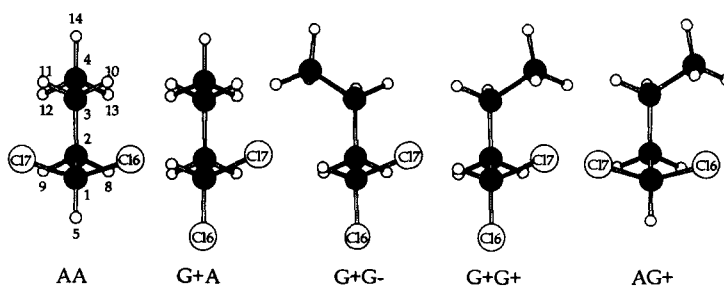


Fig. 1. Diagrams of the five different conformers of 1,1-dichlorobutane.

Fig. 1). 1,1-Dichlorobutane has previously been investigated by IR and Raman spectroscopy [4]. The spectra show that, in the liquid phase, at least three of the five possible conformers are present (G + A, G + G – and AA).

2. Experimental section and data reduction

The sample of 1,1-dichlorobutane was obtained from K&K. Diffraction experiments were performed with a Balzers Eldigraph KDG-2 at the University of Oslo [5,6] on Kodak electron image plates with a

nozzle temperature of 23°C. The voltage/distance calibration was carried out with benzene as reference and the electron wavelength was 0.058608 Å. The nozzle-to-plate distances were 498.79 mm and 248.96 mm for the long and short camera experiments respectively. Six plates from the long camera and five from the short camera distance were selected for use. The optical densities were measured with a Joyce LoebI microdensitometer. The data were reduced in the usual way [7–9]. The ranges of the data were $2.00 \leq s/\text{\AA}^{-1} \leq 15.50$ and $4.00 \leq s/\text{\AA}^{-1} \leq 30.25$. The data interval was $\Delta s = 0.25 \text{\AA}^{-1}$. A calculated

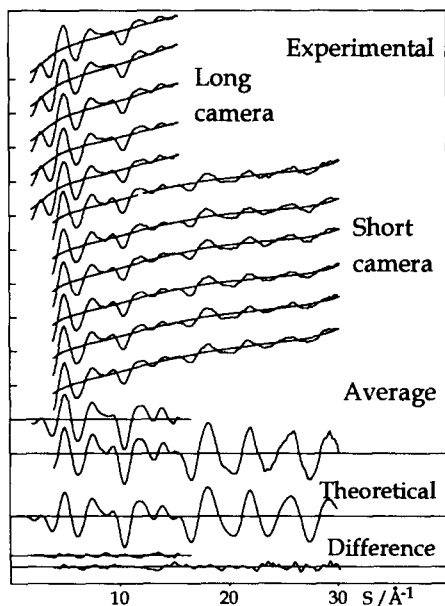


Fig. 2. Experimental intensity curves ($s^4 I(s)$) from each plate are shown magnified six times with respect to the final backgrounds on which they are superimposed. The average curves are $s I_m(s) = s(s^4 I_i - \text{background})$. The theoretical curve is for the model in Table 2.

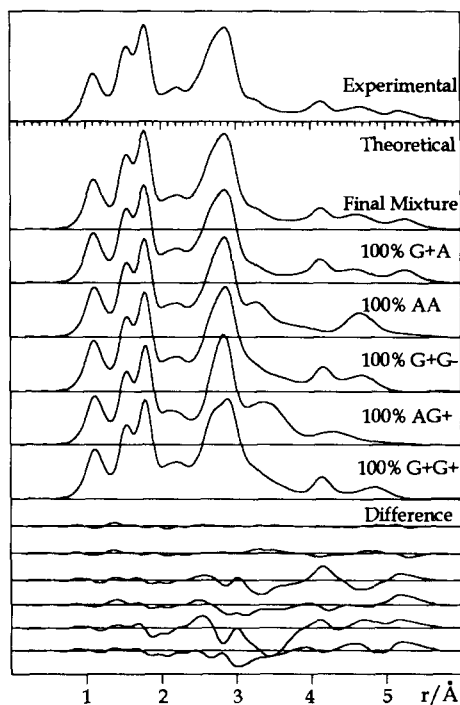


Fig. 3. Theoretical radial distribution of 1,1-dichlorobutane curves for 100% G + A, 100% AA, 100% G + G –, 100% AG + and 100% G + G +, together with the final theoretical and experimental curves.

