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Nuclear Magnetic Resonance Studies on Butane

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The NMR spectra of butane obtained at 27°C, −40°C, and −72°C have been fully analyzed by means of the computer program UEAITR. The rapidly interconverting molecule constitutes an $A_3BB'B''B'''A_3'$ spin system. This spin system has been treated theoretically by the composite particle technique. Analytical expressions have been obtained for two relatively strong A and B "doublets" of the QDDDDQ(s) and DDDDDD(s) sub-systems. From the corresponding experimental transitions in the 100 MHz spectrum we obtained the mean values $J_{AB}+J_{AB'}=7.15$ Hz and $\nu_{BA}=40.5$ Hz in satisfactory agreement with the iterated parameters.

The energy difference between the *anti* and *gauche* conformers, ΔE, has been calculated from measurements at three different temperatures. The estimated value is $\Delta E=840\pm200$ cal mol^{-1}. Using this value of ΔE the true coupling constants involved in the $-CH_2-CH_2-$ moiety of the fixed conformers, have been obtained from the measurements at 27°C and −72°C; $J_t^A=11.31$ Hz, $J_g^A=4.77$ Hz, $J_g^G=2.69$ Hz, and $J_g^{G'}+J_t^G=15.37$ Hz.

Various spectroscopy techniques have been applied in the attempt to determine energy differences between rotational isomers [1–6] of butane. From infrared and Raman spectroscopy [1] it has been concluded that liquid butane exists in two rotational isomers, one *anti* and two *gauche* forms. The energy difference, ΔE, between the *anti* and *gauche* forms (Fig. 1) is reported to be about 800 cal mol^{-1}, with the *anti* form the more stable isomer.

In a previous paper [7] we reported studies on the NMR spectrum of butane at one temperature. We have now extended this work to determine the spectral parameters at two additional temperatures. A refined analysis of the 60 MHz spectrum at 27°C is also reported. Iterative calculations have been performed on the spectra obtained at 27°C, −40°C, and − 72°C, using the iterative computer program UEAITR.[8] Analysis of the spectra of butane obtained at three different temperatures enables us to calculate ΔE as well as the true *trans* and *gauche* coupling constants of the $-CH_2-CH_2-$ moiety.

EXPERIMENTAL

The synthesis of butane and the subsequent preparation of the NMR sample, have been described in a previous paper.[7]

The 100 MHz spectra were run at ambient probe temperature (*ca.* 30°C) on a VARIAN HA-100 spectrometer. The 60 MHz spectra were recorded at 27°C, −40°C, and −72°C on a JEOL-C-60H spectrometer. The probe temperature was regulated to within 1°C using a nitrogen gas flow technique. The spectra used in the calculations were run at about 50 Hz sweep width and calibrated every 5 Hz using a frequency counter. Line positions were obtained by averaging the results of 4 scans at each temperature.

Computations were performed on an IBM/50 H computer using the UEANMR2 [9] and UEAITR [8] programs. Line-shape and "stick" plots were obtained by means of the computer program KOMBIP.[10] The iterative analyses were only carried out on the 60 MHz spectra.

The graphical output was obtained using a Calcomp Plotter.

THEORETICAL

Liquid butane exists in two different isomers, one *anti* form (I) of C_{2h} symmetry and two optically active *gauche* forms (II and III) of C_2 symmetry (Fig. 1).

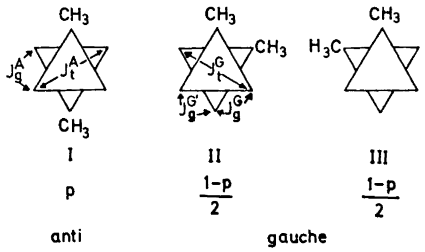


Fig. 1. The rotational isomers of butane and their relative weights.

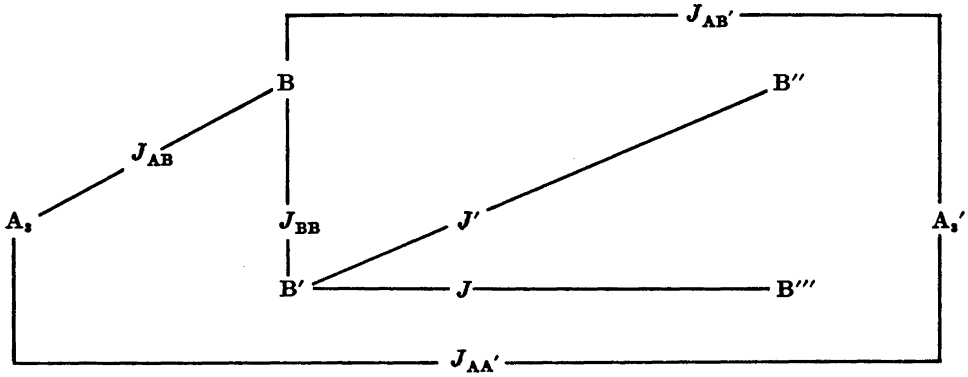
On the assumption that the three rotamers have the same partition function, it follows that the relative weight, p, of the *anti* form is given by: [11]

