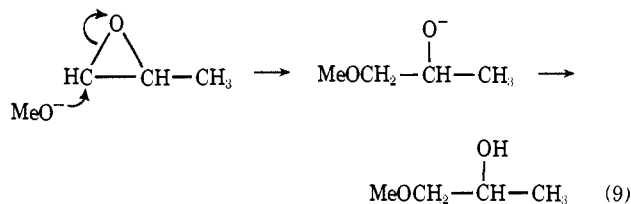
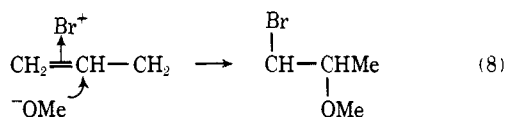


probably undergo rapid interconversion. Since the edge-protonated isomers differ little in energy, unlike the  $\pi$  complexes (Chart I), the fact that addition follows Markovnikov's rule must imply either that the  $\pi$  complex reacts more readily with nucleophiles or that one of the edge-protonated forms reacts more readily than the others.

While we have not yet calculated reaction paths for attack by nucleophiles on these ions, the calculated charge distributions in the edge-protonated dimethylcyclopropanes (Chart II, d and e) would certainly lead one to expect d to react more easily, the positive charges on the carbon atoms in the C-H-C unit being smaller in d than in e. One must therefore find some reason why the  $\pi$  complex should react more readily with nucleophiles than does an edge-protonated isomer.

One of the curious aspects of electrophilic addition to olefins is the orientation of the secondary attack by nucleophiles (10  $\rightarrow$  11). This is directly opposite to the orientation observed in the ring opening of epoxides or azirines by nucleophiles. Thus, nucleophiles attack the propene-Br<sup>+</sup>  $\pi$  complex at the substituted carbon while they attack propene oxide at the unsubstituted carbon; e.g.



This was attributed<sup>17</sup> to the relative planarity of the basal ethylene unit in the  $\pi$  complex, the approach of the reagent being normal to this plane and so relatively unhindered by methyl, whereas the opening of the ring in eq 9 is a typical S<sub>N</sub>2 process and so subject to steric hindrance ("F strain") by  $\alpha$ -methyl groups.

Our calculations (Table VI) support this intuition, the terminal groups in the ethylene units being bent out of the plane by only 17°. Now the three-center C-H-C bond in the edge-protonated cyclopropanes should behave as normal covalent bonds so far as the terminal carbon atoms are concerned; the attack by a nucleophile on such a system should therefore be analogous to a normal S<sub>N</sub>2 reaction and subject to hindrance by  $\alpha$ -methyl groups. While such hindrance should be less at the unsubstituted carbon atoms in the ions of Chart II (b-d), these atoms are predicted to carry only small positive charges. It is therefore not unreasonable to expect nucleophiles to react preferentially with the intermediate protonated cyclopropanes in their  $\pi$ -complex tautomeric forms.

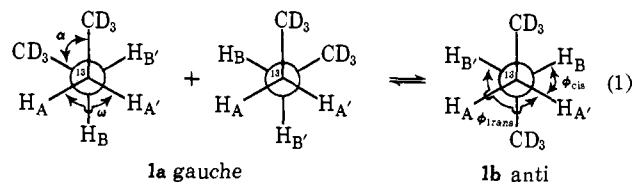
## The Conformational Analysis of *n*-Butane<sup>1</sup>

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Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. Received September 7, 1971

**Abstract:** The conformational analysis of 1,1,1,4,4,4-butane-*d*<sub>6</sub> (1) has been accomplished utilizing the temperature dependences of three nuclear magnetic resonance spectral parameters. The observed temperature dependences of the sum and the difference of the two vicinal spin-spin coupling constants and the chemical shift of the four equivalent methylene protons were correlated with the gauche  $\rightleftharpoons$  anti conformational equilibrium of 1. The enthalpy difference for this equilibrium was found to be  $-681 \pm 35$  cal/mol at  $\Delta S = -1.376$  eu. The CD<sub>3</sub>CCCD<sub>3</sub> dihedral angle in the gauche conformer was calculated to be  $66 \pm 1^\circ$ .

The simplest hydrocarbon capable of exhibiting gauche  $\rightleftharpoons$  anti conformational isomerism (eq 1)



is *n*-butane and as such it reflects the importance of nonbonded repulsive interactions that contribute to the relative stability of molecular conformers. This

(1) Presented in part by E. W. G. at the 159th National Meeting of the American Chemical Society, Feb 1969, Houston, Tex.