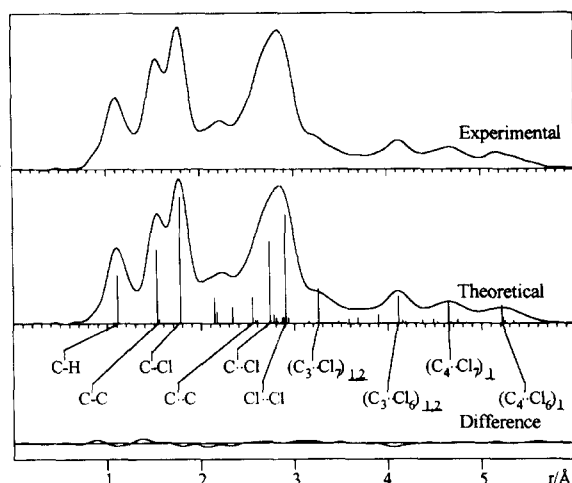


Fig. 4. Radial distribution curves for 1,1-dichlorobutane. The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region $0 \leq s/\text{\AA}^{-1} \leq 1.75$ and $B/\text{\AA}^2 = 0.0020$. Difference curve is experimental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

background [7] was subtracted from the data for each plate to yield an experimental molecular intensity curve in the form $sI_m(s)$. The experimental intensity curves are shown in Fig. 2. The data are available as supplementary material (see Section 5). Radial distribution (RD) curves (Fig. 3 and Fig. 4) were calculated in the usual way by Fourier transformation of the functions $I'_m(s) = Z_{\text{Cl}} Z_{\text{C}} (A_{\text{Cl}} A_{\text{C}})^{-1} s I_m(s) \exp(-Bs^2)$ with $B = 0.0020 \text{\AA}^{-2}$ and where $A = s^2 F$ and F is the absolute value of the complex scattering amplitudes. The scattering amplitudes and phases were taken from Ref. [10].

3. Structural analysis

From the results of earlier investigations of halogen-substituted alkanes, it is reasonable to assume that the torsion about each of the three C–C bonds in 1,1-dichlorobutane has threefold barriers. Because of symmetry, there are only five distinguishable conformers: AA, G + A, AG +, G + G + and G + G – (the first and second symbols refer to torsion about the C₁–C₂ and C₂–C₃ bonds respectively). The symbols

refer to anti (A) with H₅–C₁–C₂–C₃ and C₁–C₂–C₃–C₄ torsion angles of 180° and gauche (G+ and G–) with torsion angles of +60° and 300° (–60°) respectively (see also Fig. 1). To obtain more information about the structure and conformational composition of 1,1-dichlorobutane, ab initio molecular orbital calculations on each of the five conformers were performed. The geometry was fully optimized at the ab initio Hartree–Fock level of theory using the program GAUSSIAN 94 [11]. The 6-31G(d) basis set was used. The conformational energies obtained in these calculations and the corresponding structural parameters are given in Table 1. These results were later used to modify the theoretical model employed in the electron diffraction analysis.