$$p = \frac{1}{1 + 2\exp(-\Delta E/RT)} \tag{1}$$

where ΔE, the energy difference between the *gauche* and *anti* forms, is positive if the *anti* form is the more stable.

It has been shown previously [7] that the NMR spectrum of the rapidly interconverting molecule constitutes an $A_3BB'B''B'''A_3'$ spin system or equivalently an $[A_3[B]_2]_2$ spin system in the notation due to Haigh.[12]

It is appropriate at this stage to comment on the spectral parameters involved in the $A_3BB'B''B'''A_3'$ spin system. ν_A and ν_B represent the chemical shift of the methyl and methylene protons, respectively. There are six coupling constants that affect the spectrum. These are indicated in the diagram below.



When $\Delta E \neq 0$ the *gauche* (J_g) and *trans* (J_t) coupling constants between the methylene protons will assume different average values J and J', respectively, in the interconverting molecule. It is often assumed that there is only one value of J_g and one of J_t for a given molecule.[13] This is, however, only an approximation. It can be seen from Fig. 1 that, theoretically, there may be three different values for J_g, one for the *anti* form, J_g^A, and two for the *gauche* forms, J_g^G and $J_g^{G'}$, as indicated. Similarly, there are two values of J_t, distinguished as J_t^A and J_t^G. There are, however, only four experimentally independent coupling constants since $J_g^{G'}$ and J_t^G only occur in the relevant equations as their sum $J_g^{G'} + J_t^G = Q$.

The analysis gives the average values, J and J', which can easily be expressed in terms of the *gauche* and *trans* coupling constants of the individual rotamers (Fig. 1).

$$J = p\, J_g^A + \frac{1-p}{2} Q \tag{2}$$

$$J' = p\, J_t^A + (1-p) J_g^G \tag{3}$$

If ΔE is known, the four coupling constants are readily obtained from measurements at two temperatures, since from eqns. (2) and (3)[13]

$$J_g^G = J' - \frac{p}{\Delta p} \Delta J' \tag{4}$$

$$J_t^A = J' + \frac{1-p}{\Delta p} \Delta J' \tag{5}$$

$$J_g^A = J + \frac{1-p}{\Delta p} \Delta J \tag{6}$$

$$\frac{Q}{2} = J - \frac{p}{\Delta p} \Delta J \tag{7}$$

where ΔJ, for example, denotes the change in J resulting from a change Δp in the number of molecules in the *anti* form.

If temperature measurements over two temperature ranges 1 and 2 (three temperatures) have been performed, ΔE may be obtained using the equation:

$$2\frac{\Delta_1 p}{\Delta_2 p} = \frac{\Delta_1 J}{\Delta_2 J} + \frac{\Delta_1 J'}{\Delta_2 J'} \tag{8}$$

This expression is not explicit for ΔE, but the latter may be obtained by a trial-and-error method using eqns. (1) and (8).

The $A_3BB'B''B'''A_3'$ spin system can be analyzed by the composite particle technique.[14,15] There are four overall spin states, namely: QDDDDQ, DDDDDQ, QDDDDD, and DDDDDD with statistical weights 1, 2, 2, and 4, respectively, that is

$$A_3BB'B''B'''A_3' = QDDDDQ + 2DDDDDQ + 2QDDDDD + 4DDDDDD$$

The composite particles are referred to in the order A_3, B, B', B'', B''', A_3'. The total relative intensities (normalized to $n \times 2^{n-1}$ for an n-spin system) attributable to the four spin states QDDDDQ, DDDDDQ, QDDDDD, and DDDDDD are 1792, 1280, 1280, and 768, respectively. The pair of spin states DDDDDQ and QDDDDD are degenerate and cannot mix. In principle, it is possible to obtain all the spectral parameters from the DDDDDD sub-spectrum.

