degassed by three freeze–pump–thaw cycles and then sealed. (B) **1** (0.01 mmol), di-*tert*-butyl diperoxyoxalate (0.01 mmol), and benzene (0.40 mL) were placed in an ESR cell, and the solution was degassed as above and then sealed. (C) Dimer **3** (0.01–0.03 mmol) and solvent (0.40 mL) were placed in an ESR cell, and the solution was degassed as above and then sealed.

Measurement of Equilibrium Constants. Dimer **3** (0.64×10^{-2}–2.51×10^{-2} mmol) was dissolved in solvent (total volume 10 mL). The solution (0.20 mL) was placed in an ESR cell and integrated signals were recorded on the ESR instrument equipped with a JES-ID-2 integrator. Areas under the integrated curves were determined by their weights. Calibration curves were obtained as follows: 0.20 mL of 1,3,5-triphenylverdazyl solutions (0.20–1.00 mM) was placed in the same cell used for the dimer solutions, and integrated signals were recorded with the same instrument settings.

Registry No. 1a, 74282-58-9; **1b**, 74282-59-0; **1c**, 74282-60-3; **1d**, 74282-61-4; **1e**, 74282-62-5; **1f**, 74282-63-6; **1g**, 74282-64-7; **1h**, 74282-65-8; **2a**, 74282-66-9; **2b**, 74282-67-0; **2c**, 74282-68-1; **2d**, 62991-69-9; **2e**, 62991-70-2; **2f**, 74282-69-2; **2g**, 74282-70-5; **2h**, 62991-71-3; **3a**, 74282-71-6; **3b**, 74282-72-7; **3c**, 74282-73-8; **3d**, 74282-74-9; **3e**, 74282-75-0; **3g**, 74282-76-1; **4**, 62991-73-5; 3,5-di-*tert*-butylaniline, 2380-36-1; benzenesulfenyl chloride, 931-59-9; benzene-*2,3,4,5,6*-d_5-sulfenyl chloride, 74282-77-2; 4-methylphenylsulfenyl chloride, 933-00-6; 4-chlorophenylsulfenyl chloride, 933-01-7; 4-bromophenylsulfenyl chloride, 1762-76-1; 4-nitrophenylsulfenyl chloride, 937-32-6; 2,4-dichlorophenylsulfenyl chloride, 38064-02-7; 3,5-dichlorophenylsulfenyl chloride, 74282-78-3.

Alkane Stereodynamics: Nuclear Magnetic Resonance and Empirical Force Field Studies of 2,2,3,3-Tetramethylpentane and 3,3,4,4-Tetramethylhexane

C. Hackett Bushweller,*[1a] Warren G. Anderson,[1a] Martin J. Goldberg,[1a] Mona W. Gabriel,[1a]
Laura R. Gilliom,[1b] and Kurt Mislow*[1b]

Departments of Chemistry, University of Vermont, Burlington, Vermont 05405, and Princeton University, Princeton, New Jersey 08544

Received February 27, 1980

The two title compounds have been studied by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by empirical force field calculations using Allinger's 1971, Allinger's MM2, and Bartell's MUB-2 force fields. The experimental work on 2,2,3,3-tetramethylpentane shows restricted *tert*-butyl rotation with $\Delta G^{\ddagger} = 9.4$ kcal/mol. 3,3,4,4-Tetramethylhexane exists as a statistical mixture of gauche and anti conformers, with rotation about the central bond requiring $\Delta G^{\ddagger} = 10.4$ kcal/mol. The calculated barriers are critically compared with the experimentally determined values. In conjunction with this work, the barrier to central-bond rotation in hexamethylethane has been estimated at 8.4–8.8 kcal/mol.

Studies in static and dynamic stereochemistry which combine experimental measurements with empirical force field (EFF) calculations[2] are finding increasing use in the conformational analysis of substituted alkanes. Experimental work has confirmed the theoretical predictions of ground-state structures in symmetrically substituted tetraalkylethanes,[3,4] tetraarylethanes,[5] and related systems.[6-9a] The barrier to rotation about the central bond calculated by the EFF method has been experimentally verified for many of these systems,[3b,6a,9b] usually by dynamic NMR (DNMR) studies.[10]

Table I. EFF Minima for TMP and TMH from ALL-71

	descriptor[a]	symmetry[b]	steric energy[c]
TMP	(a)	C_s	6.1
	(+)	C_s	7.8
TMH	G(a)(a)	C_2	9.1
	G(+)(+)	C_2	12.7
	G(−)(−)	C_2	12.8
	A(a)(a)	C_{2h}	9.2
	A(+)(−)	C_i	12.7
	A(−)(−)	C_2	13.0
	A(+)(+)	C_2	12.4

[a] A implies an anti conformation with respect to $\phi = C_{Et}$-C-C-C_{Et}. G implies a gauche conformation. We define torsion angle δ such that for TMP δ = C2-C3-C4-C5 and for TMH δ = C1-C2-C3-C4 (or (equivalently) δ = C3-C4-C5-C6. The three descriptors +, −, and a (for anti) refer to $0° < \delta < 120°$, $-120° < \delta < 0°$, and $|\delta| \geq 120°$, respectively. [b] Refers to symmetry of input structure. [c] In kcal/mol.

