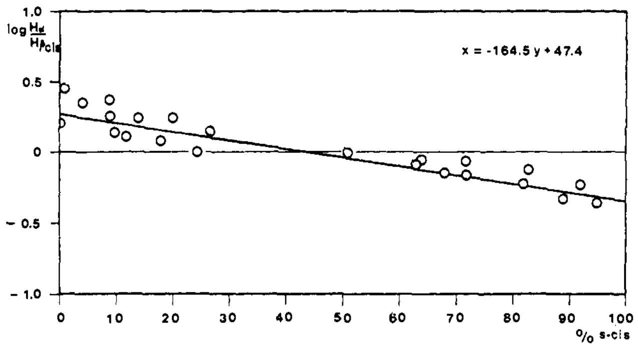

Figure 2. Plot of the percentage molar fraction of s-cis form *vs.* log $H_\alpha/H_{\beta\text{-cis}}$ for the title compounds. H_α and $H_{\beta\text{-cis}}$ are respectively the observed LIS for the protons in α and β-cis positions to the carbonyl.

methyl substituted amides (compound XXIX, Table I) and the s-trans form becomes preferred.

Discussion

The general agreement between population data presented in Table I and those available in the literature illustrates the wide applicability of the LIS method to the title compounds and also its reliability.

In fact, the LIS analysis is meaningful and its results are reliable only if the conformational equilibria in the substrate molecule are not perturbed by the lanthanide addition. Our results show that, at least for the important classes of compounds considered here, no unusual perturbation of the conformational equilibria occurs.

The reliability of our estimates is shown not only by the agreement with data from other techniques, but also by their internal consistency, as shown in Figure 2. In fact, the molar fraction of s-cis forms calculated for each vinyl compound are plotted *vs.* log $H_\alpha/H_{\beta\text{-cis}}$, where H_α is the observed LIS for the proton in α position to the carbonyl, and $H_{\beta\text{-cis}}$ is the observed LIS for the β proton in cis position to the carbonyl. A fairly linear relation exists (correlation coefficient 0.9293) among all the points in Figure 2, independent of the particular class to which they belong (aldehydes, ketones, esters, amides) and also from the lanthanide shift reagent used to obtain the experimental LIS. Although we have no theoretical explanations at hand to account for the linear behavior in Figure 2, some kind of correlation between the two parameters had to be expected since the $H_\alpha/H_{\beta\text{-cis}}$ ratio is clearly a function of the relative abundance of the s-cis and s-trans conformers in each compound, regardless of the functional group attached to the carbonyl.

Accordingly, the relation in Figure 2 can be used to determine the s-cis/s-trans population ratio *directly* from the experimental LIS data in the title compounds. This remarkable result, and its implications about further quantitative applications of the LIS method, is not the only interesting point here. Our data (Table I; Figure 2) cover the relative population range from one extreme to the other. Starting from the notion that, in absence of interferences, the s-trans form is favored over the s-cis, we have a complete set of results which illustrate the steric inhibition of one form up to the complete inversion of stability of the two forms.

Conformational Analysis of 1,3-Butadiene[1]

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Abstract: The conformational analysis of 1,3-butadiene has been accomplished using the temperature dependences of two nuclear magnetic resonance spectral parameters, δ_{AB} and $J_{CC'}$, obtained from 2,3-dideuterio-1,3-butadiene (**2**) and 1,1,4,4-tetradeuterio-1,3-butadiene (**3**), respectively. These parameters have been correlated with the trans $\rightleftharpoons$ cis conformational equilibrium (eq 1). The magnitude of the derived vicinal 2,3 proton–proton coupling of the minor conformer indicates that it is nonplanar (skew). The enthalpy difference for the trans $\rightleftharpoons$ skew equilibrium (**1a** $\rightleftharpoons$ **1c**, **1d**) was found to be +2105 ± 44 cal/mol at $\Delta S = +1.376$ eu.

The compound 1,3-butadiene is generally represented as a mixture of two planar conformers, **1a** (s-trans) and **1b** (s-cis), in mobile equilibrium.[3] Hückel, using theoretical considerations, suggested the possibility of two such forms as early as 1932.[4]

Considerable experimental evidence supporting the existence of a major conformer having a trans-coplanar conformation has been obtained from electron diffraction,[5] infrared and Raman,[6] microwave,[7] far-infrared,[8]

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[1] Presented in part by E. W. G. at the 160th National Meeting of the American Chemical Society, Houston, Texas, Feb 1969.

[2] Correspondence may be directed to E. W. G., Center for Applied Research in Environmental Sciences, St. Michaels, Md. 21663.