The secular matrices of the QDDDDQ and DDDDDD sub-spectra can be reduced by considering additional symmetry not included in the particle notation. By classifying the wave functions according to the symmetry species A_1, A_2, B_1 and B_2 of the C_{2v} point group, the secular matrices of the QDDDDQ and DDDDDD sub-system can be considerably reduced, *viz.*

$$QDDDDQ = \sum_i QDDDDQ(\Gamma_i)$$

$$DDDDDD = \sum_i DDDDDD(\Gamma_i)$$

where Γ_i denotes the four species A_1, A_2, B_1 and B_2.

The QDDDDQ(A_1) and DDDDDD(A_1) sub-systems. The Hamiltonians of the QDDDDQ (A_1) and DDDDDD(A_1) sub-systems are thus factorized into energy level diagrams with groupings (1 : 2 : 7 : 10 : 16 : 16 : 16 : 10 : 7 : 2 : 1) and (1 : 2 : 6 : 6 : 6 : 2 : 1), respectively.

It is convenient to define a magnetic quantum number $m_T = \sum_i m_i$ where the summation is over the six composite particle states. The spin state $Q^{\frac{1}{2}}D^{\frac{1}{2}}D^{\frac{1}{2}}D^{\frac{1}{2}}D^{\frac{1}{2}}Q^{\frac{1}{2}}$ has, for example, $m_T = 4$. Closed form expressions can easily be obtained for the energy levels corresponding to $m_T = \pm 4$ and ± 2 for the QDDDDQ(A_1) and DDDDDD(A_1) sub-systems, respectively, since this only involves solving secular equations of second order. The frequencies of the 4 transitions $m_T = 4 \rightarrow 5$ and $m_T = -5 \rightarrow -4$ for the QDDDDQ(A_1) sub-spectrum are then readily obtained on analytical form. The 4 transitions $m_T = 2 \rightarrow 3$ and $m_T = -3 \rightarrow -2$ for the DDDDDD(A_1) sub-spectrum are similarly obtained on analytical form.

The following expressions have been obtained for the 4 transitions of the QDDDDQ(A_1) and DDDDDD(A_1) sub-spectra.

A transitions:

$$\nu_{\pm}(\mathrm{A}) = \tfrac{1}{2}[\nu_{\mathrm{A}} + \nu_{\mathrm{B}} \pm (\mathrm{m_i} + 1)N - R_{\pm}{}^{\mathrm{m_i}}] \tag{9}$$

B transitions:

$$\nu_{\pm}(\mathrm{B}) = \tfrac{1}{2}[\nu_{\mathrm{A}} + \nu_{\mathrm{B}} \pm (\mathrm{m_i} + 1)N + R_{\pm}{}^{\mathrm{m_i}}] \tag{10}$$

where

$$R_{\pm}{}^{\mathrm{m_i}} = \tfrac{1}{2}[(\tfrac{1}{2}N \pm \nu_{\mathrm{BA}})^2 + 4\mathrm{m_i}N^2]^{\frac{1}{2}};(R_{+}{}^{\mathrm{m_i}})^2 - (R_{-}{}^{\mathrm{m_i}})^2 = 2N\nu_{\mathrm{BA}} \tag{11}$$

$$N = J_{\mathrm{AB}} + J_{\mathrm{AB}'},\ \nu_{\mathrm{BA}} = \nu_{\mathrm{B}} - \nu_{\mathrm{A}} \tag{12}$$

and $\mathrm{m_i} = \frac{3}{2}$ and $\frac{1}{2}$ for the QDDDDQ(s) and DDDDDD(s) sub-systems, respectively.

It follows from eqns. (9) and (10) that the $R_{\pm}{}^{\mathrm{m_i}}$s are given as the separation between corresponding A and B transitions, *viz.*

$$R_{\pm} = \nu_{\pm}(\mathrm{B}) - \nu_{\pm}(\mathrm{A}) \tag{13}$$

The separations $S_{\mathrm{A}}{}^{\mathrm{m_i}}$ and $S_{\mathrm{B}}{}^{\mathrm{m_i}}$ between the A doublets and B doublets, respectively, follow from eqns. (9) and (10).

$$S_{\mathrm{A}}{}^{\mathrm{m_i}} = \nu_{+}(\mathrm{A}) - \nu_{-}(\mathrm{A}) = (\mathrm{m_i} + 1)N - \tfrac{1}{2}(R_{+} - R_{-}) \tag{14}$$

$$S_{\mathrm{B}}{}^{\mathrm{m_i}} = \nu_{+}(\mathrm{B}) - \nu_{-}(\mathrm{B}) = (\mathrm{m_i} + 1)\mathrm{N} + \tfrac{1}{2}(R_{+} - R_{-}) \tag{15}$$

In order to find the frequencies of the transitions $\mathrm{m_T} = \pm 3 \rightarrow \pm 4$ and $\mathrm{m_T} = \pm 1 \rightarrow \pm 2$ for the A_2, B_1 and B_2 symmetry species of the QDDDDQ(Γ_i) and DDDDDD(Γ_i) sub-systems, respectively, it would be necessary to diagonalize 2×2, 3×3 and 4×4 matrices.

