

## Rotational Isomerism and Nuclear Magnetic Resonance Spectra of Propyl and Butyl Derivatives

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The 60 MHz NMR spectra of eleven propyl and butyl derivatives have been fully analyzed by means of the computer program UEAITR. A theoretical analysis of the propyl spectrum has also been carried out by the combined use of the composite particle technique, good quantum numbers and symmetry. The spectral parameters of the strongly coupled protons follow from this "direct" analysis. The chemical shifts and coupling constants of the eleven compounds are discussed in terms of substituent and conformational effects.

Rotamer energies of the energetically favoured forms of three butyl halides have been calculated using a semi-empirical method. The calculations indicate that, whereas the *anti* form predominates about the  $\text{CH}_3\text{CH}_2-\text{CH}_2\text{CH}_2\text{X}$  bond by 0.7–1.1 kcal/mol, the *gauche* form is preferred about the  $\text{CH}_3\text{CH}_2\text{CH}_2-\text{CH}_2\text{X}$  bond by 0.1–0.3 kcal/mol. It is found that rotamers having an *anti* arrangement of the carbon skeleton contribute as much as 77 % in the gas phase. However, the NMR data suggest an increase of *gauche*-methyl forms by 10 % in the liquid phase owing to dipole interactions.

Rotational isomerism about single C–C bonds in alkanes and their derivatives has been extensively studied by electron diffraction and various spectroscopy methods.<sup>1</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 spectra of compounds containing three or more strongly coupled methyl or methylene protons are, nevertheless, very complex. Although it might be possible to calculate some of the spectral parameters directly from the spectrum only an "indirect" computer analysis will yield precise parameters.

Experimental and theoretical studies of halogenated ethanes, propanes, and butanes generally agree in indicating that halogen stabilizes *gauche* conformations.<sup>1</sup> However, electron diffraction data on butyl bromide<sup>2</sup> suggest that the distribution of conformers is the same as for pentane<sup>3</sup> in contrast to the situation in butyl chloride.<sup>4</sup> It therefore seemed of interest to investigate the conformations of the butyl halides using NMR and the semi-empirical

method due to Scott and Scheraga.<sup>5</sup> The latter method has been found to reproduce experimental barrier heights and differences in conformational energy satisfactorily for a series of halogenated ethanes and propanes.<sup>6</sup>

The following propyl and butyl derivatives have been studied in this paper: I: propyl chloride; II: propyl bromide; III: propyl iodide; IV: propyl alcohol; V: tripropyl phosphate; VI: tripropyl thiophosphate; VII: butyl chloride; VIII: butyl bromide; IX: butyl iodide; X: butylamine; XI: butyl cyanide.

Twelve years ago Cavanaugh and Dailey<sup>7</sup> studied the NMR spectra of some propyl derivatives on the basis of a perturbation treatment of the  $A_3B_2C_2$  spin system. When the present work was initiated, however, no precise NMR data on these compounds were available. During the course of this investigation Schruppf<sup>8</sup> reported NMR data for several propyl derivatives, including compounds I–III. Schruppf analyzed the spectra of the propyl halides as  $A_3B_2C_2$  systems by iterative fitting of only 30–70 lines mainly in the B region.

The present paper also reports a theoretical sub-spectral analysis of the propyl spectrum on the basis of the  $A_3BB'XX'$  approximation. This approximation is far better than the one used by Schruppf in his sub-spectral treatment. This investigation is a continuation of previous work on related compounds.<sup>9–13</sup>

## EXPERIMENTAL

All the compounds were obtained from Fluka AG except V and VI which were provided by one of us (D.W.A.). Compounds V and VI have b.p.<sub>10</sub> 89–90°C and b.p.<sub>8</sub> 102–104°C, respectively. The propyl compounds I–VI were examined as 25 % v/v solutions in methylene chloride whereas compounds VII–XI were studied as neat liquids added 1 % v/v benzene. A trace of trifluoroacetic acid was added to IV to ensure rapid exchange of the hydroxyl proton. A small amount of TMS added to all samples served as internal standard. The samples were thoroughly degassed and sealed under vacuum.

The NMR spectra were run at ambient probe temperature (*ca.* 27°C) on a JEOL-C-60H spectrometer. The spectra used for the analyses were recorded at 54 Hz sweep width and calibrated, relative to the locking substance, 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. The graphical output was obtained on a Calcomp Plotter.

## ROTAMER ENERGIES OF BUTYL HALIDES

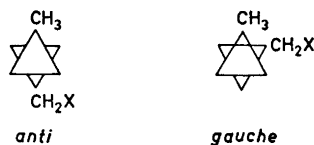
In previous papers the semi-empirical method due to Scott and Scheraga<sup>5</sup> has been used to calculate rotamer energies in halogenated butanes.<sup>6,11,12</sup>

In these calculations the energy ( $E$ ) of a given molecular conformation is broken down into additive non-bonded interactions plus the torsional strain as shown in eqn. (1).