The structural parameters chosen to define the geometry of each conformer were as follows: $r(\text{C}_2\text{--C}_3)$, $\Delta r_1(\text{C--C}) = r(\text{C}_2\text{--C}_3) - r(\text{C}_1\text{--C}_2)$, $\Delta r_2(\text{C--C}) = r(\text{C}_2\text{--C}_3) - r(\text{C}_3\text{--C}_4)$, $r(\text{C}_1\text{--H})$, $\Delta r_1(\text{C--H}) = r(\text{C}_1\text{--H}) - r(\text{C}_2\text{--H})$, $\Delta r_2(\text{C--H}) = r(\text{C}_1\text{--H}) - r(\text{C}_3\text{--H})$, $\Delta r_3(\text{C--H}) = r(\text{C}_1\text{--H}) - r(\text{C}_4\text{--H})$, $r(\text{C--Cl}) = (r(\text{C--Cl}_6) + r(\text{C--Cl}_7)) \times 0.5$, $\Delta r(\text{C--Cl}) = r(\text{C--Cl}_6) - r(\text{C--Cl}_7)$, $\angle \text{CCC} = (\angle \text{C}_1\text{C}_2\text{C}_3 - \angle \text{C}_2\text{C}_3\text{C}_4) \times 0.5$, $\Delta \angle(\text{CCC}) = (\angle \text{C}_1\text{C}_2\text{C}_3 - \angle \text{C}_2\text{C}_3\text{C}_4)$, $\angle \text{CCX} = (\angle \text{CCCl}_6 + \angle \text{CCCl}_7) \times 0.5$, $\Delta \angle(\text{CCCl}) = (\angle \text{CCCl}_6 - \angle \text{CCCl}_7)$, $\Delta \angle_1(\text{C--H}) = \angle \text{CC}_1\text{H} - \angle \text{CC}_4\text{H}$, $\angle \text{HC}_{2,3}\text{H} = (\angle \text{HC}_2\text{H} + \angle \text{HC}_3\text{H}) \times 0.5$, $\Delta(\angle \text{HC}_{2,3}\text{H}) = \angle \text{HC}_2\text{H} - \angle \text{HC}_3\text{H}$, $\angle \text{ClCCl}_{\text{proj}}$, $\Phi_1(\text{H}_5\text{--C}_1\text{--C}_2\text{--C}_3 \text{ torsion angle})$, $\Phi_2(\text{C}_1\text{--C}_2\text{--C}_3\text{--C}_4 \text{ torsion angle})$ and $\Phi_3(\text{C}_2\text{--C}_3\text{--C}_4\text{--H}_{14} \text{ torsion angle})$.

One weakness of the electron diffraction method is that it is very difficult to determine small differences in distances (Δr). Fortunately, it has been shown that ab initio molecular orbital calculations can predict these difference values quite well, even with relatively small basis sets [12]. Therefore we used the results from the ab initio calculations as constraints in our model. It should be mentioned that by using the results from the ab initio molecular orbital calculations, Δr_e is assumed to be equal to Δr_{α} , assuming that the vibrational corrections are negligible. For the $r(\text{C--H})$ distances and the $\angle \text{HCH}$ and $\angle \text{CCH}$ angles on the same carbon atom, average values were used. The differences between the corresponding parameters in the different conformers (e.g. C₁–C₂ in the different conformers) were also kept constant at the values calculated by the ab initio molecular orbital calculations.

Table 1

Structural parameters for 1,1-dichlorobutane obtained by ab initio calculations at the Hartree–Fock level of theory with the 6-31G(d) basis set

Parameter ^a	AA	G + A	G + G –	AG+	G + G +
$r(\text{C}_1\text{--C}_2)$	1.5241	1.5224	1.5236	1.5280	1.5232
$r(\text{C}_2\text{--C}_3)$	1.5288	1.5308	1.5329	1.5339	1.5436
$r(\text{C}_3\text{--C}_4)$	1.5289	1.5287	1.5297	1.5297	1.5296
$r(\text{C--Cl}_6)$	1.7846	1.7842	1.7845	1.7837	1.7834
$r(\text{C--Cl}_7)$	1.7846	1.7838	1.7837	1.7852	1.7846
$r(\text{C}_1\text{--H})^b$	1.0745	1.0751	1.0736	1.0743	1.0750
$r(\text{C}_2\text{--H})^b$	1.0866	1.0849	1.0848	1.0862	1.0842
$r(\text{C}_3\text{--H})^b$	1.0843	1.0858	1.0852	1.0855	1.0861
$r(\text{C}_4\text{--H})^b$	1.0857	1.0855	1.0856	1.0845	1.0848
$\angle \text{C}_1\text{C}_2\text{C}_3$	116.66	113.64	115.02	119.52	114.32
$\angle \text{C}_2\text{C}_3\text{C}_4$	111.42	111.68	114.59	116.80	114.51
$\angle \text{CCCl}_6$	112.24	110.63	110.24	113.64	110.43
$\angle \text{CCCl}_7$	112.24	112.14	112.08	112.47	112.91
$\angle \text{CC}_1\text{H}^b$	110.37	111.80	112.44	109.45	111.45
$\angle \text{C}_3\text{C}_2\text{H}^b$	109.67	110.11	109.78	105.84	107.22
$\angle \text{C}_3\text{C}_3\text{H}^b$	109.69	109.70	108.37	109.12	109.5
$\angle \text{CC}_4\text{H}^b$	111.16	111.10	111.29	111.11	111.03
$\Phi(\text{C}_1\text{--C}_2\text{--C}_3\text{--C}_4)$	180.0	183.74	– 61.16	68.74	102.65
$\Phi(\text{Cl}_6\text{--C}_1\text{--C}_2\text{--C}_3)$	– 62.51	171.75	175.24	– 74.50	173.53
$\Phi(\text{Cl}_7\text{--C}_1\text{--C}_2\text{--C}_3)$	62.51	– 65.33	– 62.04	51.81	– 63.19
$\Phi(\text{C}_2\text{--C}_3\text{--C}_4\text{--H}_{14})$	180.0	180.07	186.42	168.63	178.68
Energy ^c	2.3	0.0	3.3	14.6	12.6

