

## Rotational Isomerism and Nuclear Magnetic Resonance Spectra of 1,4-Dichlorobutane

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Rotamer energies of the energetically favoured forms, and one *cis* conformation of 1,4-dichlorobutane, have been calculated using a semi-empirical method. When the multiplicity is taken into account, it is found that the (*a,a,g*) rotamer predominates although the all-*anti* conformation has the lowest energy. The relative populations of the seven energetically favoured forms of 1,4-dichlorobutane have also been calculated. The obtained distribution of rotamers is similar to that reported for hexane.

The rapidly interconverting 1,4-dichlorobutane molecule constitutes an AA'BB'B''B'''A''A''' spin system. A complete analysis of the 60 MHz NMR spectrum has been performed by means of the computer program LACX. The obtained spectral parameters are similar to those found for 1,4-dibromobutane. The theoretical approach and the NMR measurements both predict that the *anti* form is preferred about the central C-C bond and that the four rotamers of this type contribute as much as 77 %.

Electron diffraction studies on 1-chloropropane<sup>1</sup> and 1-chlorobutane<sup>2</sup> have shown that chlorine stabilizes *gauche* conformations. In contrast, in 1-bromobutane<sup>3</sup> the rotamer populations are nearly identical with those in pentane.<sup>4</sup> A previous study on 1,4-dibromobutane<sup>5</sup> indicates, however, significant contributions from rotamers possessing bromine *gauche* at each end of the molecule. It, therefore, seems of interest to determine to what extent chlorine influences the stability of *gauche* conformations in 1,4-dichlorobutane.

The semi-empirical method due to Scott and Scheraga<sup>6-8</sup> will be used to calculate rotamer energy differences.

Rotational isomerism about C-C single bonds has been extensively studied by NMR.<sup>9</sup> Since the barrier to internal rotation about the C-C bond is low, only time-average NMR parameters are usually measured at room temperature.

The analysis of the NMR spectrum of 1,4-dibromobutane was reported in a previous paper.<sup>5</sup> Since the distribution of rotamers is different for 1,4-

dichlorobutane this molecule may not constitute the same type of spin system as 1,4-dibromobutane. This investigation is a continuation of previous work on similar compounds.<sup>5,10</sup>

### ROTAMER ENERGIES

In 1,4-dichlorobutane an ethane-like situation exists about three C–C bonds. With respect to the central C–C bond the three staggered rotamers shown in Fig. 1 are the energetically favoured forms. If the orientation of the

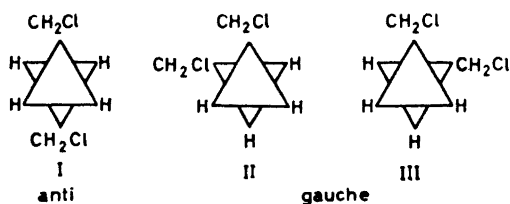


Fig. 1. The preferred conformations about the central C–C bond of 1,4-dichlorobutane.

chlorine atoms is taken into account, eleven different staggered rotamers result as for hexane<sup>4</sup> ( $3^3 = 27$  states altogether). Four of these different rotational isomers have adjacent  $g, g'$  interactions and can be rejected by steric requirements in the case of 1,4-dibromobutane and 1,4-dichlorobutane as H-halogen distances of about 1.9 Å in length would result unless the molecules are badly distorted. The remaining seven rotamers are listed in Table 1. The various rotamers are specified by italics as previously described.<sup>5</sup>

Table 1. Calculated rotamer energies for the energetically favoured forms and one *cis* conformation of 1,4-dichlorobutane (kcal/mol).

Rotamer	Dihedral angles (deg.)	Calculated contributions				Total energy
		Steric	Polar		Torsional	
			Cl...Cl	H...Cl		
<i>(a,a,a)</i>	180,180,180	1.68	1.15	-7.90	0	-5.07
<i>(a,a,g)</i>	180,180, 60	2.38	1.41	-8.27	0	-4.48
<i>(g,a,g)</i>	60,180, 60	3.05	1.61	-8.67	0	-4.01
<i>(g,a,g')</i>	60,180,300	3.13	1.39	-8.78	0	-4.26
<i>(a,g,a)</i>	180, 68,180	2.35	1.23	-8.13	0.11	-4.43
<i>(a,g,g)</i>	180, 68, 60	3.36	1.55	-8.53	0.11	-3.51
<i>(g,g,g)</i>	60, 68, 60	4.46	1.51	-9.12	0.11	-3.04
<i>(a,e,a)<sup>a</sup></i>	180, 0,180	4.30	1.27	-8.28	2.65	-0.07

<sup>a</sup> *cis* form ( $\tau = 0$ ).