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

The significance of the various terms in eqn. (1) and of the parameters has been described previously.<sup>6</sup>  $E$  can be calculated once  $V_0$ ,  $a_{ij}$ ,  $b_{ij}$ ,  $c_{ij}$ ,  $d_{ij}$  and the molecular geometry are known.

In butyl halides an ethane-like situation exists about two C–C bonds if the orientation of the substituent X is taken into account. It is thus seen that five different staggered rotamers result ( $3^2 = 9$  rotamers altogether). With respect to the central C<sub>2</sub>–C<sub>3</sub> bond two different rotational isomers are found:



In Table 1 the staggered rotamers are specified by italics *a* (*anti*) and *g* (*gauche*) which refer to the relevant dihedral angles. The first italic refers to the dihedral angle ( $\tau$ ) of the C<sub>1</sub>–C<sub>2</sub> bond relative to the C<sub>3</sub>–C<sub>4</sub> bond and the second italic refers to the dihedral angle of the X–C<sub>1</sub> bond relative to the central C<sub>2</sub>–C<sub>3</sub> bond.

Average values of bond lengths and angles have been measured for butyl chloride<sup>4</sup> and bromide<sup>5</sup> in the gas phase at room temperature. The corresponding parameters of the butyl halides in the liquid phase have, however, not been reported. For our comparative studies we have therefore found it advantageous to use the same standard values as in previous calculations on similar molecules,<sup>6,11,12</sup> viz.: Bond lengths (Å): C–C = 1.53, C–H = 1.09, C–Cl = 1.77, C–Br = 1.93, and C–I = 2.13. Bond angles (degrees): C–C–H = H–C–H = 109.47 and C–C–X = 111.0 (X = C, Cl, Br, or I). These standard values do not, in fact, differ significantly from the reported values of gaseous

Table 1. Calculated rotamer energies (kcal/mol) for the staggered forms of butyl halides.

Substituent	Rotamer	Dihedral angles (deg.)		Calculated contributions			Total energy
				Steric	Polar H...X	Torsional	
Cl		180,	180	1.31	–4.37	0	–3.06
Br	<i>(a,a)</i>	180,	180	0.84	–3.88	0	–3.03
I		180,	180	0.79	–3.05	0	–2.27
Cl		68,	180	2.02	–4.52	0.11	–2.39
Br	<i>(g,a)</i>	68,	180	1.55	–4.00	0.11	–2.34
I		68,	180	1.45	–3.15	0.11	–1.59
Cl		180,	74	1.62	–4.78	0	–3.16
Br	<i>(a,g)</i>	180,	74	1.06	–4.26	0	–3.21
I		180,	76	1.03	–3.36	0	–2.33
Cl		68,	74	2.77	–4.95	0.11	–2.06
Br	<i>(g,g)</i>	68,	70	2.24	–4.56	0.11	–2.20
I		68,	74	2.10	–3.45	0.11	–1.24
Cl		70,	300	28.16	–5.90	0.18	22.43
Br	<i>(g,g')</i> <sup>a</sup>	70,	310	21.17	–5.52	0.18	15.83
I		70,	310	27.46	–4.42	0.18	23.22

<sup>a</sup> (*g,g'*) represents the form in which the methyl and halogen approach most closely.

butyl chloride and bromide. The calculated energy differences have, nevertheless, been found to be fairly insensitive to the choice of bond lengths and bond angles for the range of conformations in which steric interactions are not strong, that is, at the energy minima.<sup>14</sup>

The rotamer energies listed in Table 1 were calculated from eqn. (1) using the previously quoted values of the parameters  $V_0$ ,  $a_{ij}$ ,  $b_{ij}$ ,  $c_{ij}$ , and  $d_{ij}$ .<sup>6</sup> The calculated energies are relative and have no absolute significance. The computer program COORD<sup>15</sup> was used for calculating the interatomic distances for a given molecular geometry.

The ratio of the mol fractions of the  $i$ 'th and  $j$ 'th rotamers is given by eqn. (2).

$$n_i/n_j = Q_i'(Q_j')^{-1} \exp[-(E_i - E_j)/RT] \quad (2)$$

where  $Q_i'$  is the partition function for a particular rotamer  $i$ , excluding the steric interaction energy term. It has, however, been shown that the  $Q_i'$ 's are fairly constant for alkane isomers with the same degree of branching.<sup>16</sup> Errors introduced by assuming that the  $Q_i'$ 's are independent on conformation in the butyl halides are small compared to the approximations involved in eqn. (1). The distribution of rotamers listed in Table 2 was obtained using eqn. (2) and the rotamer energies in Table 1.

Table 2. Distribution of rotamers (%) for butyl halides and pentane at 27°C. The figures take into account the multiplicity.

Rotamer	Multiplicity	Mol fraction	Substituent			
			Cl	Br	I	CH <sub>3</sub> <sup>a</sup>
( <i>a,a</i> )	1	$n_0$	22.8	20.7	23.7	45.7
( <i>g,a</i> )	2	$n_1$	14.8	13.0	15.2	24.0
( <i>a,g</i> )	2	$n_2$	53.9	56.0	52.4	24.0
( <i>g,g</i> )	2	$n_3$	8.5	10.3	8.7	6.3

<sup>a</sup> Based on an assumed difference in energy between *anti* and *gauche* conformations of 0.8 kcal/mol.