^aDistances are in angstroms and angles in degrees.^bAverage values.^cEnergies are in kJ mol^{–1} relative to the conformer with the lowest energy.

Refinements of the structure 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 of the two camera distances), using a unit weight matrix [13]. The geometry of each of the conformers was calculated on the basis of the r_α parameters. These were converted to the r_a type required by the scattered intensity formula using values of the centrifugal distortion constants (δr), perpendicular amplitude corrections (K) and root-mean-square amplitudes of vibration (l) obtained by force field calculations [14]. Except for the torsional force constants, the same force field was used for the different conformers. The force constants were taken from related molecules [15]; the torsional force constants were obtained from ab initio molecular orbital calculations. 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 force field calculations. Those amplitudes which could not be refined

were kept constant at the calculated values (see Table 3). In the final refinement, both the $(\text{C}_4\text{--Cl})_{\text{anti}}$ and $(\text{C}_1\text{--C}_4)_{\text{anti}}$ amplitudes were refined. Because the refined values were quite large, we also tried to constrain these at the calculated values. This constraint increased the amount of the AA and G + G – conformers in the refinement, but other than that the structure did not change significantly. The least-squares refinements also indicated that the mole fractions of G + G + and AG+ were probably less than 0.05; these conformers were therefore excluded from the theoretical model in the final refinement. It was very difficult to refine the torsional angles together with the other structural parameters. However, it was possible to refine the torsional angles in separate refinements. The uncertainties in these refinements were very large and, since the values obtained were not significantly different from the values calculated by the ab initio method, these parameters were constrained at the ab initio values. The conformational composition changed slightly using these constraints; other than that the results were the same. In the final refinement, three

Table 2

Structural parameters for the G + A conformer of 1,1-dichlorobutane

Parameter ^a	Electron diffraction/ ab initio	Ab initio ^b
$r(C_2-C_3)$	1.524(4)	1.531
$\Delta r_1(C-C)$	[0.008]	0.008
$\Delta r_2(C-C)$	[0.002]	0.002
$\langle r(C-Cl) \rangle$	1.776(3)	1.784
$\Delta r(C-Cl)$	[- 0.001]	- 0.001
$r(C_1-H)$	1.068(6)	1.075
$\Delta r_1(C-H)$	[- 0.010]	- 0.010
$\Delta r_2(C-H)$	[- 0.011]	- 0.011
$\Delta r_3(C-H)$	[- 0.010]	- 0.010
$\langle \angle(CCC) \rangle$	113.4(12)	112.7
$\Delta \angle(CCC)$	[2.0]	2.0
$\langle \angle(CCCl) \rangle$	111.2(4)	111.4
$\Delta \angle(CCCl)$	[- 1.5]	- 1.5
$\angle CC_1H$	109.5(47)	111.8
$\Delta \angle(CCH)$	[1.0]	1.0
$\langle HC_2,3H \rangle$	[107.0]	107.0
$\Delta \angle(HC_2,3H)$	[0.5]	0.5
$\angle ClC_1Cl$	109.6(5)	109.8
Conformational composition		
x_{G+A}	0.85 \pm 0.40	
x_{G+G-}	0.15 \pm 0.37	

^aDistances (r_a) are in angstroms and angles (\angle_a) are in degrees. Values in parentheses are the estimated 2σ and include estimates of uncertainties in voltage/camera heights and data correlation. Values in brackets were kept constant at the calculated values.

^bAb initio calculations with 6-31G(d) basis set.

distances, four angles, eleven amplitudes and three conformational parameters were refined simultaneously. The results of this refinement are shown in Table 2, together with the results for the G+A conformer obtained from the ab initio molecular orbital calculations. In Table 3, the final values for some selected distances and angles are shown, together with refined and/or calculated amplitude values. The intensity curves calculated for the final model are shown in Fig. 2, together with the theoretical and difference curves. Fig. 4 shows the corresponding RD curves, and the correlation matrix for the refined parameters is shown in Table 4.