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system has been the subject of a rather large number of theoretical calculations directed at accurately determining the correct form of the potential function for internal rotation about the central C-C bond and semi-empirically estimating the conformational geometry and energy of the molecule.<sup>3</sup> In contrast, reports of direct experimental measurements regarding conformation and the barrier to internal rotation are somewhat meager.<sup>4</sup> The energy difference between the gauche

(3) (a) J. R. Hoyland, *J. Chem. Phys.*, **49**, 2563 (1968); (b) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7036 (1967); (c) P. Geneste and G. Lamaty, *Bull. Soc. Chim. Fr.*, 4456 (1967); (d) R. A. Scott and H. Scheraga, *J. Chem. Phys.*, **44**, 3054 (1966); (e) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 631 (1966); (f) A. Opschor, *Makromol. Chem.*, **85**, 249 (1965); (g) N. P. Borisova and M. V. Volkenstein, *Zh. Strukt. Khim.*, **2**, 469 (1961).

(4) (a) G. J. Szasz, N. Sheppard, and D. H. Rank, *J. Chem. Phys.*, **16**, 1704 (1948); (b) N. Sheppard and G. J. Szasz, *ibid.*, **17**, 86 (1949); (c)

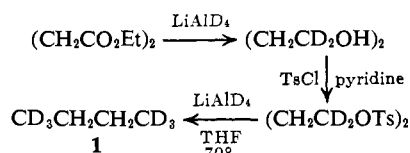
(1a) and most stable anti (1b) conformers is reported to be  $770 \pm 90$  cal/mol as calculated from the temperature dependence of Raman transition intensities for neat *n*-butane.<sup>4a</sup> The corresponding energy difference for gaseous *n*-butane is about 600 cal/mol.<sup>4c,e</sup> Electron diffraction data analyses<sup>4c</sup> indicate that the gauche potential energy minimum occurs when  $\alpha = 67.5 \pm 1.1^\circ$  in eq 1.

We now wish to report the use of the temperature dependences of nuclear magnetic resonance spectral parameters in obtaining an additional experimental measure of  $\Delta H$  for the equilibrium  $1a \rightleftharpoons 1b$  and an estimate of  $\alpha$  in 1a.

## Results and Discussion

The synthesis of 1 was accomplished by the sequence shown in Scheme I.

### Scheme I



The deuterium-decoupled pmr spectrum of neat 1 consists of a single resonance. The deuterium-decoupled  $^{13}\text{C}$ -H (natural abundance) spectrum is of the AA'A''A'''X type where X =  $^{13}\text{C}$  and the  $^{13}\text{C}$  isotope effect on the bonded hydrogen nuclei is negligible for the practical purposes of spectral analysis. The simplest method of accomplishing the analysis of the spectrum arising from this spin system is to treat it as an AA'BB' ( $^{13}\text{C}_A\text{H}_A\text{-CH}_B\text{H}_{B'}$ ) one.<sup>5</sup> The A,A' transitions are enantiomerically disposed on either side of the center band by approximately 62 Hz ( $1/2 J_{^{13}\text{C-H}}$ ) and the B,B' transitions are centered near the center band and are not observable when working with natural abundance  $^{13}\text{C}$ .

As  $M = (J_{AA'} - J_{BB'}) = 0$  in 1, the *a*-quartet which consists of transitions arising from the antisymmetric spin states collapses to a doublet exhibiting a separation exactly equal to  $L = (J_{AB} - J_{AB'})$ .<sup>5</sup> Also, there is a pair of transitions arising from the symmetric spin states whose separation gives  $N = (J_{AB} + J_{AB'})$  exactly. Since  $K = (J_{AA'} + J_{BB'}) \gg L$ , the outside transitions of the *s*-quartet are expected to have vanishing intensities.<sup>5</sup> Consequently, the geminal coupling constant,  $J_{AA'}$  ( $J_{BB'}$ ), cannot be determined accurately through spectral analysis.