Hexamethylethane (HME), a key compound in studies of carbon–carbon single bond rotation, is not amenable to analysis by the DNMR approach for reasons of symmetry. We have therefore examined two structurally similar but less symmetric systems, 2,2,3,3-tetramethylpentane (TMP) and 3,3,4,4-tetramethylhexane (TMH), by this technique and have compared the results with the predictions of EFF calculations.

Results and Discussion

2,2,3,3-Tetramethylpentane (TMP). Three different EFF's were employed in a study of TMP: Allinger's 1971[11]

---

(1) (a) University of Vermont. (b) Princeton University.

(2) For recent reviews of the EFF method, see: (a) Dunitz, J. D.; Bürgi, H. B. *MTP Int. Rev. Sci.: Org. Chem., Ser. One* **1976**, 81; Ermer, O. *Struct. Bonding (Berlin)* **1976**, *27*, 161; (b) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1; Altona C.; Faber, D. H. *Fortschr. Chem. Forsch.* **1974**, *45*, 1. See also: *Comput. Chem.* **1977**, *1*, 139.

(3) (a) Jacob, E. J.; Thompson, H. B.; Bartell, L. S. *J. Chem. Phys.* **1967**, *47*, 3736. (b) Ōsawa, E.; Shirahama, H.; Matsumoto, T. *J. Am. Chem. Soc.* **1979**, *101*, 4824 and references therein.

(4) Baxter, S. G.; Fritz, H.; Hellmann, G.; Kitschke, B.; Lindner, H. J.; Mislow, K.; Rüchardt, C.; Weiner, S. *J. Am. Chem. Soc.* **1979**, *101*, 4493.

(5) Finocchiaro, P.; Gust, D.; Hounshell, W. D.; Hummel, J. P.; Maravigna, P.; Mislow, K. *J. Am. Chem. Soc.* **1976**, *98*, 4945. Dougherty, D. A.; Mislow, K.; Blount, J. F.; Wooten, J. B.; Jacobus, J. *Ibid.* **1977**, *99*, 6149. Dougherty, D. A.; Llort, F. M.; Mislow, K.; Blount, J. F. *Tetrahedron* **1978**, *34*, 1301.

(6) (a) Baxter, S. G.; Dougherty, D. A.; Hummel, J. P.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 7795. (b) Baxter, S. G.; Mislow, K.; Blount, J. F. *Tetrahedron* **1980**, *36*, 605.

(7) Ardebili, M. H. P.; Dougherty, D. A.; Mislow, K.; Schwartz, L. H.; White, J. G. *J. Am. Chem. Soc.* **1978**, *100*, 7994.

(8) Beckhaus, H.-D.; McCullough, K. J.; Fritz, H.; Rüchardt, C.; Kitschke, B.; Lindner, H. J.; Dougherty, D. A.; Mislow, K. *Chem. Ber.* **1980**, *113*, 1867.

(9) (a) Aime, S.; Harris, R. K.; McVicker, E. M.; Fild, M. *J. Chem. Soc., Chem. Commun.* **1974**, 426. (b) Brunelle, J. A.; Bushweller, C. H.; English, A. D. *J. Phys. Chem.* **1976**, *80*, 2598.

(10) Jackman, L. M.; Cotton, F. A., Eds.; "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1975.

(11) Allinger, N. L.; Tribble, M. T.; Miller, M. A.; Wertz, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 1637.

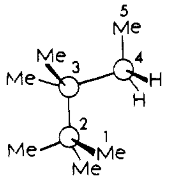
0022-3263/80/1945-3880$01.00/0 © 1980 American Chemical Society

Table II. Rotation Barriers[a] in Several Simple Hexaalkylethanes

	calculated			exptl[b]	
	ALL-71	MM2	MUB-2	^{1}H DNMR	^{13}C{^{1}H} DNMR
HME	6.2	5.3[c]	10.5		
TMP	7.2	6.0	11.1	9.4[d]	9.6
TMH, G → $\bar{G}$	8.6	7.1	11.9	10.4	10.5
G → A	8.1	6.8	11.7	10.4	10.5

[a] In kcal/mol. [b] $\Delta G^\ddagger$ values. See reference 27. [c] Reference 3b. [d] Reference 19.