4. Discussion

The electron diffraction investigation showed that the G+A conformer dominated the conformational composition in the gas phase. The investigation also

Table 3

Selected distances, amplitudes and important valence angles for the G + A conformer of 1,1-dichlorobutane

Parameter ^a	r_g/\angle_a	l_{refined}	l_{calc}
$r(C_1-C_2)$	1.521(4)	0.051	(5) 0.048
$r(C_2-C_3)$	1.539(4)	0.051	
$r(C_3-C_4)$	1.546(4)	0.051	
$r(C-Cl_6)$	1.782(3)	0.048	(4) 0.049
$r(C-Cl_7)$	1.782(3)	0.048	
$r(C_1-H)$	1.082(6)	0.061	(6) 0.078
$r(C_2-H)$	1.102(6)	0.061	
$r(C_3-H)$	1.117(6)	0.061	
$r(C_4-H)$	1.120(6)	0.061	
$r(Cl_6, Cl_7)$	2.908(9)	0.077	(7) 0.078
$r(C_2, Cl_6)$	2.715(9)	0.081	(8) 0.072
$r(C_2, Cl_7)$	2.739(9)	0.082	
$r(C_1, C_3)$	2.562(18)	0.088	(13) 0.075
$r(C_2, C_4)$	2.549(18)	0.088	
$\angle C_1C_2C_3$	114.4(13)		
$\angle C_2C_3C_4$	112.5(13)		
$\angle CC_1Cl_6$	110.4(7)		
$\angle CC_1Cl_7$	111.9(7)		
$\angle CC_1H$	108.9(47)		
Dependent distances for G + A and G + G - conformers			
$r(C_3, Cl_7)_{G+A}$	3.261(22)	0.120	(31) 0.159
$r(C_3, Cl_7)_{G+G-}$	3.237(22)	0.127	
$r(C_3, Cl_6)_{G+A}$	4.116(13)	0.089	(25) 0.075
$r(C_3, Cl_6)_{G+G-}$	4.122(13)	0.088	
$r(C_1, C_4)_{G+G-}$	3.135(45)	[0.152]	0.152
$r(C_1, C_4)_{G+A}$	3.908(23)	0.158 (102)	0.077
$r(C_4, Cl_7)_{G+G-}$	3.875(39)	[0.313]	0.313
$r(C_4, Cl_7)_{G+A}$	4.653(32)	0.134	(51) 0.173
$r(C_4, Cl_6)_{G+G-}$	4.721(44)	0.122	
$r(C_4, Cl_6)_{G+A}$	5.221(20)	0.161 (118)	0.100

^aDistances (r_g) and amplitudes (l) are in angstroms and angles (\angle_a) are in degrees. Values in parentheses are 2σ and include uncertainties in the voltage/nozzle height and correlation in the experimental data. Values in brackets were kept constant at the calculated values. For constraints used in the refinements, see text.

indicated that certain amounts of the G+G - and AA conformers might be present (see Table 2), but these were very uncertain. The refined results for these conformers depended to some extent on which vibrational amplitudes were refined and which were not. In the final model, there was a small amount of the G+G - conformer present in the theoretical model, but, as shown in Fig. 3, it was possible to obtain a good fit to the experimental data with only the G+A conformer present. The fact that the G+A conformer was the low-energy form was also in good agreement with the results from the ab initio molecular orbital calculations.

Table 4
Correlation matrix ($\times 100$) for parameters refined in the final least-squares refinement for 1,1-dichlorobutane