The two pairs of transitions that are necessary for the determination of  $N$  and  $L$  were characterized after analyzing the 46 and  $-80^\circ$   $^{13}\text{C}$ -H satellite spectra of 1 as a AA'A''A'''X system using LAOCN 3.<sup>6,7</sup> Values of  $N$  and  $L$  were found to be insensitive to the values assumed ( $-5$  to  $5$  Hz) for  $J_{^{13}\text{C-C-H}}$ , and, as expected,

L. S. Bartell and D. A. Kohl, *ibid.*, **39**, 3097 (1963); (d) R. A. Bonham and L. S. Bartell, *J. Amer. Chem. Soc.*, **81**, 3491 (1959); (e) K. Kuchitsu, *Bull. Chem. Soc. Jap.*, **32**, 748 (1959); (f) K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940).

(5) E. W. Garbisch, Jr., *J. Chem. Educ.*, **45**, 311 (1968).

(6) S. M. Castellano and A. A. Bothner-By in "Computer Programs for Chemistry," D. F. Detar, Ed., Vol. I, W. A. Benjamin, New York, N. Y., 1968, pp 10-39.

(7) Computations were performed on a CDC-6600 computer. The plotting program was provided by S. Castellano and modified for our use by B. Hawkins.

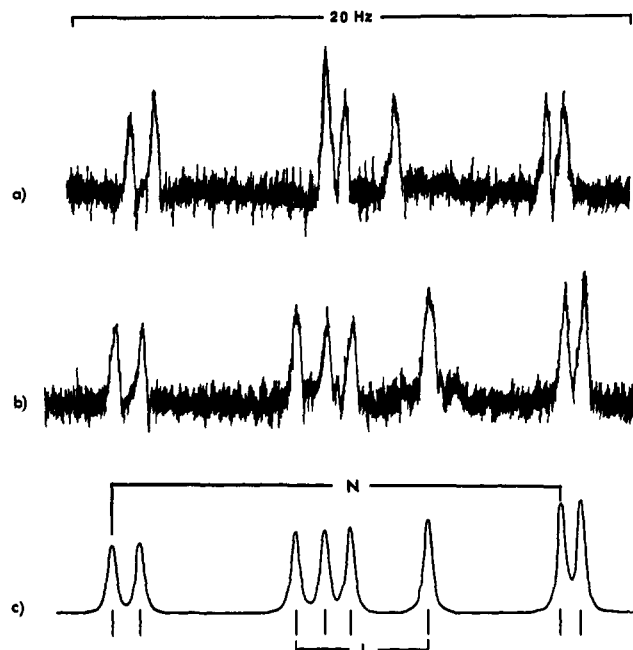


Figure 1. The low-field half of the deuterium-decoupled  $^{13}\text{C}$ -H satellite spectrum of neat 1 at (a)  $46^\circ$  and (b)  $-80^\circ$ , and (c) the computed spectrum at  $-80^\circ$  where those transitions which give exact values of the parameters  $N$  and  $L$  are indicated.

the geminal coupling constant was determined to be negative, but with a high ( $\pm 2$  Hz) probable error associated with its magnitude. Figure 1 shows the low-field halves of the experimental deuterium-decoupled  $^{13}\text{C}$ -H satellite spectra of 1 taken at 46 and  $-80^\circ$  together with the LAOCN 3 computed spectrum which is to be compared with the experimental one taken at  $-80^\circ$ .

Spectral parameters  $N$  and  $L$ , and the center band frequency,  $\nu_H$ , were determined at 12 temperatures between  $-91$  and  $63^\circ$ . Figure 2 shows the temperature dependences of these parameters.

The data summarized in Figure 2 were subsequently used to determine  $\Delta H$  for the equilibrium  $1a \rightleftharpoons 1b$  by obtaining the best solution values of the unknowns<sup>8</sup> ( $P_{aj}$ ,  $P_{bj}$ ,  $\Delta H$ , and  $\Delta S$ ) for eq 2, where  $P_{aj}$  and  $P_{bj}$  are

$$\ln \left( \frac{P_{aj} - P_{ij}^{\text{obsd}}}{P_{ij}^{\text{obsd}} - P_{bj}} \right) = \frac{-\Delta H}{RT_{ij}} + \frac{\Delta S}{R} \quad (2)$$

the  $j$ th of  $l$  intensive parameters of conformers 1a and 1b, respectively;  $P_{ij}^{\text{obsd}}$  is the  $j$ th of  $l$  observed parameters at the  $i$ th of  $k$  temperatures,  $T_{ij}$ . The best solution values of the unknowns are considered to be those which generate a minimum value of the residual,  $\phi$ , as given by<sup>9</sup>

$$\phi = \sum_{i=1}^k \sum_{j=1}^l (P_{ij}^{\text{obsd}} - P_{ij}^{\text{calcd}})^2 \quad (3)$$

(8) The use of the temperature dependence of  $P_{ij}^{\text{obsd}}$  in obtaining solutions to eq 2 was first utilized by W. W. Wood, W. Fickett, and J. G. Kirkwood, *J. Chem. Phys.*, **20**, 561 (1952).