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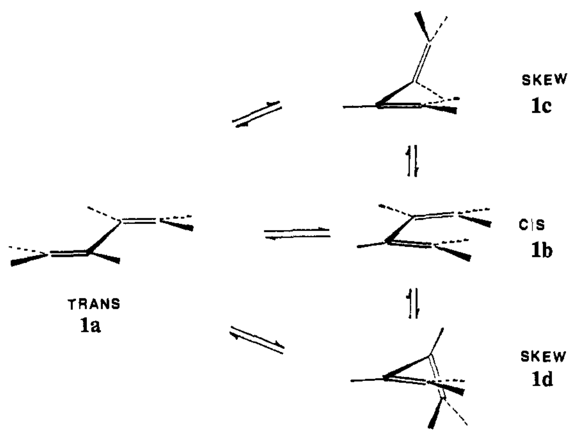
[4] E. Huckel, *Z. Phys.*, 76, 630 (1932).

[5] (a) V. Schomaker and L. Pauling, *J. Amer. Chem. Soc.*, **61**, 1769 (1939); (b) A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, 12, 1221 (1958); (c) W. Haugen and M. Traetteberg, *Acta Chem. Scand.*, 20, 1726 (1966); (d) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, 1, 463 (1968).

[6] (a) K. Bradacs and L. Kahovec, *Z. Phys. Chem., Abt. B*, **48**, 63 (1940); (b) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 131 (1947); (c) C. M. Richards and J. R. Nielsen, *J. Opt. Soc. Amer.*, **40**, 438 (1950); (d) M. I. Bateuv, A. S. Onishchenko, A. D. Matveeva, and N. I. Aronova, *Proc. Acad. Sci. USSR, Chem. Soc.*, 132, 543 (1960); (e) D. J. Marais, N. Sheppard, and B. P. Stoicheff, *Tetrahedron*,



(1)

nmr,[9] and calorimetry.[10] The existence of **1a** as the major conformer is also in agreement with most theoretical calculations.[11] There is, unfortunately, little direct experimental evidence for the least stable conformer, as it is undetectable in most cases because of its low concentration at temperatures generally employed in spectral determinations. The only direct experimental evidence for a second conformer is from the calorimetric studies of Aston, *et al.*,[10a] and Sverdlov and Bolotina.[10b] Both groups of investigators calculated the single bond torsional potential functions for trans and cis conformers which best fit the third-law entropy and gaseous heat capacities. In both studies, the fundamental torsional frequency for the central C–C single bond was assigned to the trans conformer as 170 cm^{-1} from a Raman overtone. More recently, Fateley, *et al.*, reported an experimental value of 163 cm^{-1} for this torsional frequency from far-infrared measurements.[8]

An additional uncertainty is related to the conformation of the least stable isomer of butadiene. There is not strong evidence to consider solely the coplanar structure **1b**. The possibility of two dissymmetric skew conformers **1c** and **1d** has been proposed by Lide,[7a] Fateley, *et al.*,[8] and most recently by Segre.[9b]

In this work, we have measured the temperature dependences of the averaged conformer nmr parameters for butadiene over a temperature range of 198.7°, and related these dependences to changes in conformer population.

In order to simplify spectral analysis, two deuterium-labeled derivatives, **2** and **3**, were synthesized, and the proton spectra were recorded with deuterium decoupling. The chemical shifts ν_A and ν_B arose from the analysis of the AA′BB′ nmr spectrum of **2**. The normal nmr spectrum of **3** afforded ν_C, and $J_{CC'}$ was determined directly from the ^{13}C-satellite spectrum of **3**.

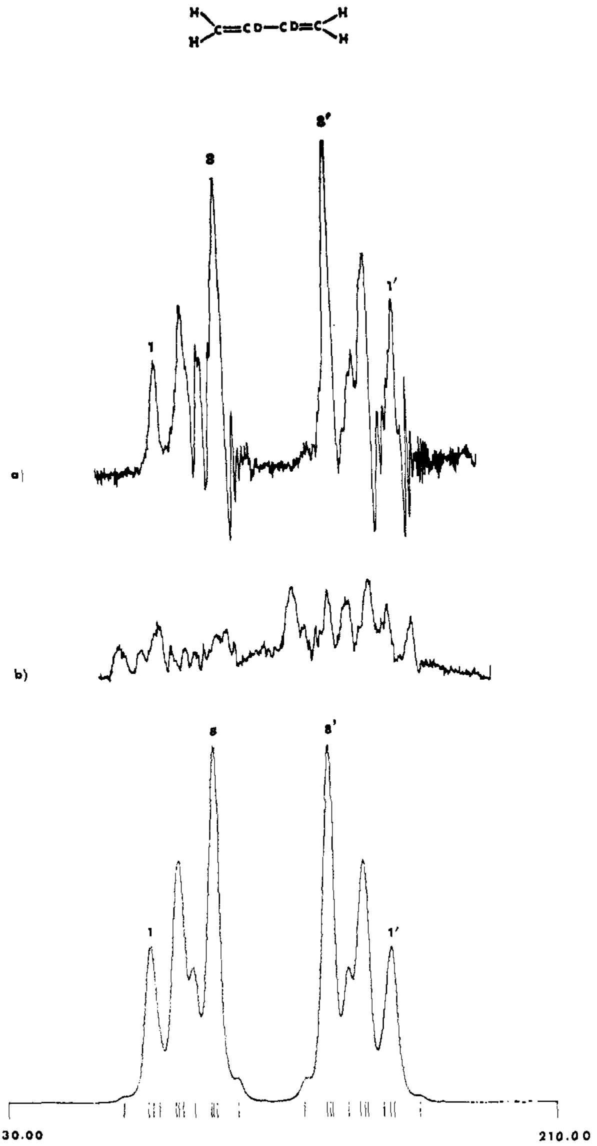
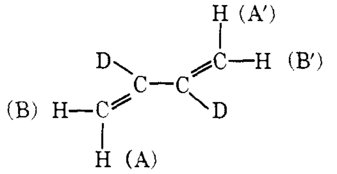