The energy ( $E$ ) of a given molecular conformation will be calculated using the method of classical mechanics which explicitly breaks down the energy into additive interactions as shown in eqn. (1).<sup>5-8</sup>

$$E = \frac{V_0}{2} (1 + \cos 3\tau) + \sum [a_{ij} \exp(-b_{ij}r_{ij}) - c_{ij}/r_{ij}^6 + d_{ij}/r_{ij}] \quad (1)$$

The significance of the first and second term, involving the summation, of eqn. (1) and of the parameters  $V_0$ ,  $\tau$ ,  $a_{ij}$ ,  $b_{ij}$ ,  $c_{ij}$ , and  $d_{ij}$  has been described previously.<sup>5-8</sup>  $E$  can be calculated once the molecular geometry and the parameters of eqn. (1) are known. For the range of conformations in which steric interactions are not strong, calculated energy differences are found to be fairly insensitive to the choice of bond lengths and bond angles.<sup>11</sup>

Since the molecular geometry of 1,4-dichlorobutane is not known, it is necessary to use standard values of bond lengths and bond angles. This will be useful in comparing with the results of previous studies based on the same standard values.<sup>5,8</sup> The computer program *COORD*<sup>12</sup> was used for calculating the interatomic distances for a given molecular geometry. The rotamer energies listed in Table 1 were then calculated from eqn. (1) using the previously quoted values for the parameters.<sup>8</sup>

The population ratio can be obtained from the simplified equation

$$n_i/n_j = \exp[-(E_j - E_i)/RT] \quad (2)$$

on the assumption that the various rotamers are equal in entropy which is often justified.<sup>13</sup> Using eqn. (2) and the rotamer energies compiled in Table 1 a fair estimate of the distribution between rotational isomers has been obtained (Table 2). For comparison the results for 1,4-dibromobutane<sup>5</sup> and hexane<sup>4</sup> are also quoted. When the multiplicity is taken into account, it is

Table 2. Distribution of rotamers at 20°C for three symmetrically 1,4-disubstituted butanes.

Rotamer	Multi- plicity	Mol fraction <sup>a</sup>	Substituents		
			CH <sub>3</sub> <sup>c</sup>	Cl	Br <sup>d</sup>
			% rotamers <sup>b</sup>		
(a,a,a)	1	$n_0$	29	23.4	15.2
(a,a,g)	4	$n_1$	34	34.0	35.0
(g,a,g)	2	$n_2$	} 10	7.6	12.1
(g,a,g')	2	$n_3$		11.6	16.6
(a,g,a)	2	$n_4$		17	15.6
(a,g,g)	4	$n_5$	10	6.4	8.1
(g,g,g)	2	$n_6$	0	1.4	3.1

<sup>a</sup> Configurations with g and g' adjacent are given zero weight.

<sup>b</sup> Takes into account the multiplicity.

<sup>c</sup> Data from Ref. 4.

<sup>d</sup> Calculated using eqn. (2) and the rotamer energies quoted in Ref. 5.

seen that the  $(a,a,g)$  rotamer predominates although the all-*anti* conformation has the lowest energy. Table 2 shows that rotamers having an *anti* arrangement of the terminal  $\text{CH}_2\text{X}$  groups with respect to the central C—C bond account for as much as 73 % to 79 % of the staggered forms. This is mainly due to increased interaction between these bulky groups in the *gauche* forms. The mutual avoidance of the terminal  $\text{CH}_2\text{X}$  groups is also implied by the value of the dihedral angle  $\tau$  (*ca.*  $70^\circ$ ) being considerably greater than  $60^\circ$  for these compounds.