### SPECTRAL ANALYSIS

The NMR spectra of the eleven compounds were analyzed by means of the UEANMR II<sup>17</sup> and UEAITR<sup>18</sup> computer programs. These programs make use of magnetic equivalence factoring to reduce the size of the secular matrices. The UEANMR II program was, however, only used in conjunction with the sub-routine KOMBIP<sup>19</sup> to obtain stick- and line-shape plots. The iterative fitting of experimental and calculated transitions was performed by means of the UEAITR program.

(a) *Propyl spectra*. Generally, the protons of a rapidly rotating propyl group constitute an A<sub>3</sub>BB'CC' spin system. However, when a strongly electro-negative substituent is attached to the propyl fragment the NMR spectra can be fairly accurately analyzed on the basis of an A<sub>3</sub>BB'XX' system. This system

provides a good example of a complex system which can be simplified by the combined use of the composite particle technique, good quantum numbers and symmetry. It follows from the principles of the sub-spectral analysis that the strongly coupled  $A_3BB'$  part of the  $A_3BB'XX'$  system can be broken down into two  $a_3b_2$  and two  $a_3bc$  sub-spectra characterized by  $m(XX') = \pm 1$  and 0, respectively.<sup>20</sup>

$$A_3BB'(A_3BB'XX') = (a_3b_2)_{+1} + (a_3b_2)_{-1} + (a_3bc)_0(\text{sym.}) + (a_3bc)_0(\text{antisym.}) \quad (3)$$

These sub-spectra are characterized by the following effective spectral parameters:

$(a_3b_2)_{\pm 1}$  sub-spectra:

$$\begin{aligned} \nu_a &= \nu_A \pm J_{AX}; J_{ab} = J_{AB} \\ \nu_b &= \nu_B \pm N \end{aligned} \quad (4)$$

$(a_3bc)_0$  sub-spectra:

$$\begin{aligned} \nu_a &= \nu_A; J_{ab} = J_{AB} \\ \nu_b &= \nu_B + L; J_{ac} = J_{AB} \\ \nu_c &= \nu_B - L; J_{bc} = J_{BB'} \pm J_{XX'} \end{aligned} \quad (5)$$

where  $N = \frac{1}{2}(J_{BX} + J_{BX'})$  and  $L = \frac{1}{2}(J_{BX} - J_{BX'})$

These effective spectral parameters are identical with the corresponding transformations of the  $ABB'XX'$  system,<sup>21</sup> as expected, since the composite particle method implies identity transformations.

The problem has thus been reduced to solving the general  $A_3B_2$  and  $A_3BC$  systems. In principle, however, the relevant spectral data of these systems can be obtained from the corresponding  $ab_2$  and  $abc$  sub-spectra.

In the composite particle notation the following spin states of the  $A_3B_2$  system contribute:

$$A_3B_2 = QT + 2DT + QS + 2DS \quad (6)$$

The total relative intensities attributable to these four overall spin states are 46, 22, 10, and 2, respectively. The two latter spin states only contribute 12 intensity units at  $\nu_A$ .

The transition frequencies of the general  $a_3b_2$  system that can be obtained in analytical form are given in Table 3.<sup>22</sup> The relevant spectral lines of a given sub-spectrum can then be found by inserting the appropriate expressions for  $\nu_a$ ,  $\nu_b$ , and  $J_{ab}$  from eqn. (4).

All spectral parameters of the  $CH_3-CH_2$ -protons, except  $L$  and  $J_{BB'}$ , can be obtained from the  $(a_3b_2)_{\pm 1}$  sub-spectra by using, for example, eqns. (7) and (8).

$$\nu_A = \frac{1}{2}(a_6^+ + a_6^-); \nu_B = \frac{1}{4}(b_4^+ + b_5^+ + b_4^- + b_5^-) \quad (7)$$

$$J_{AX} = \frac{1}{2}(a_6^+ - a_6^-); N = \frac{1}{4}(b_4^+ + b_5^+ - b_4^- - b_5^-)$$

$$J_{AB} = \frac{2}{3}(a_1^+ - a_6^+ + b_1^+ - \frac{1}{2}b_4^+ - \frac{1}{2}b_5^+) \quad (8)$$

where the superscripts + and - refer to sub-spectra characterized by  $m(XX') = 1$  and -1, respectively.

Table 3. Closed-form transition frequencies for the  $a_3b_2$  spin system.