Figure 1. The 60-MHz nmr spectrum of **2** at 35.0° (a) experimental spectrum with deuterium decoupling; (b) experimental spectrum without deuterium decoupling; (c) calculated theoretical spectrum using Hobgood and Goldstein's[9a] parameters, which were obtained by extrapolation of their data at 35.0° to infinite dilution.



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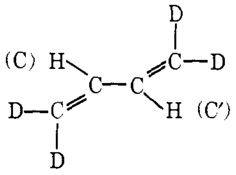

3

Results and Discussion

Figure 1 shows an undecoupled and a deuterium-decoupled nmr spectrum of 2,3-dideuterio-1,3-butadiene (**2**) along with a CALCOMP computed spectrum arising from a LAOCOON3 solution which uses the spectral parameters reported by Hobgood and Goldstein.[9a]

Although a four-spin system of the type AA′BB′ may

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(11) (a) R. S. Mulliken, *J. Chem. Phys.*, 7, 121 (1939); *Rev. Mod. Phys.*, 14, 265 (1942); (b) R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, 18, 1338 (1950); (c) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc., London, Sect. A*, 68, 601 (1955); (d) R. S. Mulliken, *Tetrahedron*, 6, 68 (1958); (e) M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, 91, 789 (1969); (f) R. Pariser and R. G. Parr, *J. Chem. Phys.*, 21, 767 (1953); (g) R. J. Buenker and J. L. Whitten, *ibid.*, 49, 5381 (1968); (h) P. A. Clark, *ibid.*, 54, 45 (1971).

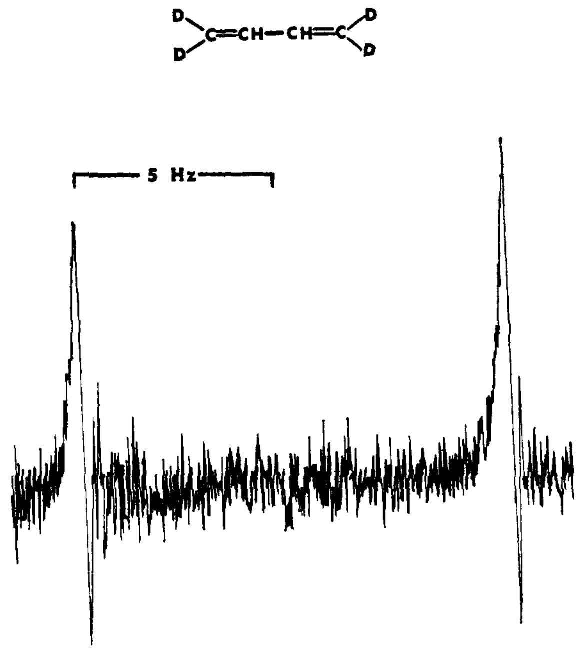

Figure 2. The low field half of the deuterium-decoupled ^{13}C–H satellite spectrum of neat **3** at −17.9°.

exhibit up to 24 transitions, it was necessary to identify only the AB subspectrum, characterized by transitions 1, 8, 1′, and 8′, in order to evaluate ν_A and ν_B using[12]

$$\nu_A = \nu_{av} + \delta_{AB}/2$$
$$\nu_B = \nu_{av} - \delta_{AB}/2$$

where $\nu_{av} = (\nu_1 + \nu_{1'} + \nu_8 + \nu_{8'})/4$ and $\delta_{AB} = [(\nu_1 - \nu_{1'})(\nu_8 - \nu_{8'})]^{1/2}$.

1,1,4,4-Tetradeuterio-1,3-butadiene (**3**) produces a singlet (the center band) in the deuterium-decoupled spectrum. The ^{13}C-satellites of this center band consist of a pair of doublets with spacings corresponding exactly to $J_{CC'}$. Figure 2 illustrates a typical deuterium-decoupled ^{13}C-satellite spectrum of **3**.