The rotamer percentages for 1,4-dichlorobutane are similar to the approximate values reported for hexane.<sup>4</sup> The  $(g,a,g)$  and  $(g,a,g')$  rotamers are, however, more predominant for 1,4-dichlorobutane at the expense of the  $(a,a,a)$  rotamer. The partial failure of the chlorine, in this case, to stabilize *gauche* conformations is of particular interest in view of the results reported for 1-chloropropane<sup>1</sup> and 1-chlorobutane.<sup>2</sup> The results for 1-bromobutane and other evidence indicate that bromine exhibits a behaviour not unlike that of a methyl group.<sup>3</sup> On this basis, 1,4-dibromobutane should have a distribution of rotamers similar to that of hexane. On the contrary, it is seen from Table 2 that rotamers possessing one or both of the bromine atoms at a *gauche* position are higher populated at the expense of the all-*anti* form than the corresponding rotamers of 1,4-dichlorobutane and hexane.

The major contribution to the calculated energy differences for 1,4-dichlorobutane and 1,4-dibromobutane arises from the steric term in eqn. (1), whereas the electrostatic term is fairly constant except for the  $(g,a,g')$  and  $(g,g,g)$  rotamers. The variation in rotamer populations between these compounds is also mainly caused by the steric term. It is, however, necessary to take the electrostatic interaction into account in order to achieve reasonable results.

It is difficult to calculate the barriers to rotation for molecules possessing more than one rotating group since the energy required to rotate one particular group depends on the orientation of the other groups.<sup>7,11</sup> It is clear that the bulky halogen substituents in 1,4-dibromobutane and 1,4-dichlorobutane significantly increase the barriers relative to butane. By assuming independent C—C rotations and defining the barrier height about the central C—C bond as  $E(0) - E(60)$  (the parenthesized figure represents  $\tau$ ) its magnitude can be estimated from eqn. (1). One obtains 4.23 kcal/mol with the terminal  $\text{CH}_2\text{Cl}$  groups in their minimum energy conformation. This value falls within the range reported for halogen-substituted ethanes, propanes and butanes.<sup>5-8,14</sup> The actual barrier height is probably smaller since the *cis* energy  $E(0)$  certainly is too high because the rigid rotor model is found to be inadequate when steric interactions are strong.<sup>11</sup>

#### SPECTRAL ANALYSIS

Since the barrier to internal rotation about the C—C single bonds in 1,4-dichlorobutane is low, only time-average NMR parameters  $P$  defined by eqn. (3) are measured at room temperature.<sup>9,15</sup>

$$P = \frac{\sum_i n_i P_i}{\sum_i n_i} \quad (3)$$

The NMR spectrum of the rapidly interconverting molecule thus constitutes an AA'BB'B''B'''A''A''' spin system.

It is appropriate at this point to define the involved spectral parameters.  $\nu_A$  and  $\nu_B$  represent the chemical shifts of the chloromethyl and methylene protons, respectively. There are eight coupling constants (neglecting the five-bond couplings) that affect the spectrum. The two geminal coupling constants are specified  $J_{AA}$  and  $J_{BB}$ , whereas  $J$  and  $J'$  represent the average vicinal coupling constants between the methylene hydrogens. Similarly, the four average coupling constants between the chloromethyl and methylene hydrogens are termed  ${}^3J_{AB}$ ,  ${}^3J_{AB'}$ ,  ${}^4J_{AB}$ , and  ${}^4J_{AB'}$ , where the superscript prefix indicates the number of intervening bonds.

The average values for the vicinal coupling constants depend on the coupling constants,  $J_g$  and  $J_t$ , for pairs of nuclei that are *gauche* and *trans* with respect to each other. Let us assume that only one pair of different *gauche* and *trans* coupling constants,  $J_g$  and  $J_t$ , exists for the coupled chloromethyl-methylene hydrogens and, similarly, one pair,  $J'_g$  and  $J'_t$ , for the coupled methylene-methylene hydrogens. By using eqn. (3) the following simplified expressions can then be obtained for the average vicinal coupling constants:

$${}^3J_{AB} = n_0J_g + n_1(3J_g + J_t) + n_2(J_g + J_t) + n_3(J_g + J_t) + 2n_4J_g + n_5(3J_g + J_t) + n_6(J_g + J_t) \quad (4)$$