(9) (a) E. W. Garbisch, Jr., B. L. Hawkins, and K. D. Mackay in "Conformational Analysis: Scope and Present Limitations," E. Chirudogu, Ed., Academic Press, New York, N. Y., 1971, pp 93-110; (b) H. Joshua, R. Gans, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4884 (1968), and references cited therein; (c) A. A. Bothner-By and D. F. Koster, *ibid.*, **90**, 2351 (1968); (d) F. Heatley and G. Allen, *Mol. Phys.*, **16**, 77 (1969).

Table I. Solution Parameters<sup>a</sup> of Equation 2 Using Temperature Dependences of  $N$ ,  $L$ , and  $\nu_H$  at Fixed Values of  $\Delta S$ 

Solution	$-\Delta S^b$ (fixed)	$-\Delta H^c$	$N_a$	$N_b$	$L_a$	$L_b$	$\nu_{H,a}$	$\nu_{H,b}$
1	1.876	637	12.06	17.45				
	1.376	551	11.41	17.71				
	0.876	472 (128) <sup>d</sup>	10.52 (0.27)	18.02 (0.81)				
2	1.876	780			-4.57	7.77		
	1.376	702			-6.02	8.08		
	0.876	631 (62) <sup>d</sup>			-7.88 (0.09)	8.42 (0.56)		
3	1.876	748					78.36	70.08
	1.376	668					79.33	69.83
	0.876	595 (38) <sup>d</sup>					80.60 (0.04)	69.56 (0.25)
4	1.876	760	12.11	16.94	-4.55	7.92	78.36	70.15
	1.376	681	11.55	17.07	-6.02	8.27	79.33	69.92
	0.876	609 (35) <sup>d</sup>	10.82 (0.07)	17.21 (0.14)	-7.91 (0.07)	8.65 (0.35)	80.57 (0.07)	69.67 (0.23)

<sup>a</sup> All nmr parameters are given in hertz. Subscripts  $a$  and  $b$  denote nmr parameters calculated for the gauche and anti conformers, respectively. <sup>b</sup> In cal/(mol deg). <sup>c</sup> In cal/mol. <sup>d</sup> Parenthetical values denote probable errors in the parameter solution values when  $-\Delta S = 1.376$  eu.

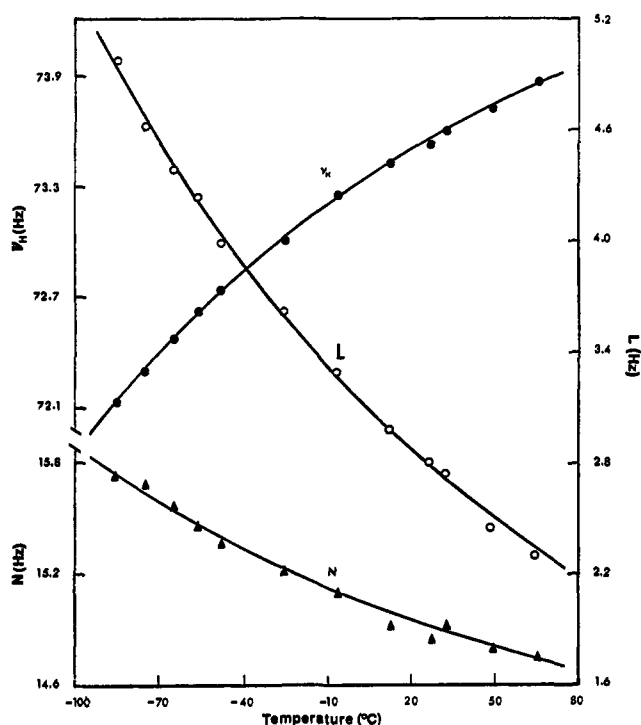


Figure 2. Observed temperature dependence of  $N$  (▲),  $L$  (○), and  $\nu_H$  (●) in neat 1. The solid lines are the calculated parameter temperature dependences for solution 4 ( $\Delta S = 1.376$  eu) in Table I.