Values of ν_A and ν_B for **2** were determined at 11 temperatures between −97.5 and 102.7°. For **3**, ν_C was determined at seven temperatures between −105.0 and 79.8°, and $J_{CC'}$ at 20 temperatures between −99.0 and 93.6°.

The applicability of the temperature dependences of intensive nmr parameters to the solution of two-conformer equilibrium problems was first suggested by Wood, Fickett, and Kirkwood,[13] and subsequently examined critically by others.[14–19] In this work, the temperature dependences of ν_A, ν_B, ν_C, δ_{AB}, and $J_{CC'}$ were used to determine ΔH for the equilibrium **1a** ⇄ **1b** (**1c**, **1d**), by solution of eq 2 where P_{aj} and P_{bj} are the

$$\ln \frac{P_{aj} - P_{ij}°}{P_{ij}° - P_{bj}} = \frac{-\Delta H}{RT_{ij}} + \frac{\Delta S}{R} \qquad (2)$$

*j*th of *l* intensive parameters of conformers **1a** and **1b**, respectively; $P_{ij}°$ is the *j*th of *l* observed parameters at the *i*th of *k* temperatures, T_{ij}.[19]

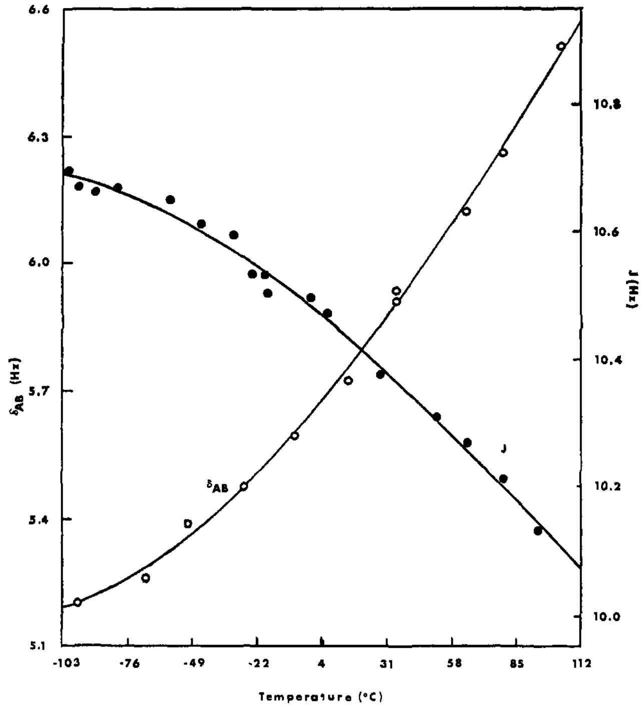

Figure 3. The experimental temperature dependences of $J_{CC'}$ (●) and δ_{AB} (○), along with their theoretical dependences. The latter were derived from the combined parameter calculation at ΔS = +1.376 eu.

Temperature dependences of parameters ν_A, ν_B, ν_C, $J_{CC'}$, $(\nu_A - \nu_B)$, and $(\nu_A + \nu_B)$ were used separately in attempts to solve eq 2 for all the unknowns. Only one of these parameter sets, $J_{CC'}$, yielded a unique solution of eq 2. The probable errors associated with the solution values of ΔH and ΔS (ΔH = +2024 ± 457 cal/mol, ΔS = −0.753 ± 8.343 eu), however, were intolerably high and for all subsequent calculations, ΔS was held fixed at either 0 or $+R$ ln 2 (+1.376), corresponding qualitatively to either one planar (**1b**), or two skew enantiomers (**1c**, **1d**) for the minor conformer.[20] Such treatment led to consistent solutions of eq 2. However, solutions of eq 2 using the ν_A, ν_B, and ν_C parameter sets yielded values of ΔH having 10–60% associated probable errors. As solution values of ΔH arising for the δ_{AB} and $J_{CC'}$ parameter sets exhibited only 3–4% associated probable errors, these parameter sets were retained for further considerations and the others discarded.

Table I shows the solution parameters of eq 2 using the temperature dependences of δ_{AB} and $J_{CC'}$. As the values of ΔH arising for the δ_{AB} and $J_{CC'}$ parameter sets are the same within their probable error limits, solution of eq 2 using the combined sets is considered justified[19] and should generate the most reliable value of ΔH.[19] Solution 3 in Table I shows the results of this calcula-

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(17) G. Govil and H. J. Bernstein, *ibid.*, **47**, 2818 (1967).

(18) (a) J. Jonas and H. F. Gutowsky, *ibid.*, **42**, 140 (1965); (b) H. S. Gutowsky, J. Jonas, F. Chen, and R. Meinzer, *ibid.*, **42**, 2625 (1965).