(ALL-71), Allinger's 1977[12] (MM2), and Bartell's modified Urey–Bradley[13] (MUB-2) force fields. Calculations were carried out as previously described,[14] with input structures[15] optimized by the pattern-search minimization technique. To ensure that the search reached a true minimum, in every calculation structures with torsional angles "on both sides" of the supposed minimum were input and optimized. The full relaxation technique was used, and all structures were optimized without symmetry constraints. Each of the three force fields yields a ground-state geometry for TMP with C5 anti to C2 (see idealized structure I and Table I). ALL-71 and MM2 predict a twisted ground state (ϕ = C1–C2–C3–C4 = 41.2 and 43.9°, respectively); MUB-2 predicts a broad minimum centered at ϕ = 60°. To study rotation in TMP, we used



I

incremental group driving calculations. The torsion angle ϕ was frozen at decreasing values[16] and the resulting structures were minimized with respect to all other internal parameters. The difference between the steric energy of the "transition state" so obtained and that of the ground-state structure was taken as an approximation to the rotation barrier. These calculated barrier heights for rotation about the C2–C3 bond through ϕ = 0° are listed in Table II.

Examination of the ^{1}H NMR spectrum (60 MHz) of TMP in CH_2CHCl at 206 K shows the expected *tert*-butyl singlet (δ 0.84), 3,3-dimethyl singlet (δ 0.75), and A_2C_3 spin system for the ethyl group (δ_A 1.28, δ_C 0.81, $^3J_{AC}$ = 7.3 Hz; see Figure 1). A theoretical decomposition of this spectrum is shown in the left column of Figure 2.[17] The spectrum of TMP at 206 K is consistent with rapid *tert*-butyl group rotation on the NMR time scale.

At lower temperatures (Figure 1), the *tert*-butyl resonance undergoes a decoalescence phenomenon. A complete line-shape simulation[17] of the spectrum revealed that the 3,3-dimethyl and ethyl subspectra had remained unchanged but that the *tert*-butyl peak was separated at 136 K into two singlets at δ 0.82 (6 H) and δ 0.87 (3 H). A theoretical decomposition of the spectrum at 136 K is presented in the right hand column of Figure 2. The ^{1}H DNMR behavior for TMP can be simulated accurately by using a model incorporating three superimposed subspectra, two of which are not subject to exchange effects (i.e., ethyl and 3,3-dimethyl) and one of which is subject to exchange effects (i.e., *tert*-butyl), consistent with slowing the rotation illustrated in eq 1.[18] The activation param-

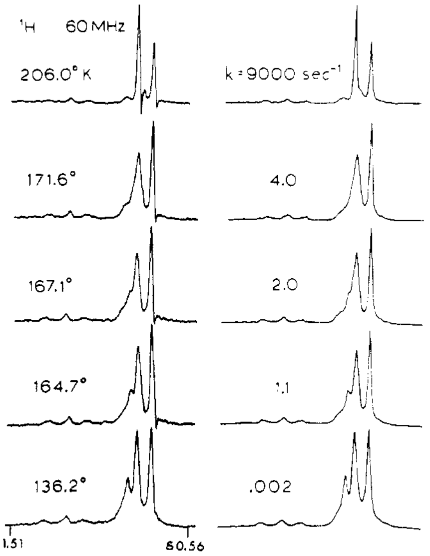


Figure 1. Experimental ^{1}H DNMR spectra (60 MHz) of 2,2,3,3-tetramethylpentane (5% v/v in CH_2CHCl; left column) and theoretical spectra calculated as a function of the rate of *tert*-butyl group rotation (*k* is the first order rate constant for conversion of one topomer to the other; right column).

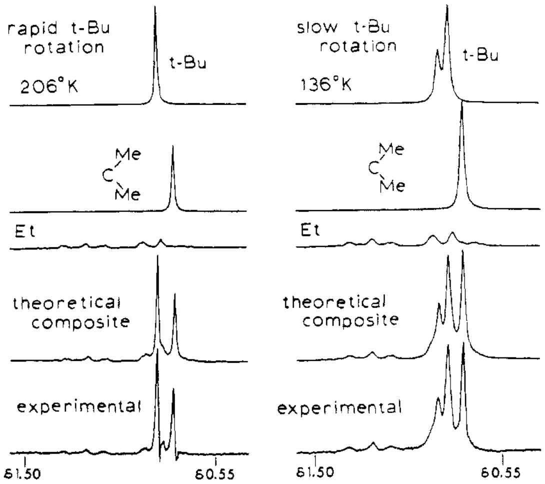


Figure 2. Decomposition of the ^{1}H DNMR spectrum of 2,2,3,3-tetramethylpentane under conditions of rapid *tert*-butyl group rotation at 206 K (left column) and slow *tert*-butyl group rotation at 136 K (right column).