where  $P_{ij}^{\text{calcd}}$  may be written as

$$P_{ij}^{\text{calcd}} = \frac{P_{aj} - P_{ij}^{\text{obsd}}}{1 + \exp\left(\frac{-\Delta H}{RT_{ij}} + \frac{\Delta S}{R}\right)} + P_{bj}$$

after rearrangement of eq 2 and substituting  $P_{ij}^{\text{calcd}}$  for  $P_{ij}^{\text{obsd}}$ . An iterative least-squares approach employing a Fortran IV computer program (CONAL2)<sup>10</sup> was used to solve eq 2 for up to  $(2l + 2)$  unknowns ( $P_{aj}$ ,  $P_{bj}$ ,  $\Delta H$ , and  $\Delta S$ ;  $j = 1, 2, \dots, l$ ) by applying corrections to the unknowns in such a manner that  $\phi$  is minimized.

The requirements which lead to the applicability of this approach to conformational analysis have been

(10) Details of CONAL2 can be found in ref 9a.

enumerated and discussed critically.<sup>9a,c,11</sup> One of the essential assumptions is that the property parameters  $P_{aj}$  and  $P_{bj}$  be temperature independent so that any temperature dependence of the observed parameter  $P_{ij}^{\text{obsd}}$  reflects a change in conformer populations with temperature. The vicinal proton coupling constants in cyclohexane have been found to be constant over a 141° temperature range while the proton chemical shift relative to TMS underwent a 0.5-Hz downfield shift with a 90° increase in temperature.<sup>12</sup> The former observation provides some justification for ascribing the observed temperature dependence of  $N$  and  $L$  in 1 to changes in conformer populations with temperature. Since the origin of the temperature dependence of the proton resonance frequency of cyclohexane is unknown, the use of chemical shifts in this approach to conformational analysis has been cautioned. It has, however, been demonstrated that the temperature dependences of the chemical shifts of a variety of saturated hydrocarbons can be correlated with the temperature dependence of the relative conformer populations and lead to values of  $\Delta H$  for the conformational equilibria which are compatible with those obtained from the temperature dependence of proton coupling constants.<sup>9a,13</sup>

The temperature dependences of  $N$ ,  $L$ , and  $\nu_H$  for 1 were processed separately and collectively by an iterative least-squares approach.<sup>9a</sup> Solution values of  $\Delta H$  and the corresponding six unknown intensive parameters of the gauche and anti conformers, holding  $\Delta S$  constant between  $-1.876$  and  $-0.876$  eu, are collected in Table I. Varying all unknowns including  $\Delta S$  failed to lead to unique solutions of eq 2.<sup>9a</sup> The values of  $\Delta H$  derived from single parameter set calculations (Table I; solutions 1, 2, and 3) all lie within the probable error limits of each other for any fixed value of  $\Delta S$ . These

(11) (a) H. S. Gutowsky, G. G. Belford, and P. W. McMahon, *J. Chem. Phys.*, **36**, 3353 (1962); (b) R. S. Newmark and C. H. Sederholm, *ibid.*, **39**, 3131 (1963); (c) G. Govil and H. J. Bernstein, *ibid.*, **47**, 2818 (1967); (d) J. Jonas and H. F. Gutowsky, *ibid.*, **42**, 140 (1965); (e) H. S. Gutowsky, J. Jonas, F. Chen, and R. Meinzer, *ibid.*, **42**, 2625 (1965).

(12) E. W. Garbisch, Jr., and M. G. Griffith, *J. Amer. Chem. Soc.*, **90**, 6543 (1968).

(13) E. W. Garbisch, Jr., with P. B. Woller, R. L. Lipnick, H. W. Tan, B. L. Hawkins, and K. D. Mackay, unpublished results.

results suggest that conformational equilibrium is responsible for the observed temperature dependences of  $N$ ,  $L$ , and  $\nu_H$  and provide justification for considering the value of  $\Delta H$  obtained from the combined parameter set calculation (Table I; solution 4) to be the most reliable.<sup>9a</sup> The latter calculation, although dominated by the temperature dependence of  $L$ , and to a lesser extent by  $\nu_H$ , affords values of the property parameters for the gauche and anti conformers which are in good agreement with those same values given by solutions 1, 2, and 3 at corresponding values of  $\Delta S$ .