Parameter	σ_{LS}^2	r_1	r_2	r_3	\angle_4	\angle_5	\angle_6	\angle_7	\angle_8	l_9	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}	l_{15}	l_{16}	l_{17}	l_{18}	x_{G+A}	x_{G+G-}
1 $r(C_2-C_3)$	0.0013	100	33	-10	-15	-20	-13	-10	0	-23	-1	3	1	3	5	-2	0	13	3	24	-20
2 $r(C-C1)$	0.0009		100	-8	16	-35	8	-41	21	-1	15	26	19	16	2	5	5	19	-2	30	-33
3 $r(C-H)$	0.0021			100	-5	12	-12	3	-12	9	1	-5	-5	-5	6	-2	-3	-9	-4	-15	23
4 $\angle(CCC)$	0.4173				100	0	8	18	-3	-7	17	19	26	20	-12	-7	-8	18	2	45	-52
5 $\angle CCCI$	0.2232					100	-25	84	-11	-13	-15	12	-27	-30	4	-13	-14	-17	-3	-18	35
6 $\angle CC_1H$	1.6693						100	-27	-12	1	-15	40	-17	-26	-12	4	-14	1	-7	12	-11
7 $\angle C1C_1Cl_{\text{free}}$	0.4355							100	-5	-4	-6	15	-13	-15	-8	-17	-1	-8	13	-7	0
8 $\angle(C_1-C_2)$	0.0015								100	-2	26	-14	25	20	4	-8	10	3	9	0	-8
9 $\angle(C-C1_6)$	0.0013									100	27	-12	21	16	4	-5	9	1	9	-10	1
10 $\angle(C-H)$	0.0022										100	-19	78	60	11	-25	7	8	1	9	-9
11 $\angle(C1_6-C1_7)$	0.0023											100	-26	-33	-11	6	-13	-6	-2	-1	0
12 $\angle(C_2-C1_6)$	0.0047												100	82	9	25	12	12	4	16	-21
13 $\angle(C_1-C_3)$	0.0086													100	12	-17	13	16	-1	20	-21
14 $\angle(C_3-C1_6)_{G+A}$	0.0085														100	-21	35	16	-29	21	8
15 $\angle(C_3-C1_7)_{G+A}$	0.0108															100	-8	-7	9	-16	-1
16 $\angle(C_1-C_4)_{G+A}$	0.0560																100	9	5	6	-19
17 $\angle(C_4-C1_6)_{G+A}$	0.0356																	100	4	55	47
18 $\angle(C_4-C1_7)_{G+A}$	0.0178																		100	-23	-8
19 x_{G+A}	0.1257																			100	35
20 x_{G+G-}	0.1199																				100

*Standard deviations from least-squares refinements. Distances (r) and amplitudes (l) are in angstroms and angles (\angle) in degrees.

Table 5

Structural parameters of butane, 1-chlorobutane, 1,1-dichlorobutane, 1,4-dichlorobutane and 1,3-dichlorobutane

Parameter ^a	Butane	1-Chlorobutane	1,1-Dichlorobutane	1,4-Dichlorobutane	1,3-Dichlorobutane
$r(C_1-C_2)$	1.531(2) ^b	1.519(3)	1.521(4)	1.529(3)	1.525(3)
$r(C_2-C_3)$		1.530(3)	1.539(4)	1.529(3)	1.527(3)
$r(C_3-C_4)$		1.543(3)	1.546(4)		1.530(3)
$r(C_1-Cl)$		1.800(4)	1.783(3)	1.802(3)	1.799(3)
$r(C_3-Cl)$					1.810(3)
$\angle C_1C_2C_3$	113.8(5) ^b	114.3(6)	117.5(12)	114.0(6)	114.5(7)
$\angle C_2C_3C_4$		112.0(6)	112.2(12)		111.0(7)
$\angle CC_1Cl$		112.3(5)	112.0(6)	112.8(4)	112.1(6)
Ref.	[17]	[1]	This work	[2]	[3]

^aDistances (r_g) are in angstroms and angles (\angle_α) are in degrees. Values in parentheses are 2σ and include uncertainties in the voltage/nozzle height and correlation in the experimental data. The parameters are for the conformer of each molecule with a planar carbon framework and with the C–X bond(s) gauche to a C–C bond.

^bAverage values.

In Table 2, the structural parameters obtained from the electron diffraction analysis and from the ab initio calculations are compared. Most bond distances were calculated to be slightly longer than those observed experimentally. For the valence angles, the results obtained by these two methods were within experimental error limits. An earlier investigation of 1,1-dichlorobutane [4] in the liquid state indicated that three conformers, G + A, G + G – and AA, were present.