---

(12) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

(13) Fitzwater, S.; Bartell, L. S. *J. Am. Chem. Soc.* **1976**, *98*, 5107.

(14) Andose, J. D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 2168. All calculations used the program BIGSTRN (Program No. 348, Quantum Chemistry Program Exchange, Indiana University).

(15) Two C_s input structures were used in searching for the ground state for TMP: torsion angle δ = C2–C3–C4–C5 = ca. 0 and ca. 180°.

(16) The torsional angle ϕ was held fixed at a given value (ϕ_0) by imposing a large quadratic potential, $E_{\text{fix}} = 10000(\phi - \phi_0)^2$ kcal/mol. This technique is a modified version of one originally employed by: Wiberg, K. B.; Boyd, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 8426.

(17) The computer program used to simulate the DNMR spectra is a substantially modified local version of DNMR3 by: Kleier, D. A.; Binsch, G. *J. Magn. Reson.* **1970**, *3*, 146 (Program No. 165, Quantum Chemistry Program Exchange, Indiana University). Our local modifications are described in: Bushweller, C. H.; Bhat, G.; Letendre, L. J.; Brunelle, J. A.; Bilofsky, H. S.; Ruben, H.; Templeton, D. H.; Zalkin, A. *J. Am. Chem. Soc.* **1975**, *97*, 65.

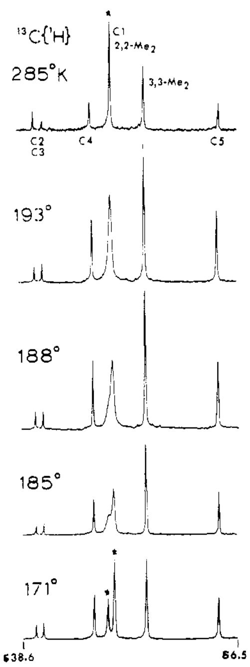
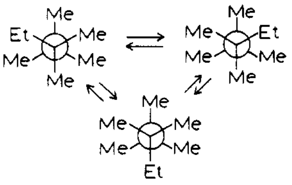


Figure 3. Experimental $^{13}C\{^1H\}$ DNMR spectra (22.64 MHz) of 2,2,3,3-tetramethylpentane (30% v/v in 50/50 CD_2Cl_2/CS_2). The resonances due to the *tert*-butyl methyl carbons are indicated by asterisks.

eters for *tert*-butyl rotation in TMP derived from the DNMR line-shape analysis are $\Delta H^\ddagger = 9.6 \pm 0.4$ kcal/mol, $\Delta S^\ddagger = 1 \pm 3$ gibbs/mol, and $\Delta G^\ddagger = 9.4 \pm 0.1$ kcal/mol at 172 K.[19]



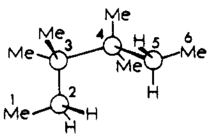
(1)

A $^{13}C\{^1H\}$ DNMR investigation (22.64 MHz) of TMP in CD_2Cl_2/CS_2 gave results completely in accord with the ^1H DNMR study. Consistent with the calculated preferred geometry, the C2 (δ 37.31, Me_4Si reference), C3 (δ 35.96), C4 (δ 28.85), 3,3-dimethyl (δ 20.70), and C5 (δ 9.33) $^{13}C\{^1H\}$ resonances remained unchanged as the temperature was lowered. However, the signal for the three *tert*-butyl methyl carbons (δ 25.72 at 285 K) was separated at 171 K into two singlets at δ 25.99 (1C) and 24.94 (2C), as indicated by the asterisks in Figure 3. The free energy of activation ($\Delta G^\ddagger$) for *tert*-butyl rotation as determined from a two-site DNMR simulation at 188 K is 9.6 ± 0.2 kcal/mol, in excellent agreement with the ^1H DNMR data.

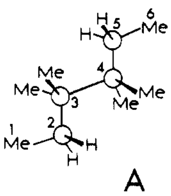
Comparison of the calculated and experimental values for the rotation barrier (Table II) shows that the magnitudes predicted by the Allinger fields are low while MUB-2 gives a high value. The tendency for MM2 to underestimate barrier heights has previously been noted and discussed.[3b]

3,3,4,4-Tetramethylhexane (TMH). TMH is of interest not only because of its structural relationship to HME but also because it is capable of gauche and anti conformers and has two possible itineraries for rotation about its central bond.