As the steric isotope effect between deuterium and hydrogen is likely to be negligible,<sup>14</sup> the value of  $\Delta H$  obtained for eq 1 can be equated with that involving  $n$ -butane. Thus, for  $\Delta S = -1.376$  eu,<sup>15</sup> the experimental value of  $\Delta H = -681 \pm 35$  cal/mol obtained from the temperature dependence of three nmr spectral parameters of neat **1** compares well with  $\Delta H = -770 \pm 90$  cal/mol for neat  $n$ -butane as established by the Raman spectral work of Szasz, Sheppard, and Rank<sup>4a</sup> as well as the mean value of  $-650$  cal/mol from theoretical calculations.<sup>3</sup>

The decreased stability of the gauche conformer of  $n$ -butane relative to that of the anti one has been ascribed in part to nonbonded repulsive interactions between the gauche methyl groups,<sup>15</sup> The magnitude of these repulsive interactions may be sufficiently large so that a minimum in torsional plus nonbonded potential energies is realized at a torsional angle,  $\alpha$ , somewhat greater than the idealized angle at  $60^\circ$  (see eq 1). An estimate of the angle  $\alpha$  in the least stable gauche conformer, **1a**, may be obtained using eq 4, which de-

$$\frac{J_{a,t}}{J_{a,c}} = \frac{0.5[\cos^2(\omega + \alpha) + n \cos(\omega + \alpha)] + 0.5[\cos^2(\omega - \alpha) + n \cos(\omega - \alpha)]}{\cos^2 \alpha + n \cos \alpha} \quad (4)$$

rives from eq 5,<sup>16</sup> where  $J_{a,c}$  and  $J_{a,t}$  in eq 4 are the cis

$$J = A[\cos^2 \phi + n \cos \phi] \quad (5)$$

and trans proton couplings, respectively, in **1a**. Assuming that  $\phi_{\text{cis}}$  and  $\phi_{\text{trans}}$  in **1b** are  $60^\circ$  and  $180^\circ$ , respectively, and using the values of the cis ( $J_{b,c}$ ) and trans ( $J_{b,t}$ ) proton couplings derived from the values of  $N_b$  and  $L_b$  given in Table I (solution 4 at  $\Delta S = -1.376$  eu), eq 5 was solved to give  $A = 12.56$  and  $n = 0.11$ . From the experimental value of 3.17 for ( $J_{a,t}/J_{a,c}$ ) obtained from Table I (solution 4 at  $\Delta S = -1.376$  eu) and using eq 4 with  $n = 0.11$  and  $\omega = 120^\circ$ ,  $\alpha$  was calculated to be  $66^\circ$ . An estimate of the uncertainty in  $\alpha$  was obtained by applying the probable errors in  $N_a$  and  $L_a$  to calculate minimum and maximum values of the vicinal couplings. Using these data and eq 4,  $\alpha = 66 \pm 1^\circ$ . This value of  $\alpha$  is in good agreement with the experimental one of  $67.5 \pm 1.1^\circ$  established by Kuchitsu<sup>4e</sup> from electron-diffraction data of gaseous  $n$ -butane.

(14) K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *J. Amer. Chem. Soc.*, **86**, 1733 (1964).

(15) The value of  $\Delta S$  for the equilibrium under consideration was taken as  $R \ln 2$ , the entropy of mixing. See E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, pp 11-12.

(16) M. Barfield and D. M. Grant, *Advan. Magn. Resonance*, **1**, 149 (1965).

## Experimental Section

**1,4-Butanediol-1,1,4,4-*d*<sub>4</sub>**. A 9.5-g (5.45 mmol) sample of diethyl succinate (Eastman Organic Chemicals) in 50 ml of anhydrous ether was added dropwise to a stirred suspension of 3.0 g (71.0 mmol) of lithium aluminum deuteride (Stohler Isotope Chemicals) in 500 ml of refluxing ether. After addition was complete (4 hr), the resulting mixture was refluxed for 8 hr and the excess reducing agent destroyed by the addition of powdered  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ . After thoroughly stirring the resulting mixture, the inorganic salts were removed by filtration through Celite. The solvent then was removed by distillation at atmospheric pressure and the residue was distilled under vacuum to afford 4.6 g (90%) of diol, bp  $89^\circ$  (1.0 mm).

