

## The Nuclear Magnetic Resonance Spectrum of Butane

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The application of infra-red and Raman spectroscopy to the determination of the energy differences between the rotational isomers of butane has been reported.<sup>1</sup> It was concluded from Raman spectroscopy<sup>1</sup> that liquid butane exists in two different rotational isomers, one anti form (I) of  $C_{2h}$  symmetry and two optically active gauche forms (II and III) of  $C_2$  symmetry (see Fig. 1). The energy difference between the two different isomers is about 770 cal/mol.

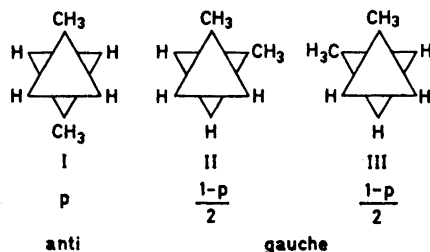


Fig. 1. The rotational isomers of butane and their relative weights.

As butane is the simplest hydrocarbon of which rotational isomers occur, it is of interest to study the NMR spectrum of this molecule. This paper reports the analysis of the 60 and 100 MHz NMR spectra of liquid butane at 27°C.

The analysis of the proton spectrum of butane is very challenging owing to the large number of strongly coupled nuclei. The most reasonable approach is to apply the composite particle technique.

The appearance of the NMR spectrum gives information about the isomers as the spin system is dependent on the relative weight of the isomers and the rate of rotation about the single C—C bonds. Butane constitutes an  $[A_3[B]_2]_1$  spin system if rapid rotation occurs about the single C—C bonds. Slow rotation about the central C—C bond, however, results

in two different spin systems,  $[A_3[B]_2]_1$  and  $[ABC_2]_1$  for the anti and gauche isomers, respectively. We have assumed that the methyl groups always rotate rapidly. No NMR spectrum of liquid hydrocarbons indicating slow rotation at room temperature, has, to the authors knowledge, been observed as yet. The low energy barrier between the isomers of butane also suggests rapid rotations about all the C—C bonds. There is no evidence in the spectrum of butane that any isomer is sufficiently long-lived to give its own NMR spectrum. It is therefore concluded that the NMR spectrum can be analyzed on the basis of an  $[A_3[B]_2]_1$  spin system. The theoretical spectrum was analyzed applying the composite particle technique and the computer program UEA NMR2.<sup>2</sup> The following spin states are possible:

QDDDDQ  
DDDDQ QDDDD  
DDDDDD

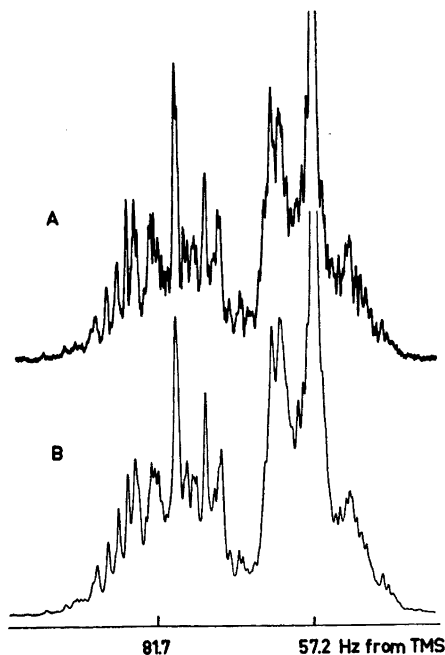


Fig. 2. 60 MHz spectrum of butane; A, observed; B, computed with the parameters of Table 1 (with 0.5 Hz half-width).

The excellent fit between the experimental and calculated spectra in Fig. 2 confirms the correctness of the spectral parameters listed in Table 1. Furthermore, the 100 MHz spectrum calculated on the basis of the same parameters also displayed the same excellent agreement with the experimental spectrum. These spectral parameters are quite close to the corresponding parameters of propane,<sup>4-6</sup> as expected.

Table 1. Coupling constants and the chemical shift difference in Hz, obtained at 60 MHz.

$\nu_{\text{CH}_2} - \nu_{\text{CH}_3}$	$J'$	$J$	$^3J_{\text{CH}_2, \text{CH}_3}$	$^4J_{\text{CH}_2, \text{CH}_3}$
24.5	8.6	5.7	7.4	-0.2

When rapid internal rotation is occurring, the *trans* and *gauche* coupling constants of the methylene hydrogens assume average values  $J'$  and  $J$ , respectively, of the corresponding parameters  $J_T$  and  $J_G$  in the fixed isomeric states. The analysis gives the average values  $J'$  and  $J$  which can easily be expressed in terms of  $J_T$  and  $J_G$  (see Fig. 1):

$$J' = pJ_T + (1-p)J_G$$

and

$$J = pJ_G + \frac{1}{2}(1-p)(J_T + J_G)$$

where  $p$  is the relative weight of the anti isomer I.