(19) E. W. Garbisch, Jr., B. L. Hawkins, and K. D. MacKay in "Conformational Analysis: Scope and Present Limitations," E. Chiurdogu, Ed., Academic Press, New York, N. Y., 1971, pp 93–110; P. B. Woller and E. W. Garbisch, *J. Amer. Chem. Soc.*, **94**, 5310 (1972).

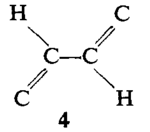
(20) The entropy of mixing is normally used to account for any entropy differences between conformers. See E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, pp 11–12.

Table I. Solution Parameters[a] of Equation 2 Using Temperature Dependences of δ_{AB} and $J_{CC'}$ at Fixed Values of ΔS for Equation 1

Solution	ΔS^b (fixed)	ΔH^c	$(\delta_{AB})_a$	$(\delta_{AB})_b$	$(J_{CC'})_a$	$(J_{CC'})_b$	RMS
1	0	2037 ± 66	5.14 ± 0.02	27.21 ± 1.74			0.021
	1.376	2118 ± 63	5.15 ± 0.02	17.96 ± 0.93			0.021
2	0	1987 ± 84			10.72 ± 0.01	1.48 ± 0.96	0.015
	1.376	2059 ± 78			10.71 ± 0.01	5.39 ± 0.50	0.015
3	0	2026 ± 46	5.14 ± 0.01	26.91 ± 1.21	10.71 ± 0.01	1.03 ± 0.58	0.018
	1.376	2105 ± 44	5.15 ± 0.01	17.77 ± 0.64	10.71 ± 0.01	5.10 ± 0.31	0.018

[a] All nmr parameters are given in hertz. Subscripts a and b denote nmr parameters calculated for the trans and cis conformers, respectively. See **2** and **3** for chemical shift assignments. ± figures denote probable errors. [b] In cal/(mol deg). [c] In cal/mol.

tion where ΔS was held constant at 0 and + 1.376 eu. Figure 3 shows the experimental and calculated temperature dependences of $J_{CC'}$ and δ_{AB} for solution 3 (ΔS = + 1.376 eu) of Table I. It is noteworthy that solution 3 of Table I shows that both ΔH and $(J_{CC'})_a$ are insensitive to ΔS. Consequently, these parameters have been accurately determined. Since the steric isotopic effect between deuterium and hydrogen is likely to be negligible,[21] the solution 3 value of ΔH in Table I may be equated to that for eq 1 involving 1,3-butadiene, and compared with the value +2.3 kcal/mol obtained by both Aston[10a] and Sverdlov[10b] in their calorimetric studies. The most stable, or trans conformer, of butadiene has been established as being coplanar,[21] so $(J_{CC'})_a$ or J_{trans} for the coplanar fragment, **4**, may be considered to be 10.7 Hz.



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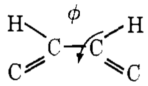
Furthermore, we are able to conclude that the least stable conformer is probably skew (**1c**, **1d**), rather than cis (coplanar), and that the solution obtained when ΔS = +1.376 eu is probably the most reliable one. From a series of model compounds exhibiting cis diene configurations, **5**, Bothner-By and Moser have estimated J_{cis} (ϕ = 0°) and J_{skew} ($\phi \approx$ 20°) as being 5.9–6.5 and 5.1–5.4 Hz, respectively.[23] The solution value of $J_{CC'}$ which is obtained when ΔS is held constant at 0 eu[24] corresponds to that for J_{cis} and is 1.03 ± 0.58 Hz. The magnitude of this coupling is in poor agreement with that expected for the cis conformer. However, the solution value of $J_{CC'}$ which is obtained when ΔS is held constant at 1.376 eu,[25] corresponds to that for J_{skew} and is 5.1 ± 0.3 Hz. This value of the vicinal coupling agrees well with that expected for the skew conformer, where ϕ is about 20°.[23]



5

The existence of a potential energy maximum corresponding to a planar cis conformation is not unreasonable. Eliel has suggested the possibility of nonplanarity of the minor conformer arising from nonbonded interactions between the internal syn hydrogens.[26] If one assumes that the bond angles and bond distances given by Haugen and Traetteberg for the trans conformer[5c] are the same for a cis coplanar conformer, this leads to a syn hydrogen, hydrogen nonbonded distance of 1.92 Å which should lead to a significant interaction energy.[27] In addition, repulsive electrostatic interactions may be significant in the cis conformer. These effects and possibly others may be sufficient to cause the cis conformation to be a potential energy maximum one.