In keeping with our earlier observation[6a] that the global minima of many substituted ethanes correspond to symmetric structures containing either a center of inversion or a two-fold rotation axis, we considered only three C_2 gauche and four anti (two C_2, one each C_i and C_{2h}) input structures for TMH. Relaxation of these structures yielded seven unique minima. The structures corresponding to the lowest energy minima are a C_2 gauche (idealized sketch, G) conformer[20] and a C_{2h} anti (idealized sketch, A) conformer.[21]



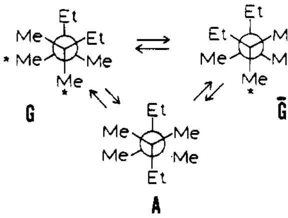
G



A

As indicated in Table I, the other minima are of significantly higher energy and are not further considered. Since the steric energies of G and A differ by less than 0.2 kcal/mol for all three force fields, we expect a statistical mixture of gauche and anti conformers.

In discussing central-bond rotation for a similar system, we previously found it useful to examine the two pathways producing enantiomerization.[6a] The molecule can rotate directly through $\phi = 0°$ (in the case of TMH, $\phi = C_{Et}$–C–C–C_{Et}) in a gauche-to-gauche mechanism ($G \rightleftarrows \bar{G}$) or it can rotate through $\phi = 180°$ in a gauche-to-anti-to-gauche mechanism ($G \rightleftarrows A \rightleftarrows \bar{G}$); see eq 2. The calculated barrier heights for conformer interconversion for TMH, obtained as described above, are presented in Table II. While it appears that the $G \rightarrow \bar{G}$ barrier is slightly greater than the $G \rightarrow A$ barrier, this difference lies well with the error limits of the method,[2a,6a,22] and the magnitudes of the two barriers should therefore be considered equal.



(2)

The high-field ^1H NMR spectrum (270 MHz) of TMH in CH_2CHCl at 229 K shows a singlet for the 3,3,4,4-tetramethyl protons (δ 0.74) and an A_2X_3 pattern for the ethyl groups (δ_A 1.29, δ_X 0.81, $^3J_{AX} = 7.5$ Hz) as illustrated at the top of the center column of Figure 4. At lower temperatures, the spectrum undergoes exchange broadening and then is sharpened into a complex spectrum at 159 K (Figure 4). This spectrum can be decomposed by line-shape analysis into just two subspectra which corre-

---

[18] The singlet resonances for the *tert*-butyl and 3,3-dimethyl groups as well as the A_2C_3 spectrum for ethyl at 136 K indicate that all protons on any given methyl group are equivalent; i.e., all individual methyl rotations are fast on the NMR time scale at this temperature.

[19] Bushweller, C. H.; Anderson, W. A. *Tetrahedron Lett.* **1972**, 1811. In this paper there is a typographical error. The $\Delta G^\ddagger$ value for TMP on p 1813 should be 9.3 kcal/mol (−102 °C).

[20] Calculations using both Allinger fields uncovered two gauche minima, G1 at $\phi \simeq 40°$ and G2 at $\phi \simeq 80°$, where ϕ is the C_{Et}–C–C–C_{Et} torsion angle. The difference in the calculated steric energy for the structures corresponding to these two minima is less than 0.05 kcal/mol. Interconverting G1 and G2 by driving ϕ through $\phi = 60°$ yielded barriers of 2.7 (ALL-71) and 1.4 kcal/mol (MM2). A barrier of this magnitude would not be detectable by DNMR, and in describing the gauche conformer (G), we are therefore considering the time average of G1 and G2. In calculating rotation barriers, we have assigned the steric energy of G2 to G. In contrast to the Allinger fields, MUB-2 produced a single broad minimum centered around $\phi \simeq 60°$.

[21] ALL-71 and MM2 also yielded a twisted anti minimum, $\phi \simeq 160°$, with barriers to enantiomerization through the C_{2h} structure of 3.0 and 1.4 kcal/mol, respectively. MUB-2 yields a single anti minimum centered around $\phi \simeq 180°$.

[22] Jacobus, J. *Tetrahedron Lett.* **1976**, 2927.