DISCUSSION

The 4 transition frequencies $\nu_{\pm}(\mathrm{A})$ and $\nu_{\pm}(\mathrm{B})$ for the DDDDDD(s) sub-system account for 48 intensity units. With the aid of the estimated intensities and eqns. (13)–(15), the 4 transitions may be picked out of the experimental spectrum quite easily (Fig. 2). The super-position of the other sub-spectra, however, introduces some inaccuracy in the experimental transitions. From these 4 experimental transitions in the 100 MHz spectrum, it follows that $R_{+}{}^{\frac{1}{2}} = 45.5$ Hz, $R_{-}{}^{\frac{1}{2}} = 38.4$ Hz, $\mathrm{N} = 7.1$ Hz, and $\nu_{\mathrm{BA}} = 40.6$ Hz.

The corresponding 4 A and B transitions of the QDDDDQ(s) sub-system account for only 20 intensity units and are not as easy to discern. However, using the information obtained from the DDDDDD(s) sub-system, the relevant transitions have been found (Fig. 2). One obtains $N = 7.2$ Hz and $\nu_{\mathrm{BA}} = 40.4$ Hz in good agreement with the results from the DDDDDD(s) sub-system. Using this information, satisfactory trial spectra at 60 MHz were easily obtained at the three measured temperatures by varying J and J' and putting

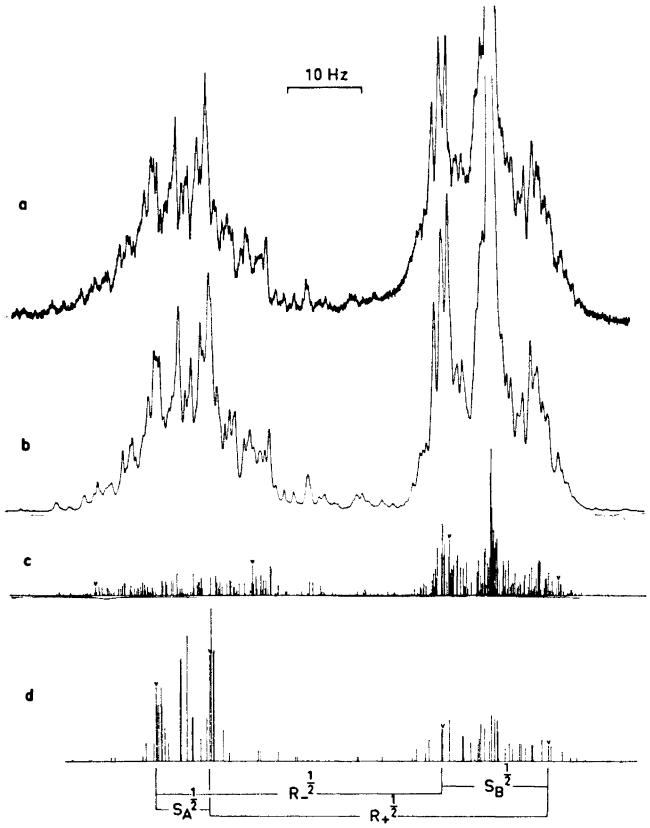


Fig. 2. The 100 MHz spectrum of butane at 30°C; a, experimental spectrum; b, computed total spectrum; c, computed composite QDDDDQ sub-spectrum; d, computed composite DDDDDD sub-spectrum. The spectra b – d are based on the 60 MHz parameters in Table 1. The A and B doublets are indicated in the two sub-spectra.

$J_{AB'} = J_{AA'} = 0$. The final NMR parameters, listed in Table 1, were obtained by iteration on about 600 transitions at each temperature. The root-mean-square deviations for the experimental and calculated transitions were 0.1 Hz or less. The calculated probable errors were 0.01 Hz or less.

The agreement between the experimental and computed spectra in Figs. (2) and (3) is very good. The excellent fit between the experimental 100 MHz

Table 1. Spectral parameters (in Hz) measured at 60 MHz of neat butane.