In general, the torsional potential $V(\phi)$ hindering internal rotation about a single bond can be represented by eq 3.[28] The second and third terms correspond to

$$V(\phi) = \frac{V_1}{2}(1 - \cos\phi) + \frac{V_2}{2}(1 - \cos 2\phi) + \frac{V_3}{2}(1 - \cos 3\phi) \quad (3)$$

the resonance and torsional contributions and the first term relates to additional interactions which affect the potential energy at the cis conformation (*i.e.*, nonbonded and electrostatic interactions). In principle, if all three term coefficients V_1, V_2, and V_3 were known, the potential minima in eq 3 for α = 0–180° would identify the conformers involved in the butadiene equilibrium.

For eq 3, $d(V(\phi))/d\phi$ is always zero at ϕ = 180°; therefore, the cis conformation exists at either a potential maximum or minimum. Furthermore, the sign of $d^2V(\phi)/d\phi^2$ at ϕ = 180° allows us to determine whether the cis conformer is a potential maximum or minimum one. If $4V_2 > (V_1 + 9V_3)$, the cis conformer is a potential minimum one, and if $4V_2 < (V_1 + 9V_3)$, the cis conformer is a potential maximum one. The value of the experimental torsional barrier for propene (2.0 kcal/mol) will be assigned to the third term coefficient V_3.[29] Fateley, *et al.*, have shown that for butadiene $V_1 + 4V_2 + 9V_3$ = 28.1 kcal/mol, by assuming the harmonic oscillator approximation, and relating this potential to the observed torsional fundamental at 163 cm^{-1}.[8] If we use for V_1 the value of 0.77 kcal/mol calculated for the syn H, H nonbonded interaction in the cis

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

(22) See, *e.g.*, ref 5d.

(23) A. A. Bothner-By and E. Moser, *J. Amer. Chem. Soc.*, **90**, 2347 (1968).

(24) This neglects a small contribution to ΔS of about 0.4 eu that was calculated as arising from the difference in moments of inertia of the two butadiene conformers.

(25) This ΔS arises from + R ln 2, the entropy of mixing the *dl* pair of skew conformers.

(26) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 331–332.

(27) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961), eq 3.

(28) R. A. Pethrick and E. Wyn-Jones, *Quart. Rev., Chem. Soc.*, **23**, 304 (1969).

(29) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957); D. R. Herschbach and L. C. Krisher, *ibid.*, **28**, 728 (1958); J. E. Kilpatrick and K. S. Pitzer, *J. Res. Nat. Bur. Stand.*, **37**, 163 (1946).

conformer,[27] a value of 2.3 kcal/mol is estimated for V_2 and the minor conformer is expected to be skew. This value of V_2 falls between the values calculated for the theoretical delocalization energy (0.7 kcal/mol)[11e] and the empirical resonance energy (3.5 kcal/mol) of butadiene.[30,31]

While this argument lends support to an equilibrium involving the trans, **1a**, and two skew enantiomorphic conformers, **1c** and **1d**, it does not rule out entirely the possibility that the cis conformer is the least stable potential minimum one. If $4V_2$ is only slightly greater than $(V_1 + 9V_3)$, the differences in shape of a shallow cis *vs.* a steeper trans potential could well result in large differences in their respective vibrational partition functions. Calculations in which the two wells are approximated by harmonic oscillators indicate qualitatively that $S_{\text{VIB}} \approx R \ln 2$ for values of $V_2 \approx$ 4.0–4.6 kcal/mol.

Nmr Spectral Determinations. All nmr spectra were determined at 60 MHz with deuterium decoupling on a Varian A-60 spectrometer equipped with a V-6040 temperature controller, a V-6058A homonuclear decoupler, and an nmr specialties HD-60A heteronuclear spin decoupler.

The temperature for each experiment, taken as the average of measurements before and after, was determined using a copper–constantan thermocouple which was enclosed in an empty nmr tube and inserted directly into the probe. The thermocouple output was measured with a Honeywell 2725-3 potentiometer. Temperatures are thought to be accurate to ± 1°.

For 2,3-dideuterio-1,3-butadiene (**2**), spectra were determined using an 8.3% (w/w) solution of **2** in carbon disulfide containing 4.6% (w/w) hexamethyldisilane (HMDS) as an internal standard. At each temperature, HMDS side band calibrated spectra were determined with alternate upfield and downfield sweeps, and the average frequency for transitions 1, 8, 8′, and 1′ were calculated relative to HMDS, with all line measurements made at the peak center at half-height. Any values for each line whose deviations were equal to or greater than twice the standard deviation for that line were discarded, and the line frequency was recalculated. This process was repeated until all deviations from the average were less than twice their corresponding standard deviations. Final standard deviations for each line ranged from 0.02 to 0.06 Hz, and were generally around 0.03 Hz. Data for **3** were discarded by the same statistical process. The nmr data for **2** are shown in Table II.

Nmr spectra for 1,1,4,4-tetradeuterio-1,3-butadiene (**3**) were determined using a neat sample of **3** containing 11% (w/w) of HMDS, as described previously. HMDS side band calibrated nmr spectra were taken of the deuterium-decoupled H_1 singlet as described for **2**.