$${}^3J_{AB'} = n_0J_t + 2n_1(J_g + J_t) + 2n_2J_g + 2n_3J_g + 2n_4J_t + 2n_5(J_g + J_t) + 2n_6J_g \quad (5)$$

$$J = \frac{1}{2}(1 + p)J'_g + \frac{1}{2}(1 - p)J'_t \quad (6)$$

$$J' = (1 - p)J'_g + pJ'_t \quad (7)$$

where  $p = n_0 + 4n_1 + 2n_2 + 2n_3$ , that is, the relative population of the *anti* form (I). It follows from eqns. (4)–(7) that

$$2{}^3J_{AB} + {}^3J_{AB'} = 2J_g + J_t \quad (8)$$

$$2J + J' = 2J'_g + J'_t \quad (9)$$

A complete analysis of the NMR spectrum using iterative fitting of experimental and calculated transitions has been performed by means of the computer program LACX.<sup>16</sup> The analysis was carried out as previously described.<sup>5</sup> About 300 transitions were matched. The root-mean-square deviation was 0.072 Hz. The calculated spectral parameters are listed in Table 3. The agreement between the experimental and computed spectra in Figs. 2 and 3 is satisfactory.

By using eqn. (8) and the data in Table 3 it follows that  $2J_g + J_t = 19.1$  Hz. From this value and from analogy with similar compounds,<sup>9</sup> it can be assumed that  $J_g \simeq 4$  Hz and  $J_t \simeq 11$  Hz. By inserting these values in eqns. (4) and (5) and using the rotamer populations listed in Table 2, it is found that  ${}^3J_{AB} = 5.4$  Hz, and  ${}^3J_{AB'} = 8.1$  Hz for 1,4-dichlorobutane. Increasing populations of the (*g,a,g*), (*g,a,g'*) and (*g,g,g*) rotamers at the expense of the all-*anti* form would make  ${}^3J_{AB}$  and  ${}^3J_{AB'}$  more similar. The effect of this population change is seen for 1,4-dibromobutane where a corresponding evaluation yields  ${}^3J_{AB} = 5.9$

Table 3. NMR spectral parameters (in Hz) at 60 MHz of 1,4-dichlorobutane in 25 % v/v methylene chloride solution.

$\nu_A - \nu_B$	${}^3J_{AB}$	${}^3J_{AB'}$	$J$	$J'$	$J_{AA}^a$	$J_{BB}$	${}^4J_{AB}$	${}^4J_{AB'}$
98.68	6.25	6.62	5.57	9.51	-10	-11.44	-0.19	-0.30

<sup>a</sup> Approximate value.

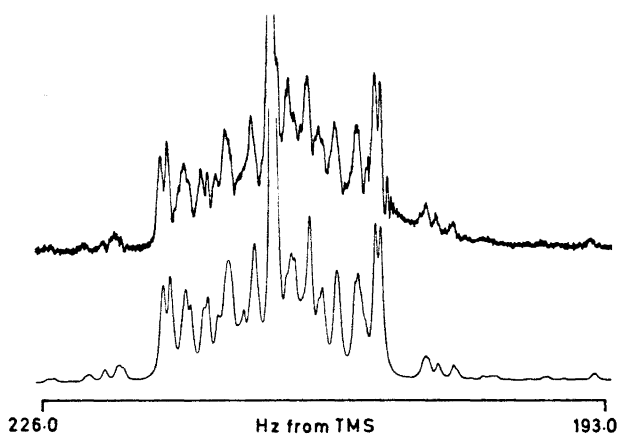


Fig. 2. Experimental (upper part) and calculated (lower part) chloromethyl proton spectra at 60 MHz of 25 % v/v 1,4-dichlorobutane in methylene chloride.