Line	Origin	Frequency <sup>a</sup>
$a_1$	$QT$	$\frac{1}{2}(\nu_a + \nu_b + \frac{5}{2}J_{ab} + R_-)$
$a_2$	$DT$	$\frac{1}{2}(\nu_a + \nu_b + \frac{3}{2}J_{ab} + S_+)$
$a_3$	$QT$	$\frac{1}{2}(\nu_a + \nu_b - \frac{5}{2}J_{ab} + R_+)$
$a_4$	$DT$	$\nu_b + \frac{1}{2}(S_+ + S_-)$
$a_5$	$DT$	$\frac{1}{2}(\nu_a + \nu_b - \frac{3}{2}J_{ab} + S_-)$
$a_6$	$QS + DS$	$\nu_a$
$b_1$	$QT$	$\frac{1}{2}(\nu_a + \nu_b + \frac{5}{2}J_{ab} - R_-)$
$b_2$	$DT$	$\frac{1}{2}(\nu_a + \nu_b + \frac{3}{2}J_{ab} - S_+)$
$b_3$	$QT$	$\frac{1}{2}(\nu_a + \nu_b - \frac{5}{2}J_{ab} - R_+)$
$b_4$	$DT$	$\nu_b + \frac{1}{2}(S_- - S_+)$
$b_5$	$DT$	$\nu_b - \frac{1}{2}(S_- - S_+)$
$b_6$	$DT$	$\frac{1}{2}(\nu_a + \nu_b - \frac{3}{2}J_{ab} - S_-)$

$$^a R_{\pm} = [(\nu_a - \nu_b \pm \frac{1}{2}J_{ab})^2 + 6J_{ab}^2]^{\frac{1}{2}} \quad S_{\pm} = [(\nu_a - \nu_b \pm \frac{1}{2}J_{ab})^2 + 2J_{ab}^2]^{\frac{1}{2}}$$

The appearance of the  $(a_3b_2)_{\pm 1}$  sub-spectra depends only on  $T$ , where and

$$T = J_{AB}/(\nu_{AB} \pm (J_{AX} - N)) \quad (9)$$

$$\nu_{AB} = \nu_A - \nu_B$$

These sub-spectra have similar appearance in the investigated compounds I–IV since  $|\nu_{AB}| \gg |J_{AX} - N|$ . A fair estimate of  $T$  can be obtained directly from the experimental spectra. It was thus possible to identify most of the transitions of the  $(a_3b_2)_{\pm 1}$  sub-spectra as shown in Fig. 1 for compound I. Subsequent use of eqns. (7) and (8) then yielded the following NMR data for I:

$$\nu_A = 60.0 \text{ Hz}, \nu_B = 106.4 \text{ Hz}, J_{AB} = 7.35 \text{ Hz}, N = 6.70 \text{ Hz}, \text{ and } J_{AX} = 0.$$

The  $b$ -lines used in this calculation have been indicated with arrows in Fig. 1

Closed-form expressions for the transitions of the ABC system and hence  $A_3BC$  system, cannot be obtained, however, since secular matrices of at least third order are involved.

Compounds V and VI can, similarly, be treated as  $A_3BB'XX'P$  systems. The phosphorus-proton coupling constants can be obtained directly from the spectra with reasonable accuracy.

The experimental spectra of the terminal  $-\text{CH}_2\text{R}$  protons in compounds I–VI show that these protons are practically magnetically equivalent. The propyl protons thus constitute an  $A_3B_2X_2$  system quite closely. It is therefore of interest to look at the features of this system. It follows from eqns. (3)–(5) that the strongly coupled  $A_3B_2$  part of the  $A_3B_2X_2$  system consists of four  $a_3b_2$  sub-spectra with  $J_{ab} = J_{AB}$  and the following effective chemical shifts:

$$\nu_a = \nu_A + m(X_2)J_{AX}; \nu_b = \nu_B \pm m(X_2)J_{BX} \quad (10)$$

where  $m(X_2) = \pm 1$  and 0. The  $a_3b_2$  sub-spectrum corresponding to  $m(X_2) = 0$  are doubly degenerate. Closed-form transition frequencies can be obtained

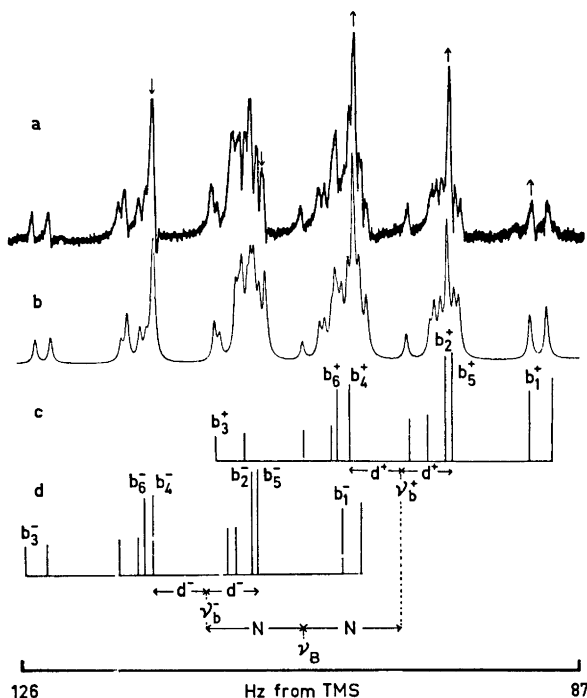


Fig. 1. The BB' region of the 60 MHz spectrum of propyl chloride; a, experimental spectrum; b, computed total spectrum; c, and d, computed stick-plots of the  $a_3b_2$  sub-spectra characterized by  $m(XX') = 1$  and  $-1$ , respectively. The numbering of the lines refers to Table 3 and  $d = \frac{1}{2}(S_+ - S_-)$ .

from Table 3 by inserting the appropriate values of  $\nu_a$ ,  $\nu_b$ , and  $J_{ab}$  from eqn. (10).