Table II. Temperature Dependences of the Pmr Parameters of **2**

Temp[a]	ν_A[b]	ν_B[b]	δ_{AB}	N[b,d]
−97.5	305.850	300.648	5.202 (14)[c]	2.296
−69.0	305.202	299.941	5.261 (10)	2.241
−51.5	305.189	299.800	5.389 (14)	2.243
−28.6	304.972	299.497	5.475 (13)	2.298
−7.0	304.576	298.983	5.594 (12)	2.239
15.0	304.432	298.706	5.726 (14)	2.289
34.5	304.106	298.194	5.912 (11)	2.262
35.0	304.591	298.656	5.935 (13)	2.301
63.3	304.044	297.921	6.123 (13)	2.282
79.2	303.895	297.636	6.259 (10)	2.277
102.7	303.881	297.368	6.513 (12)	2.281

[a] In °C; accurate to ±1°. [b] In hertz. Chemical shift assignments are based on the work of Hobgood and Goldstein,[9a] where ν_A appears at lower field than ν_B. This is also in agreement with temperature dependence, where ν_A could be expected to exhibit the larger temperature dependence. [c] Values in parentheses indicate number of traces used. [d] Values obtained using the relationship: $N = (J_{AB} + J_{AB'}) = (\nu_8 - \nu_1) = (\nu_{8'} - \nu_{1'})$. See structure **2** and Figure 1.

Table III. Temperature Dependences of the Pmr Parameters of **3**

Temp[a]	Scale factor[b]	$J_{CC'}$[c]	$J_{C,^{13}C}$[h]	ν_C[i]
93.9		10.136 (8)[d]		
79.8	0.992	10.216[f] (8)	153.329	372.816
64.3		10.272 (13)		
51.7		10.312 (16)		
28.6	0.992	10.378[f] (10)	153.349	373.105
15.1	0.985	10.396[e,g] (21)		373.194
7.1		10.473 (30)		
5.7		10.518[e] (15)		
0.0	0.990	10.497[f] (8)	153.258	
−17.9	0.987	10.504[g] (10)		373.389
−18.9		10.533 (32)		
−24.5		10.534 (14)		
−32.3		10.596 (21)		
−38.0	0.988	10.651[e,f] (10)	153.328	373.552
−45.2		10.613 (29)		
−58.4		10.651 (28)		
−80.0		10.670 (27)		
−89.0		10.663 (17)		
−96.4	0.975	10.671[f] (12)	153.329	374.016
−99.0		10.696 (16)		
−105.0				374.238

[a] In °C; accurate to ±1°. [b] In Hz/cm; standard deviations 0.02–0.06 Hz; unless otherwise indicated, an average value of 0.99 was used as described above. [c] In hertz; standard deviations 0.02–0.06 Hz; unless otherwise indicated, $J_{CC'}$ was measured using an audio side band from one of the satellite transitions as described in the text. [d] Values in parentheses indicate the number of traces used. [e] Dropped statistically in final calculations. [f] Recorded with side bands from center band as described in the text. [g] Average scale factor (Hz/cm) determined from 19 to 21 separate calibration spectra as described in the text. [h] In hertz; these values were extracted directly for the satellite spectra. When the values for all temperatures were averaged and treated as an AA′X spin system, LAOCOON3 gives a $J_{C,^{13}C}$ value of 152.56 ± 0.4 Hz. [i] In hertz; standard deviations 0.02–0.04 Hz.

Temperature measurements of the downfield ^{13}C-satellite doublet were made in three ways. At five temperatures, nmr spectra were determined with audio side bands from H_C, and provided values for $J_{CC'}$ and $J_{C,^{13}C}$. For each of these five temperatures, $J_{CC'}$ was calculated in two ways: (1) individual scale correction of each sweep and averaging of these corrected couplings; (2) separate averaging of all scale factor corrections, and application of this average scale factor to the average unscaled coupling. Final values of $J_{CC'}$ obtained by each method were always within 0.005 Hz of one another. All values for $J_{CC'}$ used in subsequent calculations were derived using method 2.

For two temperatures, the downfield satellite doublet was determined without audio side bands. Average

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(30) G. W. Wheland, "Resonance in Organic Chemistry," Wiley, New York, N. Y., 1955, p 80.

(31) For a critical discussion of the applicability of theoretical resonance energies and empirical resonance energies, see L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, p 97.

scale factors were obtained before and after each experiment from separate audio side band spectra which were derived from H_1 and located within several hertz of the original satellites. In each case, the before and after scale factors agreed to less than 0.001 Hz/cm.