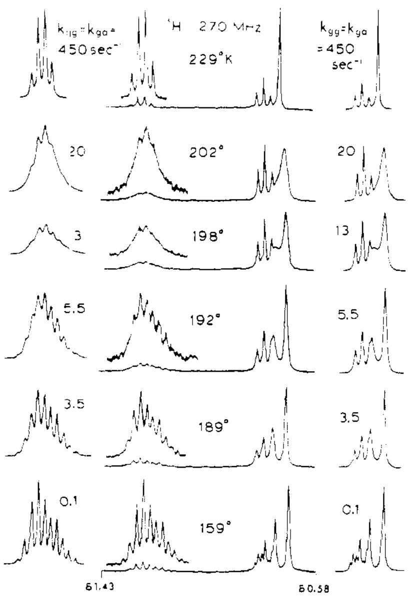


Figure 4. Experimental ^{1}H DNMR spectra (270 MHz) of 3,3,4,4-tetramethylhexane (4% v/v in CH_2CHCl; see middle column). The methylene protons' signal is recorded at increased amplitude above each complete spectrum. Theoretical DNMR spectra for the methylene protons (left column) and all methyl groups (right column) are computed as a function of the rate of the direct G → $\bar{G}$ (k_{gg}) and G → A (k_{ga}) processes.

spond to the two different molecular geometries.

One subspectrum is composed of an A_2X_3 spin system (δ_A 1.28, δ_X 0.80, $^3J_{AX}$ = 7.3 Hz) for the ethyl groups and one singlet (δ 0.69) for the 3,3,4,4-tetramethyl protons. The area ratio of the A_2X_3 spectrum to the singlet is 5:6, and thus this subspectrum corresponds to the A conformation of TMH. The two equivalent protons on a given methylene group give rise to the A_2X_3 subspectrum for the ethyl groups while the four equivalent 3,3,4,4-tetramethyl groups give rise to the singlet. This theoretically dissected subspectrum is shown in Figure 5.

The second subspectrum is composed of a BCY_3 spin system (δ_B 1.27, δ_C 1.19, δ_Y 0.79, $^2J_{BC}$ = 13.5 Hz, $^3J_{BY}$ = $^3J_{CY}$ = 7.3 Hz) for the ethyl protons and two singlets of equal area for the 3,3,4,4-tetramethyl groups (δ 0.75, 0.70) as illustrated in the middle spectrum of Figure 5. The area ratio of the BCY_3 spectrum to the two singlets combined is 5:6. Thus, this subspectrum corresponds to the gauche rotamer of TMH (G). In principle, the two protons on a given methylene group of G should be nonequivalent, and, in fact, this is reflected in the BCY_3 subspectrum of the ethyl groups at 159 K. Also, the two different types of 3,3,4,4-tetramethyl protons in G are indicated by the two observed singlets.

The ^{1}H DNMR spectrum of TMH at 159 K is consistent with slow rotation about the C3-C4 bond and reflects not only a slow G ⇄ A process but also slow G ⇄ $\bar{G}$ interconversion. If the former process were slow at 159 K and the latter were fast, the spectrum of the gauche rotamers would collapse to a B_2Y_3 spin system for the ethyl groups and to one singlet for the 3,3,4,4-tetramethyl protons. If the G ⇄ $\bar{G}$ process were slow and the G ⇄ A equilibrations remained fast, no changes at all would be observed in the variable-temperature ^{1}H NMR spectrum of TMH.

The composite spectrum in Figure 5 is an accurate simulation of the experimental spectrum at 159 K (Figure 4) and is composed of a superposition of two spectra corresponding to 30% anti and 70% gauche rotamers; K_{eq} = [gauche]/[anti] = 2.33, and $\Delta G°$ = −0.27 kcal/mol ($\Delta G°$ = −0.22 kcal/mol for a purely statistical mixture). This result is in fair agreement with the EFF prediction of a statistical distribution of rotamers.

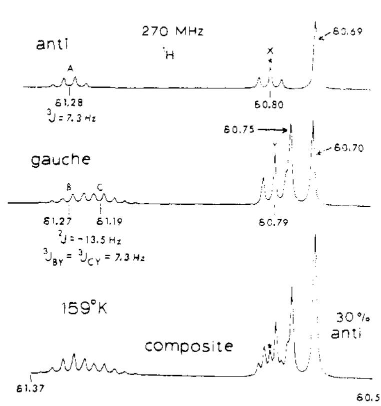


Figure 5. Decomposition of the slow-exchange ^{1}H NMR spectrum of 3,3,4,4-tetramethylhexane at 159 K.

The kinetic model that best simulated the ^{1}H DNMR spectrum of TMH employed equal barriers for the G ⇄ $\bar{G}$ and G ⇄ A processes (see Figure 4). Activation parameters derived from the line-shape analyses for these processes are $\Delta H^{\ddagger}$ = 9.8 ± 0.4 kcal/mol, $\Delta S^{\ddagger}$ = −3 ± 2 gibbs/mol, and $\Delta G^{\ddagger}$ = 10.4 ± 0.1 kcal/mol at 190 K.