The  $\text{CH}_3 - \text{CH}_2$ -region of the propyl spectrum can therefore be reproduced reasonably well as a superposition of three similar  $a_3b_2$  sub-spectra. These sub-spectra contribute a total of 48 intensity units at  $\nu_A$  and account fully for this strong peak.

The final spectral parameters of compounds I–IV obtained from the iterative analyses of the  $A_3BB'CC'$  and  $A_3BB'CC'P$  spin systems are listed in Table 4. The experimental and calculated B spectra of I and VI are shown in Figs. 1 and 2. It is seen that the doublets at the wings of the spectrum in Fig. 1 are further split into quartets in Fig. 2 due to the  $J_{BP}$  coupling.

(b) *Butyl spectra.* Again, rotational averaging simplifies the NMR spectrum to one of the  $A_3BB'CC'DD'$  type. All the experimental spectra were, however, satisfactorily reproduced on the basis of an  $A_3BB'CC'D_2$  spin system. This implies that the terminal  $-\text{CH}_2$  R protons are magnetically equivalent within the accuracy of the experiment.

The secular matrices of this spin system can be considerably reduced by means of a procedure similar to the one used for the propyl spectra. The

Table 4. 60 MHz NMR spectral parameters (Hz) of six propyl derivatives in 25 % v/v methylene chloride solution.

Compound	I	II	III	IV	V <sup>b</sup>	VI <sup>b</sup>
$\nu_A$ <sup>a</sup>	60.02	59.96	58.05	52.58	53.94	55.49
$\nu_B$	106.55	111.10	109.12	90.76	97.99	99.44
$\nu_C$	209.23	202.46	190.12	209.23	237.92	237.24
$\nu_{\alpha\beta}$ <sup>c</sup>	102.68	91.36	81.00	118.47	139.93	137.70
$J_{AB}$	7.34	7.30	7.31	7.39	7.36	7.38
$J_{AC}$	-0.04	-0.04	-0.04	-0.05	-0.03	-0.07
$J_{BB'} - J_{CC'}$	-0.95	-0.90	-1.02	-0.92	-0.99	-0.94
$J_{BC}$	6.60	6.64	6.73	6.59	6.39	6.67
$J_{BC'}$	6.72	6.76	6.90	6.87	6.54	6.48
$J_{BP}$	—	—	—	—	-0.20	-0.71
$J_{CP}$	—	—	—	—	8.60	8.86
Assigned lines	130	148	147	130	205	244
RMS error	0.06	0.06	0.07	0.09	0.09	0.10
Max. prob. error	0.033	0.022	0.044	0.037	0.051	0.038

<sup>a</sup> Chemical shifts downfield from TMS. <sup>b</sup>  $J_{AP}=0$ . <sup>c</sup>  $\nu_{\alpha\beta}=\nu_C-\nu_B$ , i.e., the internal shift difference of protons positioned  $\alpha$  and  $\beta$  to the substituent.

simplest possible spin state, however, comprises an ABB'CC' system and is unamenable to calculation by hand. It is thus necessary to use computer analysis in order to obtain the spectral data. The trial values were obtained either from the experimental spectra or else by a tedious trial-and-error procedure. The refined parameters listed in Table 5 were all obtained from the iterative computations. Figs. 3 and 4 show satisfactory agreement between the experimental and calculated spectra of X.

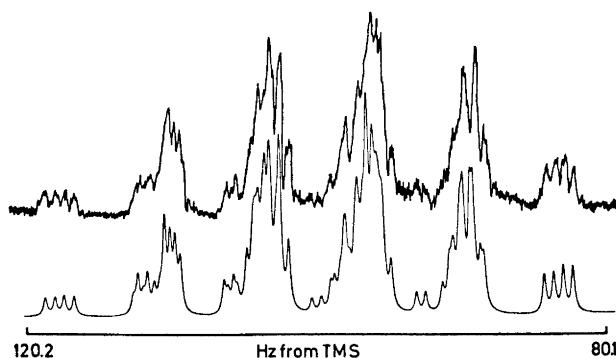


Fig. 2. Experimental (upper trace) and calculated (lower trace) 60 MHz spectrum of the BB' region in tripropyl thiophosphate. Note that the doublets at the wings of the propyl spectrum (Fig. 1) are further split into quartets due to the proton-phosphorus coupling.



Table 5. 60 MHz NMR spectral parameters (in Hz) of neat 1-substituted butanes.