**1,4-Butane-1,1,4,4-*d*<sub>4</sub> Ditosylate**. A stirred solution of the deuterium-labeled diol (4.4 g, 47.0 mmol) in 100 ml of pyridine was cooled to  $0^\circ$  in an ice bath and 24.0 g (0.125 mol) of *p*-toluenesulfonyl chloride was added at such a rate that the temperature did not rise above  $5^\circ$ . After addition was complete, the mixture was stored at  $0^\circ$  for 48 hr and then poured into an ice-hydrochloric acid mixture. The solid material was collected, washed with water until the washings were neutral to litmus, and air dried. The crude product was recrystallized twice from absolute ethanol to afford 16.0 g (85%) of ditosylate, mp  $83-84^\circ$  [lit.<sup>17</sup> mp  $82-83^\circ$ ].

**Butane-1,1,1,4,4,4-*d*<sub>6</sub> (1)**. A solution of 3.0 g (7.5 mmol) of the ditosylate in 12 ml of anhydrous tetrahydrofuran was prepared by distillation of the solvent from lithium aluminum hydride directly into a dry pressure equilibrated dropping funnel containing the substrate. Similarly, ca. 20 ml of the same solvent was distilled into a dry three-necked 100-ml round-bottomed flask containing a stirring bar. The flask was then fitted with the dropping funnel, a water-cooled condenser, and a gas inlet tube. To the top of the reflux condenser was connected a tower of fresh Drierite, two bubblers containing ethylene glycol, and finally a second tower of Drierite through which the exiting gases passed before being collected in a constricted nmr tube containing hexamethyldisilane (HMDS) and immersed in Dry Ice-acetone coolant. The system was flushed with dry nitrogen gas, stirring was initiated, and 2.0 g (50.0 mmol) of freshly ground, finely divided lithium aluminum deuteride (Stohler Isotope Chemicals) was introduced into the flask in small portions. The resulting suspension was heated to reflux for 30 min before the substrate was added dropwise at such a rate that gentle bubbling was observed in the ethylene glycol traps. Throughout the course of addition, and for 30 min after the addition was complete, the reaction mixture was maintained at reflux by external heating. While maintaining reflux of the reaction mixture, the system finally was gently swept with dry nitrogen gas to give **1**. The nmr tubes were subsequently degassed and sealed at  $-68^\circ$ . From a typical run it was possible to obtain two samples suitable for study by nmr spectroscopy.

**Nmr Spectral Determinations**. All spectra were determined on a Varian A-60 spectrometer equipped with an NMR Specialties HD-60A heteronuclear spin decoupler, a V-6058A homonuclear decoupler, and a V-6040 temperature controller. Deuterium decoupling was accomplished on the phase-lock mode of the homonuclear decoupler for all spectral determinations. Spectra were calibrated from audio side bands of internal HMDS using a Hewlett-Packard 3300A function generator and a Hewlett-Packard 3734A electronic counter.

The probe temperatures were measured before and after each experiment by means of a calibrated copper-constantan thermocouple inserted into an empty stationary nmr tube positioned in the probe. The temperatures generally agreed within  $0.5^\circ$ . The average of the two temperatures was used as the temperature of the experiment and is believed to be accurate to  $\pm 1^\circ$ . For each experiment, the probe and sample were allowed to thermally equilibrate 4-5 hr before commencing spectral determinations.

Spectra were determined using neat samples containing ca. 15% (v/v) HMDS as internal standard and prepared as described above. In general, 18 HMDS side-band calibrated spectra were recorded for the methylene protons at each temperature by alternately sweeping upfield and downfield. The calculated transition frequencies at each temperature were then averaged and those values whose deviations were greater than or equal to twice the standard deviation were discarded. The calculation was repeated until all deviations from the average were less than the corresponding standard deviations. This procedure led to an average of 18 spectra for

(17) H. A. Staab and K. Wendel, *Justus Liebigs Ann. Chem.*, **694**, 86 (1966).