In Table 5, some of the important structural parameters of butane [16], 1-chlorobutane [1], 1,1-dichlorobutane, 1,4-dichlorobutane [3] and 1,3-dichlorobutane [2] are compared. For each molecule, the results for the conformer with the C–X bond(s) gauche to a C–C bond and the planar carbon framework are compared. For 1,1-dichlorobutane, this conformer was not present in large enough amounts for the structure to be determined independently by electron diffraction. The results in Table 5 for this molecule are the structural parameters (for the conformer with the planar carbon framework and the C–X bond(s) gauche to a C–C bond) of the low-energy form and the differences obtained by ab initio molecular orbital calculations. There are small differences between the corresponding C–C distances for 1-chlorobutane and 1,1-dichlorobutane. The C–Cl distances in 1,1-dichlorobutane are slightly shorter than those in 1-chlorobutane, 1,4-dichlorobutane and 1,3-dichlorobutane. It has previously been shown that the length of the C–X bond (X is an electronegative atom or group) decreases with increasing number of electronegative

substituents [17] on the carbon atom. This is in agreement with our observation. The $C_1C_2C_3$ angle is similar in butane, 1-chlorobutane, 1,4-dichlorobutane and 1,3-dichlorobutane (113.8–114.5°), but for 1,1-dichlorobutane a larger value is observed. The $C_1C_2C_3$ angle in the low-energy form of 1,1-dichlorobutane (G + A) is 114.4(13)°. If the CCX angles in all the molecules in Table 5 are compared, only small differences are observed.

For the previously investigated halogenated butanes (and 1,1-dichlorobutane), the conformer with the planar carbon framework and the C–X bond(s) gauche to a C–C bond is one of the low-energy forms for all of the molecules, except for 1-iodobutane. The uncertainty in the conformational composition is large for all the molecules. In 1,1-dichlorobutane, the G + A conformer (with one C–X gauche and one anti to the carbon framework) was found to be the low-energy form; this was not in agreement with that observed for 1,1-dichloropropane [18], where the two forms A (both C–X anti) and G (one C–X gauche and one anti) were found to have almost equal energy.

5. Supplementary material available

Tables of total scattered intensities, average molecular intensities and Cartesian coordinates for 1,1-dichlorobutane are available from the British Library Document Supply Centre as publication no. SUP26586 (5 pages of table).

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References

- [1] K. Aarset, K. Hagen, R. Stølevik, P.C. Sæbø, *Struct. Chem.* 6 (1995) 197.
- [2] K. Aarset, K. Hagen, R. Stølevik, *J. Phys. Chem.* 99 (1995) 11089.
- [3] K. Aarset, K. Hagen, R. Stølevik, *J. Phys. Chem.* 98 (1994) 5249.
- [4] G.A. Crowder, *J. Mol. Struct.* 70 (1981) 193.
- [5] W. Zeil, J. Haase, L. Wegmann, *Z. Instrumentenk* 74 (1966) 84.
- [6] O. Bastiansen, R. Graber, L. Wegmann, *Balzers High Vac. Rep.* 25 (1969) 1.
- [7] K. Hagen, K. Hedberg, *J. Am. Chem. Soc.* 95 (1973) 1003.
- [8] G. Gundersen, K. Hedberg, *J. Chem. Phys.* 51 (1969) 2500.
- [9] L. Hedberg, Abstracts of Papers, Fifth Austin Symposium on Gas-Phase Molecular Structure, Austin, TX, March, 1974, p. 37.
- [10] A.W. Ross, M. Fink, R. Hilderbrandt, *International Tables of Crystallography*, Vol. 4, Kluwer Academic Publishers, Dordrecht, 1992, p. 245.
- [11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, *GAUSSIAN 94*, Revision B.1, Gaussian, Inc., Pittsburgh, PA, 1995.
- [12] L. Shcäfer, J.D. Ewbank, K. Siam, N. Chiu, H.L. Sellers, in: I. Hargittai, M. Hargittai (Eds.), *Stereochemical Applications of Gas-Phase Electron Diffraction*, Part A, VCH, New York, 1988, p. 301.
- [13] K. Hedberg, M. Iwasaki, *Acta Crystallogr.* 17 (1964) 529.
- [14] R.L. Hilderbrandt, J.D. Wieser, *J. Chem. Phys.* 55 (1971) 4686.
- [15] L. Postmyr, *J. Mol. Struct.* 298 (1993) 137.
- [16] W.F. Bradford, S. Fitzwater, L.S. Bartell, *J. Mol. Struct.* 38 (1977) 185.
- [17] H.A. Bent, *J. Chem. Phys.* 33 (1960) 1259.
- [18] T. Rydland, R. Seip, R. Stølevik, *Acta Chem. Scand. A* 37 (1983) 41.