Compound	VII <sup>b</sup>	VIII	IX	X	XI
$\nu_A^a$	50.98	50.20	48.34	50.58	47.57
$\nu_B$	82.80	81.56	77.55	76.30	77.74
$\nu_C$	98.55	102.77	99.05	77.55	83.61
$\nu_D$	203.17	194.82	179.73	152.31	126.94
$\nu_{2\beta}^d$	104.62	92.05	80.68	74.76	43.33
$J_{AB}$	7.34	7.38	7.33	7.39	7.32
$J_{AC}^c$	-0.18	-0.20	-0.14	-0.17	-0.20
$J_{BB'}$	-12.47	-12.54	-12.62	-12.63	-12.74
$J_{BC}$	5.81	5.73	5.77	5.80	5.88
$J_{BC'}$	8.83	8.94	8.93	8.95	9.05
$J_{BD}$	-0.22	-0.23	-0.07	-0.20	-0.11
$J_{CC'}$	-12.53	-12.53	-12.65	-12.67	-12.73
$J_{CD}$	6.71	6.80	6.92	6.79	6.96
Assigned lines	550	446	540	566	399
RMS error	0.09	0.09	0.11	0.09	0.10
Max. prob. error	0.012	0.014	0.013	0.017	0.016

<sup>a</sup> Chemical shifts downfield from TMS. <sup>b</sup> Data from Ref. 13 with corrected shift values.  $J_{AD}=0$ . <sup>d</sup>  $\nu_{2\beta}=\nu_D-\nu_C$ .

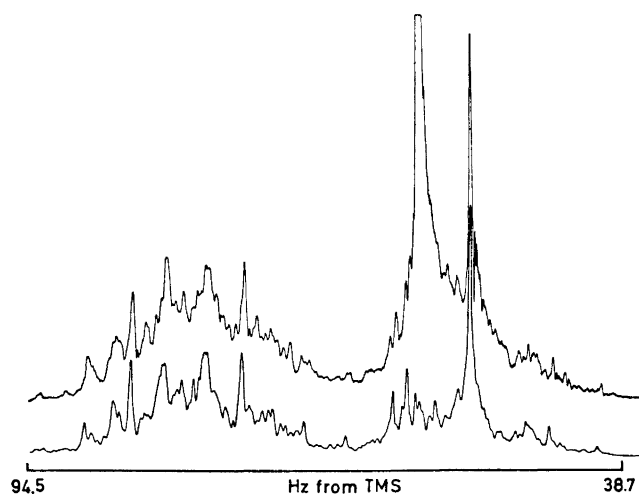


Fig. 3. Experimental (upper trace) and calculated (lower trace) 60 MHz spectrum of the  $A_3BB'CC'$  region in butylamine. The strong peak adjacent to the methyl signal is due to the  $NH_2$  protons.

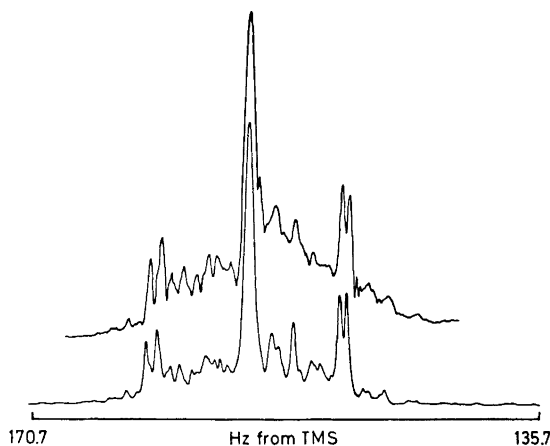


Fig. 4. Experimental (upper trace) and calculated (lower trace) 60 MHz spectrum of the  $D_2$  region in butylamine.

#### DISCUSSION

The calculated rotamer energies of the butyl halides (Table 1) show that, whereas the *anti* form predominates about the  $\text{CH}_3\text{CH}_2-\text{CH}_2\text{CH}_2\text{X}$  bond by 0.7–1.1 kcal/mol, the *gauche* form is preferred about the  $\text{CH}_3\text{CH}_2\text{CH}_2-\text{CH}_2\text{X}$  bond by 0.1–0.3 kcal/mol. When the multiplicity is taken into account it is seen from Table 2 that the (*a*, *g*) rotamer predominates although the (*a*, *a*) conformer has comparable energy for the butyl halides. In contrast, in pentane the all-*anti* conformation abounds. In these molecules the (*a*, *a*) and (*a*, *g*) rotamers contribute as much as 70–77 % of the staggered forms. This clearly shows that an *anti* or zig-zag conformation of the carbon skeleton is preferred. The calculations indicate, however, that the replacement of one methyl group by a halogen atom in pentane introduces extra stability of the (*a*, *g*) conformer at the expense of the (*a*, *a*) and (*g*, *a*) conformers.

The steric energy for the (*g*, *g'*) rotamer in Table 1 is, of course, too high since the rigid rotor model used in the present calculations is found to be inadequate when steric interactions are strong.<sup>14</sup> At any rate, however, the contribution of the (*g*, *g'*) rotamer can be rejected by steric requirements because calculations show that the H-halogen distances would be too short (*ca.* 1.8 Å) to allow the existence of this form without serious distortion of the rest of the molecule.