A $^{13}C\{^1H\}$ DNMR (50.2 MHz) study of TMH in CD_2Cl_2/CS_2 gave results consistent with the ^{1}H DNMR study discussed above. The $^{13}C\{^1H\}$ spectrum at 269 K consists of four singlets due to C3,4 (δ 38.26), C2,5 (δ 28.61), the 3,3,4,4-tetramethyl carbons (δ 20.62), and C1,6 (δ 9.32) as shown in Figure 6. At lower temperatures, the C2,5 and 3,3,4,4-tetramethyl carbon resonances broaden, and each split at 173 K into two singlets separated, respectively, by 40.5 and 43.5 Hz (Figure 6). The smaller C2,5 singlet (δ 28.47) is assigned to A and the larger C2,5 singlet (δ 27.66) to G. The smaller 3,3,4,4-tetramethyl signal (δ 20.72) is assigned to the methyl groups of G marked by asterisks in eq 2. The larger 3,3,4,4-tetramethyl singlet (δ 19.86) is due to one signal from A and a second signal from the other methyls of G in eq 2. It is apparent that these latter two singlets are nearly superimposed. The C1,6 and C3,4 signals are also separated into two singlets at 173 K but with much smaller chemical shift differences (2.9 and 2.0 Hz, respectively; see insets in spectrum at 173 K in Figure 6). The ratio of G to A rotamers as determined from the $^{13}C\{^1H\}$ spectra agree with the ^{1}H NMR data. The free energy of activation at 203 K for the G ⇄ A process as determined from a two-site DNMR simulation of the C2,5 spectrum (Figure 6) is 10.5 ± 0.3 kcal/mol, again in excellent agreement with the ^{1}H DNMR results.

Both DNMR and EFF calculation find approximately equal barriers for the G → $\bar{G}$ and G → A processes. The magnitudes of the calculated barriers differ from the DNMR results in the same way they differed for TMP: ALL-71 and MM2 yield low estimates while MUB-2 gives a high estimate.

Hexamethylethane (HME). The ground-state structure of HME has D_3 symmetry, as determined by EFF calculations and gas-phase electron diffraction.[23] As also found for the various barriers calculated in the present work, the calculated (EFF) barrier to rotation about the central carbon–carbon bond in HME[24] is highly force field dependent (Table II). An experimental attempt to estimate this barrier by extrapolation from measured rotation

---

[23] (a) Iroff, L. D.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 2121, ref 39. (b) Bartell, L. S.; Boates, T. L. *J. Mol. Struct.* **1976**, *32*, 379. Reference 3a in this paper.

[24] For other calculations of the barrier to central-bond rotation in HME see: Braun, H.; Lüttke, W. *J. Mol. Struct.* **1976**, *31*, 97; reference 3a in this paper.

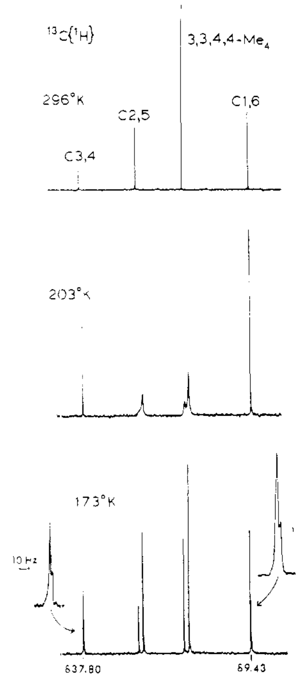


Figure 6. Experimental $^{13}C\{^1H\}$ DNMR spectra (50.2 MHz) of 3,3,4,4-tetramethylhexane (10% v/v in 50/50 CD_2Cl_2/CS_2).

barriers in similar chlorine-substituted systems led to a predicted barrier height of 9.6 kcal/mol.[25] However, we feel that an extrapolation from the experimental barrier heights for TMP and TMH, as supported by our EFF study of these compounds and of HME, provides a more reliable estimate of the barrier to central-bond rotation in HME. By examining the experimental barriers to rotation in TMP and TMH and trends in the calculated barriers for TMH, TMP, and HME (Table II), we conclude that the actual barrier to central-bond rotation in HME lies between 8.4 and 8.8 kcal/mol.

Experimental Section

The 60-MHz ^1H DNMR spectra were recorded by using a Varian HR-60A continuous-wave NMR spectrometer equipped with a custom-built variable temperature probe.[26] Temperature measurements in this probe are accurate to ± 0.2 K. The 270-MHz ^1H DNMR spectra were recorded in the pulsed Fourier transform mode on a Bruker 270-MHz NMR system at the Southern New England High Field NMR Facility at Yale University. Temperature measurements are accurate to ±2.0 K. The 22.64- and 50.2-MHz $^{13}C\{^1H\}$ DNMR spectra were recorded, respectively, on a Bruker WH-90D NMR system and a Varian XL-200 NMR spectrometer. Temperature measurements for the latter two systems are accurate to ±5.0 K.