On the assumption of a Boltzmann distribution of the isomers, and an energy difference of 770 cal/mol, we obtain  $p = 0.644$  at 27°C. Using this value of  $p$  it follows from the two equations above that  $J_T = 11.2$  and  $J_G = 4.5$  Hz. These values are quite close to the corresponding values reported for a cyclohexane derivative, ( $J_T = J_{aa} = 12.4$  Hz and  $J_G = J_{ac} = 4.25$  Hz), dioxanes<sup>8</sup> ( $J_T = J_{4a,5a} = 10.1$  Hz, and  $J_G = J_{5a,4e} = 4.8$  Hz or  $J_{4a,5e} = 3.3$  Hz) and 1-chloro-2-bromoethane<sup>9</sup> where  $J_T + 2J_G = 20.6$  Hz.

We have observed that the NMR spectrum of butane changes with the temperature in a manner expected for rapid rotation. The results of this study support the previous conclusion that butane exists as two different isomers. The calculated *trans* and *gauche* coupling

constants also indicate that 770 cal/mol is a reasonable value for the energy difference between the isomers. It is also concluded that the internal rotation is rapid in relation to the NMR time scale.

A refined analysis of the 60 and 100 MHz spectra of butane using the iterative computer program UEAITER,<sup>10</sup> is at present being carried out in this laboratory. Temperature studies of the 60 MHz NMR spectrum is also being undertaken by observing the effect of temperature changes on the spectral parameters, in order to obtain more information about the rotational isomers and the energy differences.

*Experimental.* The butane was synthesized from butyl iodide according to the conventional Grignard method. The butane was trapped and collected at -65°C. The NMR spectrum was taken as evidence of purity.

The butane was introduced into a 5 mm O.D. sample tube and small quantities of benzene and TMS were added to serve as NMR locking and reference substances, respectively. The tube was sealed under vacuum while at low temperature.

The 60 and 100 MHz spectra were recorded on JEOL-C-60H and VARIAN HA-100 spectrometers, respectively. The spectra used in the calculation were recorded at 50 Hz sweep width and calibrated every 5 Hz, using a frequency-counter accurate to  $\pm 0.1$  Hz. Computation was performed on an IBM 360/50H computer using the UEA NMR2 and UEAITR programs. The graphical output was obtained on a Calcomp Plotter.

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## An Extension of the "Uniformly Charged Sphere Approximation" to $\pi$ -Electron Calculations for Twisted Conjugated Systems

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In 1952 Parr<sup>1</sup> introduced a simple formula for evaluating two-electron two-center Coulomb integrals for use in LCAO-MO calculations involving planar  $\pi$ -electron systems:

$$(pp|qq) = (14.395/r) \left( \frac{1}{2} + \frac{1}{2} [1 + (d/r)^2]^{-\frac{1}{2}} \right) \text{eV} \quad (1)$$

Here  $r$  is the distance between the atoms  $p$  and  $q$ , and  $d$  is the diameter of two uniformly charged tangent spheres defined for each type of atom. In cases where

atoms  $p$  and  $q$  are different, eqn. (1) becomes slightly more complicated.

As eqn. (1) shows, the integral values are expressed as the repulsion energy between pairs of point charges at the sphere centers. This method has been widely used because of its simplicity and good agreement with integral values obtained theoretically from Slater orbitals.

We will here report an extension of the method for applications to twisted molecules. Let us assume the molecule to have a general formula  $R_1-R_2$ .  $R_1$  and  $R_2$  may be twisted an angle  $\phi$  relative to each other. A coordinate system is introduced with the  $z$  axis along the  $R_1-R_2$  bond, and the  $xz$  plane in the molecular plane when  $\phi=0$ .

Each integral is expressed as a sum of four inverse distances (between sphere centers), multiplied by a conversion factor, as in the planar case.<sup>1</sup> One of these distances will be given by the following expression when one atom from each of the groups  $R_1$  and  $R_2$  is involved:

$$r_1 = [(x_1 - x_2 \cos \phi \pm \frac{1}{2}d_2 \sin \phi)^2 + (\frac{1}{2}d_1 \pm x_2 \sin \phi \pm \frac{1}{2}d_2 \cos \phi)^2 + (z_1 - z_2)^2]^{\frac{1}{2}} \quad (2)$$

The atomic centers involved are labelled by the indices 1 and 2. Sphere diameters are denoted  $d_1$  and  $d_2$ . The  $x$  and  $z$  coordinates are atomic coordinates for the case  $\phi=0$ .

To obtain each separate  $r_1$  value, the three symbols  $\pm$  in (2) have to be substituted in the same order from left to right by either

$$\begin{array}{l} (1) \quad + + + \\ \text{or } (2) \quad + - - \\ \text{or } (3) \quad - + - \\ \text{or } (4) \quad - - + \end{array}$$

*Table 1.* Comparison between theoretical and approximate values of some selected two-electron integrals. All values in eV.

Molecule	Integral	Method	Angle of rotation				
			0°	30°	60°	90°	120°
3,3'-Bithienyl	(2 2/6 6)	Theoretical Eqn. (3)	5.37	5.38	5.42	5.44	5.42
			5.37	5.38	5.41	5.43	5.41
2-Fluorobiphenyl (13 13/8 8)		Theoretical Eqn. (3)	5.42	5.25	4.70	4.11	3.67
			5.42	5.24	4.74	4.15	3.69
	(13 13/7 7)	Theoretical Eqn. (3)	4.88	4.94	5.04	5.10	5.04
			4.88	4.96	5.12	5.20	5.12