The present calculations of rotamer distributions deviate, however, considerably from the results obtained from electron diffraction studies of compounds VII<sup>4</sup> and VIII.<sup>2</sup> Surprisingly, in those studies, the (*g*, *g'*) rotamer was found to contribute as much as 24 % for VII<sup>4</sup> while this rotamer was ruled out by steric requirements for VIII.<sup>2</sup> It is difficult to believe, however, that the present evaluations are so much in error since the same model has been found to reproduce experimental barrier heights and rotamer energy differences

satisfactorily for a series of halogenated ethanes and propanes.<sup>6</sup> At any rate, since the present calculations are strongly dependent upon bond angles it is certain that further improvements in the calculated molecular energies will necessitate more accurate bond angles than yet available. In the analysis of the electron diffraction data for VII a *gauche* angle of 60° was assumed.<sup>4</sup> The authors point out, however, that in the analysis of the radial distribution curve for the longer non-bonded interactions some adjustment of the *gauche* angle may be necessary. In accord with the present work, infrared, electron diffraction, microwave, and theoretical studies of halogenated propanes and butanes generally agree in indicating that fluorine, chlorine, and bromine stabilize *gauche* isomers.<sup>1,4,6,11,12,23</sup> Electron diffraction data for VIII<sup>2</sup> suggest, however, that bromine has a negligible stabilization effect on the *gauche* forms, in contrast to experimental results for propyl bromide.<sup>1,6</sup>

The results of Table 1 show that the steric or van der Waals energy is repulsive whereas the electrostatic energy is attractive for the butyl halides. It is seen that the steric repulsion which is considerable in the rotamers possessing *gauche* methyl, is not balanced by the attractive electrostatic interaction in the (*g*, *a*), (*g*, *g*) and (*g*, *g'*) rotamers. The mutual avoidance of the terminal CH<sub>2</sub>X and CH<sub>3</sub> groups is also implied by the large value of the dihedral angle  $\tau$  (68°). The attractive hydrogen-halogen interaction is comparable for VII and VIII but somewhat less for IX. The steric repulsion is, however, about the same for these molecules.

Since the barriers to internal rotation about the C–C single bonds in the propyl and butyl derivatives are low only time-average NMR parameters  $P$  defined by eqn. (20) are measured at room temperature.

$$P = \frac{\sum_i n_i P_i}{\sum_i n_i} \quad (20)$$

where the summation is over all the contributing rotamers.

Let  $J_g$  and  $J_t$  represent the *gauche* and *trans* coupling constants of the –CH<sub>2</sub>–CH<sub>2</sub>– fragment in a perfectly staggered conformation. The observed vicinal coupling constants,  $J$  and  $J'$ , can easily be expressed in terms of  $J_g$  and  $J_t$  by using eqn. (20).<sup>22</sup>

$$\begin{aligned} J &= \frac{1}{2}(1+p)J_g + \frac{1}{2}(1-p)J_t \\ J' &= (1-p)J_g + pJ_t \end{aligned} \quad (21)$$

where  $p$  is the relative population of all contributing conformers possessing an *anti* arrangement of the R–C–C–C or C–C–C–C bonds, as appropriate. Eqn. (21) is based on the assumption that  $J_t$  and  $J_g$  are invariant for a particular ethanic fragment of a given compound. This is, of course, an approximation, in particular since the present compounds are not perfectly staggered ( $\tau > 60^\circ$ ).<sup>10,24</sup> It follows from eqn. (21) that

$$2J + J' = 2J_g + J_t \quad (22)$$

It is possible to calculate  $p$  from eqns. (21) and (22) provided that  $J$ ,  $J'$  and either  $J_g$  or  $J_t$  are known.

It follows from eqn. (21) that  $J = J'$  when  $p = \frac{1}{3}$ . This is the situation when the energy difference  $\Delta E$  between the *anti* form and the two identical *gauche* forms, is zero.

The pair of vicinal coupling constants observed in the  $-\text{CH}_2-\text{CH}_2-\text{R}$  fragment of compounds I–XI have identical or nearly identical values for a particular compound. This indicates that the relevant  $\Delta E$  values are small in agreement with previous observations for propyl chloride and bromide<sup>1</sup> and 1,4-dihalobutanes.<sup>11,12</sup> Our calculations indicate that  $\Delta E = 0.1-0.3$  kcal/mol in gaseous butyl halides while the NMR data imply that  $\Delta E \simeq 0$  in the liquid phase. The small deviation in  $\Delta E$  is reasonable since dipole interactions in the liquid phase would tend to stabilize rotamers having the larger dipole moments, that is, rotamers with a *gauche* substituent.