For all seven temperature experiments described above, the average scale factor never varied by more than 0.02 Hz/cm, and most values were within 0.01 Hz/cm of the average, 0.99 Hz/cm. In the remaining temperature experiments, an audio side band, generated by a frequency of 8.6–9.2 Hz, was produced from one transition of the satellite doublet, and measured with respect to the remaining transition about 1.5 Hz away. At any temperature, a maximum expected error of 0.02 Hz/cm in the above average scale factor (0.99 Hz/cm) would introduce a maximum total scaling error of 0.03 Hz in $J_{CC'}$ but for most cases, the scaling error is thought to be less than 0.01 Hz. Nmr data for **3** are shown in Table III.

Experimental Section

2,3-Dideuterio-1,3-butadiene (2). 2,3-Dideuterio-2,3-butanediol was prepared by reduction of biacetyl with lithium aluminum deuteride according to the procedure of Loewus, Westheimer, and Vennesland.[32] The crude 2,3-dideuterio-2,3-butanediol was distilled through a Vigreux column under vacuum, and the major fraction was collected at 89–92° (21 mm) (reported 95–105° (40 mm)).

2,3-Dideuterio-2,3-butanediol was acetylated in the usual manner[33] using an excess of acetic anhydride and pyridine. The crude product was distilled through a Vigreux column, and the major fraction of 2,3-dideuterio-2,3-diacetoxybutane was collected at 94.0–94.5° (22 mm).

2,3-Dideuterio-2,3-diacetoxybutane (3 g) was added dropwise into a heated Vycor column containing Vycor chips under an atmosphere of N_2 at 585°, using the procedure of Shlechter, Othmer, and Brand.[34] The crude gaseous product was purified by passage through an ice-cooled trap, followed by a bubbler containing 10% aqueous sodium hydroxide solution and a second bubbler containing water. The wet gas was passed through a tube containing a weighed mixture of carbon disulfide and hexamethyldisilane. The nmr tube, which was immersed in a Dry Ice–acetone bath, was evacuated and sealed under vacuum. The mixture was found to be 8.3% (w/w) 2,3-dideuterio-1,3-butadiene (**2**) and 4.6% hexamethyldisilane in carbon disulfide solvent.

1,1,4,4-Tetradeuterio-1,3-butadiene (3). 2,2,5,5-Tetradeuterio-2,5-dihydrothiophene 1,1-dioxide was prepared from sulfolene by alkaline deuterium exchange according to the method of Cope, Berchtold, and Ross.[35] Eight exchanges yielded 99.3% isotopic purity (by nmr integration). Recrystallization from 2:1 THF–pentane gave a mp 63–65° (reported mp 66.8–67.3°).

The above dihydrothiophene 1,1-dioxide (5 g) was pyrolyzed at 130° to generate **3** at a convenient rate. Gaseous **3** was bubbled through two traps, each containing about 100 ml of 10% aqueous sodium hydroxide solution to remove the sulfur dioxide by-product formed in the reaction. The purified **3** was passed through a tube containing Drierite, and into two preconstricted tared nmr tubes containing known weights of hexamethyldisilane. The nmr tubes were immersed in Dry Ice–acetone contained in a dewar flask. In order to minimize boiling of **3** during high temperature experiments, one of these filled nmr tubes was sealed under nitrogen at atmospheric pressure. The second nmr tube, sealed under vacuum, was used for the remaining variable-temperature study. Both samples contained 11% (w/w) hexamethyldisilane in neat **3**.

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Conformational Analysis of 2-Methylbutane[1]

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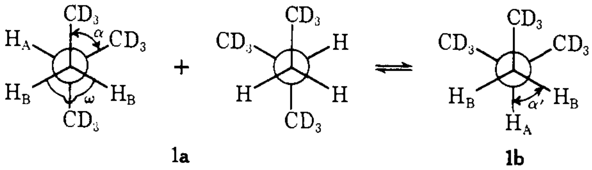
Abstract: The AB_2 deuterium-decoupled pmr spectrum of 2-methylbutane-d_9 (**1**) was determined at ten temperatures in the range −91 to +72°. The observed temperature dependences of the three nmr parameters (ν_A, ν_B, and J_{AB}) were ascribed to changes in conformer population with temperature (eq 1). These parameters were subsequently used in a least-squares analysis to obtain quantitative estimates of ΔH and the intensive nmr parameters of conformers **1a** and **1b**. The value of ΔH for the equilibrium **1a** $\rightleftharpoons$ **1b** is 888 ± 18 cal/mol ($\Delta S = -1.376$ eu). The torsional angle, α, for **1a** was estimated to fall between 60 and 72° from the calculated vicinal coupling constant.

Rotational isomerism in 2-methylbutane has been observed by Raman,[3] infrared,[4] ultrasonic,[5] and thermodynamic[6] methods, and estimates were made of both the enthalpy difference between the two possible conformers and their barrier to interconversion.

Szasz and Sheppard concluded from Raman[3] that the enthalpy difference for the equilibrium **1a** $\rightleftharpoons$ **1b** was



1a
C_i

1b
C_s

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