Temp. °C	ν_{BA}	J'	J	J_{AB}	$J_{AB'}$	J_{BB}
27	24.19	8.48	5.73	7.30	−0.20	−12.36
−40	23.55	9.25	5.51	7.46	−0.25	−12 85
−72	23.03	9.62	5.34	7.41	−0.18	−12.53

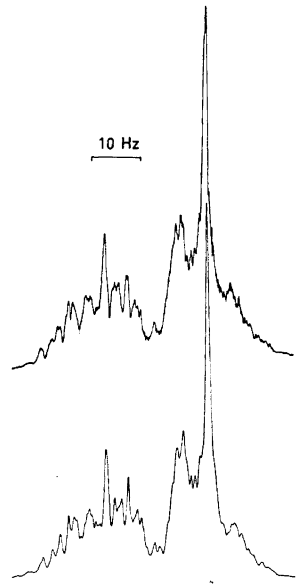


Fig. 3. Experimental (upper part) and computed (lower part) 60 MHz spectra of butane at −40°C.

spectrum and the calculated spectrum based on the 60 MHz parameters is noteworthy. It can be concluded from the 60 MHz spectra at −72°C (not shown) that the internal C−C rotations are rapid, in relation to the NMR time scale, even at this low temperature.

The value of ΔE can now be calculated using eqns. (1) and (8) and the experimental values of J and J' at the 3 measured temperatures. One obtains $\Delta E = 840 \pm 200$ cal mol^{-1}. The magnitude of ΔE obtained by the NMR method is close to the values reported by several workers.[1–6] Due to the possible cumulative effect of experimental errors in eqn. (8) the uncertainty in ΔE is considerable.

It follows from eqn. (1) that $p = 0.67$, 0.75, and 0.80 at 27°C, −40°C, and −72°C, respectively. Furthermore, from eqns. (4)−(7) we obtain $J_g^G = 2.69$ Hz, $J_g^A = 4.77$ Hz, $J_t^A = 11.31$ Hz, and $Q/2 = 7.68$ Hz. The simple treatment based on the assumption of only one set of *gauche* and *trans* coupling constants for the given molecule yields the substantially different values $J_t = 10.26$ Hz and $J_g = 4.84$ Hz.

The C−C−C−C dihedral angle is about 70° for the *gauche* isomers of butane, 1,4-dibromobutane [15] and 1,4-dichlorobutane.[16] The energy differences between *anti* and *gauche* conformations about the central C−C bond are also similar for these compounds.[15,16] This may explain why the vicinal coupling constants, J and J', have quite close values in butane, 1,4-dibromobutane [15] and 1,4-dichlorobutane.[16] The effect of the bromine and chlorine substituents on J and J' is expected to be negligible.

Valence bond calculations [17,18] predict that the vicinal coupling constants are dependent on the H−C−C−H dihedral angle θ. Use of the $\cos^2\theta$ rela-

tion [17,18] indicates that the difference in J_{vic} for $\theta = 60°$ and $\theta = 70°$ is about 1.8 Hz. The difference between J_g^A and J_g^G, about 2.1 Hz, agrees reasonable well with the relevant H–C–C–H dihedral angles assumed for *anti* and *gauche* butanes, [4,15,16] 60° and 70°, respectively. The existence of different magnitudes of the various gauche coupling constants in substituted ethanes is reported.[13] For the corresponding coupling constants in cyclohexanes where the dihedral angles are close to 60° and where the substituents at the $-CH_2-CH_2-$ moiety are similar to those in butane, are the following values reported: $J_t = J_{aa} = 12.4$ Hz and $J_g = J_{ae} = 4.25$ Hz [4] or $J_{aa} = 11.0$ Hz and $J_{ae} = 4.5$ Hz.[19] This agrees quite well with J_t^A and J_g^A obtained for butane and indicates that the relative orientation of the substituents at the $-CH_2-CH_2-$ moiety has a negligible effect on the coupling constants within that moiety. For 1,3-dioxanes,[20] the general trend in the coupling constants is $J_t = J_{aa} = 11.2$ Hz and $J_g = J_{5a4e} = 4.8$ Hz or $J_{4a5e} = 3.3$ Hz. The variation in J_g is partly due to dihedral angles less than 60° and partly to a stereospecific effect of the ring oxygen, as the oxygen is in different positions in the two coupling paths.

All coupling constants obtained for butane are within the expected ranges. The chemical shift difference $\nu_{B,A}$ is slightly temperature dependent. This is expected from the assumption that the chemical shifts are different for the *anti* butane as compared to the *gauche* butane.

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