By inserting  $p = n_0 + 2n_2$  in eqn. (21) the  $J_{\text{BC}}$  and  $J_{\text{BC}'}$  coupling constants corresponding to  $J$  and  $J'$ , respectively, are obtained. From eqn. (22) and the data of Table 5 it follows that the average value of  $2J_g + J_t = 20.44$  Hz for the butyl halides. This value is quite close to the values reported for similar compounds<sup>11,12,22</sup> with the substituents two bonds away from the ethanic fragment. There is considerable experimental evidence for assuming that  $J_t \simeq 11$  Hz,<sup>9-12,22</sup> whence  $J_g \simeq 4.7$  Hz. By inserting these values together with the average values  $J_{\text{BC}} = 5.77$  Hz and  $J_{\text{BC}'} = 8.90$  Hz for the butyl halides (Table 5) it is found that  $p = 0.67$  which is about 0.1 less than the theoretical value for the gas phase. This result is consistent with the previous conclusion that *gauche* forms are enriched in the liquid phase. However, in the symmetrically substituted 1,4-dihalobutanes<sup>11,12</sup> the change of phase was found to have little effect on the *anti-gauche* equilibrium about the central  $\text{C}_2-\text{C}_3$  bond.

The NMR parameters for compounds I–III obtained in this study, deviate considerably from those reported by Cavanaugh and Dailey.<sup>7</sup> Our results are, however, in good agreement with Schrumpfs<sup>8</sup> recent data for the propyl halides. The observed deviations in the chemical shifts can probably be largely ascribed to solvent effects. However, Schrumpf discusses at length certain aspects of the propyl spectrum on basis of the  $\text{X}_3\text{BB}'\text{CC}'$  approximation. This is a very poor approximation and the  $\text{A}_3\text{BB}'\text{XX}'$  system would have been a far better choice. Furthermore, the present work shows that the latter system is easily treated by the sub-spectral method.

The observed chemical shifts for compounds I–XI are generally in keeping with the inductive effect. When the chemical shift differences of the  $-\text{CH}_2-\text{CH}_2\text{R}$  protons were plotted against Huggins<sup>25</sup> values of the electronegativities of the first atom in the substituent, a linear relationship was found to exist for the Cl, Br, I, and OH substituents. The electron withdrawing power of the remaining substituents, however, is apparently not adequately described by the electronegativity of the first atom in the bond. Furthermore, on a quantitative basis, other substituent as well as conformational effects have to be taken into account. Specifically, for the CN group the magnetic anisotropy effect contributes significantly to the screening of the adjacent methylene protons. This effect gives rise to shielding along the  $\text{C}\equiv\text{N}$  bond direction.<sup>26</sup> However, since the shielding attenuates rapidly with the distance from the anisotropic center the  $\alpha$ -protons will experience a larger shielding than the  $\beta$ -proton resulting in a reduced value of  $\nu_{\alpha\beta}$ .

The chemical shift difference of the  $\text{CH}_3-\text{CH}_2-$  protons decreases from propyl to corresponding butyl derivatives in accord with the attenuation of

the inductive effect due to the extra intervening carbon atom.

Although it has not been possible to obtain the individual geminal coupling constants for the propyl compounds the data of Table 4 show that  $J_{CC'}$  is more positive than  $J_{BB'}$ . This observation is in agreement with the following predictions based on MO calculations:<sup>26,27</sup>

(a) Increasing the HCH angle increases the  $s$  character of the orbitals thus resulting in a positive contribution to the coupling.

(b) A substituent which withdraws electrons from the  $\sigma$  bond by the inductive effect will give a positive contribution to the coupling and vice-versa.

Strongly electronegative substituents will affect the hybridization of the adjacent carbon atom by preferring to make use of carbon  $p$  character. This results in an increase in the  $s$  character of the remaining bonds and the geminal coupling constant will get a positive contribution [(a) above]. A similar substituent effect on the geminal coupling constants has also been observed in 1,4-dichlorobutane.<sup>12</sup> In the butyl compounds, however, the measured geminal coupling constants have nearly the same values and are little affected by the substituent due to the extra intervening carbon atom.

The observed decrease in the  $-\text{CH}_2-\text{CH}_2-\text{R}$  vicinal coupling constants with increasing electronegativity of the substituent is also in agreement with valence bond calculations which predict that:<sup>27,28</sup>

(a) electronegative substituents decrease the vicinal coupling and

(b) increase of the HCC bond angles decreases the vicinal coupling.

Electronegative substituents might be expected to increase the HCC bond angle by altering the hybridization as mentioned above.

The vicinal coupling constants of the  $\text{CH}_3-\text{CH}_2$ -fragment are virtually identical in the studied compounds. The present results can therefore hardly be taken as support for the idea that strongly electronegative substituents increase vicinal coupling in  $\text{H}-\text{C}-\text{C}-\text{H}$  fragments separated by an odd number of bonds.<sup>8,29</sup>

The values of  $J_{BC}$  and  $J_{BC'}$  in the butyl compounds are determined by conformational rather than substituent effects.

The relatively small magnitude of the long-range coupling constants (0–0.23 Hz) is due to rotational averaging. Motionally averaged four-bond coupling constants of comparable magnitude and either sign, have been measured in saturated aliphatic and cyclic compounds.<sup>30</sup> However, no unambiguous substituent trends are discernible from the present data. At any rate, due to conformational effects it would be hazardous to ascribe small changes in the long-range coupling constants to definite substituent effects.

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