Table II. Temperature Dependences of the Pmr Parameters for 1

Temp, <sup>a</sup> °C	N <sup>b</sup>	L <sup>b</sup>	ν <sub>H</sub> <sup>c</sup>
63	14.764 (0.033) <sup>d</sup> [19] <sup>e</sup>	2.264 (0.033) <sup>d</sup> [24] <sup>e</sup>	73.874 (0.039) <sup>d</sup> [12] <sup>e</sup>
46	14.814 (0.073) [18]	2.419 (0.047) [19]	73.729 (0.048) [17]
30	14.939 (0.059) [17]	2.718 (0.045) [14]	73.606 (0.037) [14]
24	14.833 (0.037) [15]	2.781 (0.041) [16]	73.525 (0.044) [10]
10	14.936 (0.033) [17]	2.954 (0.023) [15]	73.423 (0.026) [9]
-10	15.126 (0.043) [15]	3.266 (0.042) [21]	73.249 (0.026) [14]
-30	15.244 (0.071) [23]	3.608 (0.061) [24]	72.998 (0.052) [12]
-53	15.389 (0.054) [21]	3.974 (0.086) [20]	72.728 (0.044) [18]
-62	15.490 (0.074) [14]	4.232 (0.018) [11]	72.603 (0.068) [13]
-70	15.592 (0.066) [24]	4.385 (0.043) [21]	72.459 (0.033) [12]
-80	15.716 (0.062) [21]	4.620 (0.059) [25]	72.285 (0.020) [9]
-91	15.765 (0.044) [22]	4.970 (0.027) [21]	72.112 (0.031) [15]

<sup>a</sup> Accurate to ±1°. <sup>b</sup> In hertz. <sup>c</sup> Downfield from HMDS in hertz. <sup>d</sup> Parenthetical values are standard deviations. <sup>e</sup> Bracketed values indicate the number of traces used.

each temperature and afforded standard deviations of less than 0.06 Hz with the majority in the range of 0.02–0.04 Hz.

For <sup>13</sup>C satellite spectra, the region in which the satellites were observed was calibrated before and after the experiment using side bands from HMDS. The average calibrations both before and after were calculated as previously described and in all cases were within the probable error of each other at a given temperature. The average of these two values provided a scale factor which was applied to the frequency separations of the transitions of interest. An average of 26 traces (13 upfield and 13 downfield) was recorded and manipulated as previously described. As a result, about 20

spectra were used for each temperature, the transition frequency separations of which exhibit standard deviations of less than 0.08 Hz with the majority between 0.02 and 0.05 Hz.

For all experiments, satellite and methylene proton absorptions exhibit widths at half-heights comparable to those of HMDS (*i.e.*, between 0.3 and 0.6 Hz). The spectral data for 1 are compiled in Table II.

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## Nmr Parameters of the Individual Fluorines of the Trifluoromethyl Group

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**Abstract:** The rotation barriers (5.2–8.5 kcal/mol) of the trifluoromethyl group and the chemical shifts of the individual fluorines have been measured by analysis of the variable temperature fluorine nmr spectra of 2,2-dichlorohexafluoropropane (1), 2,2-dibromohexafluoropropane (2), 2-iodo-2-(trifluoromethyl)hexafluoropropane (4), 1,1,1-trifluoro-2,2-dichloro-2-iodoethane (5), pentafluoroiodoethane (6), and 1,1,1-trifluoropentachloropropane (7). In addition, individual long-range coupling constants were observed for 2,2-diiodohexafluoropropane (3). The four-bond coupling constants between the fluorine nuclei of 3 are +34 and +16 Hz for eclipsed and gauche-gauche, +15 Hz for trans-trans, and -3.5 Hz for trans-gauche configurations. Chemical shift assignments have been made for each of the three distinct fluorine nuclei of 2-bromo-2-iodohexafluoropropane (11).

Fluorine nmr is an invaluable technique in structure determination,<sup>1</sup> but detailed configurational analysis is hampered by a lack of lore on specific geometric interactions. Progress has been made by investigating fluorines affixed to rigid rings,<sup>2</sup> but available synthetic methods limit the configurations attainable and unknown strain effects may be introduced by the small rings used.

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Specific interactions can be observed in nmr spectra at those temperatures where conformational averaging is slow on the nmr time scale.<sup>3</sup> We have elaborated the individual fluorine chemical shifts in trifluoromethyl groups, the stereospecific coupling constants between the individual fluorines in *gem*-trifluoromethyl groups, and the rotation barriers of these groups.

### Results

Chemical shifts and two-bond, fluorine-fluorine couplings were obtained for the compounds in Table I

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