2,2,3,3-Tetramethylpentane and 3,3,4,4-tetramethylhexane were purchased from Chemical Samples Co. and were used without further purification. All NMR samples were degassed three times and the NMR tubes sealed.

Acknowledgment. C.H.B. and K. M. are grateful for support from the National Science Foundation (Grant No. CHE78-21161 and CHE77-07665, respectively). We thank Dr. W. Jankowski of Varian Associates for running the 50.2-MHz 13C{1H} DNMR spectra of TMH and Linda D. Iroff for helpful discussions. We wish to acknowledge the support of the Southern New England High Field NMR Facility made possible by a grant from the Biotechnology Resources Program of the National Institutes of Health (RR-798).

Registry No. 2,2,3,3-Tetramethylpentane, 7154-79-2; 3,3,4,4-tetramethylhexane, 5171-84-6; hexamethylethane, 594-82-1.

---

(25) Anderson, J. E.; Pearson, H. *J. Am. Chem. Soc.* **1975**, *97*, 764. An attempt to measure the barrier height thermodynamically can be found in: Scott, D. W.; Douslin, D. R.; Gross, M. E.; Oliver, G. D.; Huffman, H. M. *J. Am. Chem. Soc.* **1952**, *74*, 883.

(26) Jensen, F. R.; Smith, L. A.; Bushweller, C. H.; Beck, B. H. *Rev. Sci. Instrum.* **1972**, *43*, 894.

(27) A more appropriate comparison might be made between the EFF barriers and $\Delta H^{\ddagger}$ obtained from the ^1H DNMR line-shape simulations. However, the overall magnitude of systematic errors in any determination of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values using the DNMR method is difficult to assess, and the most accurately determined activation parameter is consistently $\Delta G^{\ddagger}$; cf.: Shoup, R. R.; Becker, E. D.; McNeel, M. L. *J. Phys. Chem.* **1972**, *76*, 71. With regard to the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values reported in the text, the rich complexity of the ^1H NMR spectra of both TMP and TMH should lead to accurate rate constants from simulation of the exchange-broadened spectra. This situation and our efforts to measure the sample temperature as accurately as possible give us reasonable confidence in these $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, but we choose to take a conservative approach in the values used for comparison in Table II.

Acidities of Sulfoximines and Related Oxosulfonium Cations. Cyclopropyl Effects and Structures of α-Sulfonyl-Type Carbanions

Frederick G. Bordwell,*[1] John C. Branca,[1] Carl R. Johnson,*[2] and Noel R. Vanier[1]

Departments of Chemistry, Northwestern University, Evanston, Illinois 60201, and Wayne State University, Detroit, Michigan 48202

Received January 24, 1980

(Dimethylamino)methylphenyloxosulfonium cation, $PhS(O)(NMe_2)CH_3^+$, was found to be more acidic than the parent sulfoximine, $PhS(O)(NMe)CH_3$, by about 19 pK_a units. The latter is about equal in acidity to $PhS(O)CH_3$ and about 5 pK_a units less acidic than $PhSO_2CH_3$. The cyclopropyl compounds, c-PrG, with G equal to $Ph(NMe_2)SO^+$, p-$MeC_6H_4(NMe_2)SO^+$, F_3CSO_2, and $Ph(PhSO_2N)SO$, were found to be about 4–7 pK_a units less acidic than their acyclic methyl analogues, CH_3G. This is interpreted as evidence for a demand on the part of sulfone-type functions for p character in cyclopropyl carbanions. Evidence is presented to show that carbanions of the type GCH_2^-, where G is an electron-withdrawing function such as RSO_2, RS(O)(NR), RSO, Ph_2PO, $(RO)_2PO$, and the like, are planar or nearly planar. Acidity data indicate that the preferential generation of chiral, rather than achiral, planar α-sulfonyl carbanions is a consequence of a preferred kinetic pathway rather than an inherent greater thermodynamic stability. Factors controlling the stereoselective generation and reactions of carbanions are reviewed.

The sulfonyl function, SO_2G, where G is R, Ar, NRAr, or OR, has proved to be superior to other strongly electron-withdrawing functions [COPh, CN, $P(O)Ph_2$, $P(O)(OR)_2$, S(O)R, and the like] in promoting the generation

0022-3263/80/1945-3884$01.00/0