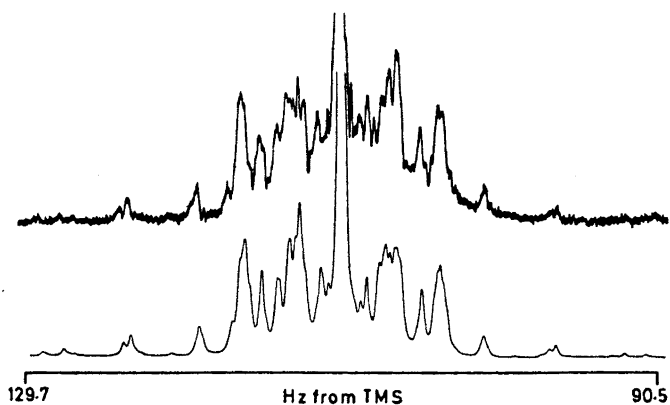


Fig. 3. Experimental (upper part) and calculated (lower part) methylene proton spectra at 60 MHz of 25 % v/v 1,4-dichlorobutane in methylene chloride.

Hz, and  ${}^3J_{AB'} = 7.3$  Hz. In calculating these coupling constants the estimated rotamer populations for the gas phase have been used. The vicinal coupling constants have, however, been measured in the liquid phase where dipole interactions would tend to stabilize the rotamers having the larger dipole moments. A stabilization in the liquid phase, of the rotamers possessing *gauche* halogens at each end of the molecule, may explain why the observed NMR spectra show that the terminal  $\text{CH}_2\text{X}$  protons are nearly magnetically equivalent.

The NMR spectrum of 1,4-dichlorobutane may be approximately treated as an  $\text{AA}'\text{XX}'\text{X}''\text{X}''' \text{A}'\text{A}''$  spin system. This system has two  $a_4$  and two  $x_4$  sub-spectra with effective Larmor frequencies  $\nu_A \pm ({}^3J_{AX} + {}^3J_{AX'} + {}^4J_{AX} + {}^4J_{AX'})$  and  $\nu_X \pm ({}^3J_{AX} + {}^3J_{AX'} + {}^4J_{AX} + {}^4J_{AX'})$ , respectively. From the experimental spectra it is found that these A and X "doublets" are separated by 12.48 Hz. This value should be approximately equal to  ${}^3J_{AB} + {}^3J_{AB'} + {}^4J_{AB} + {}^4J_{AB'} = 12.38$  Hz, as observed.

Eqn. (9) yields  $2J'_g + J'_t = 20.6$  Hz after inserting the experimental  $J$  and  $J'$  values. Since the substituent effect of the chlorine atoms on  $J'_g$  and  $J'_t$  is probably small, it can be assumed that the *trans* coupling constant has about the same value as in butane<sup>10</sup> and 1,4-dibromobutane,<sup>5</sup> that is,  $J'_t \approx 11$  Hz, hence  $J'_g \approx 4.8$  Hz. By inserting these values and the theoretical value of  $p$  in eqns. (6) and (7) one obtains  $J = 5.5$  Hz and  $J' = 9.5$  Hz in excellent agreement with the experiment. This indicates that the total population of the *anti* form (I) is about the same for the liquid and gas phase (*ca.* 77 %). Within the approximation of the calculations, the change of phase thus appears to have little effect on the *anti-gauche* equilibrium about the central C - C bond.

The magnitude of the observed chemical shift for 1,4-dichlorobutane is larger than for 1,4-dibromobutane, as expected. The coupling constants are very similar for these two compounds. The largest variation occurs in the  $\text{CH}_2 - \text{CH}_2\text{X}$  couplings being more affected by the substituents. The almost identical  $J$  and  $J'$  values observed for 1,4-dibromobutane and 1,4-dichlorobutane indicate about the same percentage of the *anti* form (I) for these compounds in agreement with calculations for the gas phase.

## EXPERIMENTAL

1,4-Dichlorobutane was obtained from EGA (purity minimum 99 %) and used without further purification. The 60 MHz NMR spectra were examined in 25 % v/v methylene chloride solution. Tetramethylsilane was used as internal reference and lock signal source. The sample was thoroughly degassed and sealed under vacuum.

The NMR spectra were run at ambient temperature (*ca.* 27°C) on a JOEL-C-60H spectrometer. The spectra used for the analysis were recorded at 54 Hz sweep width and calibrated every 5 Hz using a frequency-counter. Line positions were obtained by averaging the results of four scans.

Computations were performed on the IBM/50H computer at the University of Bergen. Graphical plots were obtained using a Calcomp Plotter.

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