J. Am. Chem. Soc. **1988**, *110*, 8029–8038

Rotational Barriers. 2. Energies of Alkane Rotamers. An Examination of Gauche Interactions

Kenneth B. Wiberg* and Mark A. Murcko

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511. *Received February 11, 1987*

Abstract: The barrier to rotation about the C2–C3 bond in *n*-butane has been calculated using several basis sets, complete geometry optimization, and correction for electron correlation. Neither the basis set size nor inclusion of electron correlation has a large effect on the magnitude of the rotational barrier or the trans/gauche energy difference. After correction for zero-point energy differences, the former is found to be 6.34 kcal/mol, while the latter is 0.86, in very good agreement with the experimental value. The trans/gauche energy difference in *n*-pentane is the same as that for butane, and similar values are found for the two gauche forms of *n*-hexane and the symmetrical gauche form of octane. The structures and energies of several conformers of pentane and hexane with two and three gauche fragments also have been obtained. It is found that the pentane rotamer with two consecutive gauche kinks has roughly twice the gauche energy, but the hexane conformer with three consecutive gauche kinks has considerably less than 3 times that value. The energy differences for the rotamers of 2-methylbutane and 2,3-dimethylbutane are well reproduced by the calculations. Vibrational frequencies are estimated at the 3-21G level for all species, and the zero-point energies and enthalpy changes ($H_{298} - H_0$) are calculated. The difference in enthalpy between an axial and equatorial methyl substituent on cyclohexane is calculated to be 2.17 kcal/mol after correcting for vibrational energy differences. The relationship between the energy of a methylene group in cyclohexane and in *trans*-*n*-alkanes is examined.

I. Butane. Butane is a key to understanding torsional interactions about carbon–carbon single bonds, and such interactions are central to all efforts in molecular modeling.[1] Torsional interactions also are of importance in studies of polymethylene chains.[2] As a result, the barrier to rotation about the C2–C3 bond in butane has been extensively studied, both experimentally[3-11] and theoretically.[12-18]

The trans/gauche energy difference in the gas phase appears to be fairly well determined from experimental measurements as 0.89 ± 0.03 kcal/mol (Table I).[3-7] The trans/syn energy difference is much more difficult to measure experimentally, and a long extrapolation of spectroscopic data led to a barrier of 4.6 kcal/mol.[6] Although it may be subject to considerable uncertainty, this value has been strongly advocated by Allinger.[1,14,18]

Ab initio molecular orbital (MO) calculations using split-valence basis sets lead to a trans/gauche energy difference of 0.9–1.2 kcal/mol and a trans/syn energy difference of 5.0–6.5 kcal/mol, which is relatively independent of the basis set used.[12-16] Raghavachari[17] has reported a detailed examination of the effect of electron correlation on the energy differences using the Moller-Plesset perturbation treatment[19] and found that it had a relatively small effect on the barrier height and that it decreased the gauche/trans energy difference to between 0.60 and 0.70 kcal/mol. This value is significantly smaller than those found experimentally, whereas the calculated barrier is larger than the experimental value. The reason for these differences has been the subject of discussion[1,14,17] and will further be considered herein.

Table I. Trans vs Gauche Energies for Butane (cal/mol)

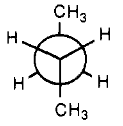
a. Experimental Values

value	phase	method	ref
966 ± 50	gas	Raman	3
887	gas	far IR	5
889 ± 29	gas	Raman	6
751 ± 235	gas	ED	7
540 ± 100	liquid	Raman	8
557 ± 13	liquid	Raman	9
571 ± 109	liquid	IR	10
537 ± 70	CH_2Cl_2 soln	Raman	11

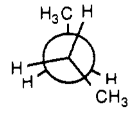
b. Calculated Values

value	details of calculation	ref
1090	4-31G std geom, CCC angles optimized only	12
950	STO-3G exp geom, rigid rotation	13
880	STO-3G using MM2-optimized geometries	14
1190	4-31G partially optimized	15
1070	4-31G fully optimized	16
600–700	MP3/6-311G**//MP2/6-31G	17

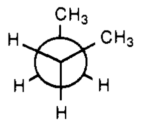
What are the sources of error in the MO calculations? Energies and geometries are dependent on basis set size as well as the possible effects of electron correlation. In order to see if the inclusion of polarization functions at hydrogen might affect the calculated geometries and relative energies, we have carried out geometry optimizations using the 6-31G** basis set for the two energy minima (trans and gauche) and for the two saddle-point conformations that separate them (A and syn).



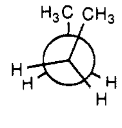
trans



A



gauche



syn

---

(1) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1981.

(2) Eliel, E. L.; Allinger, N. L.; Angyal, S. G.; Morrison, G. A. *Conformational Analysis*; Interscience: New York, 1966. Flory, P. J. *Science (Washington, D.C.)* **1965**, *188*, 1268.

(3) Verma, A. L.; Murphy, W. F.; Bernstein, H. J. *J. Chem. Phys.* **1974**, *60*, 1540.

(4) Bradford, W. F.; Fitzwater, S.; Bartell, L. S. *J. Mol. Struct.* 1977, *38*, 185.

(5) Durig, J. R.; Compton, D. A. C. *J. Phys. Chem.* **1979**, *83*, 265.

(6) Compton, D. A. C.; Montrero, S.; Murphy, W. F. *J. Phys. Chem.* **1980**, *84*, 3587.

(7) Heenan, R. K.; Bartell, L. S. *J. Chem. Phys.* **1983**, *78*, 1270.

(8) Devaure, J.; Lascombe, J. *Nouv. J. Chem.* **1979**, *3*, 579.

(9) Kint, S.; Scherer, J.; Snyder, R. G. *J. Chem. Phys.* **1980**, *73*, 2599.

(10) Colombo, L.; Zerbi, G. *J. Chem. Phys.* **1980**, *73*, 2013.

(11) Rosenthal, L.; Rabolt, J. F.; Hummel, J. *J. Chem. Phys.* **1982**, *76*, 817.

(12) Radom, L.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Chem. Soc.* **1973**, *95*, 693.

(13) Peterson, M. R.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1978**, *100*, 6911.

(14) Allinger, N. L.; Profecta, S. *J. Comput. Chem.* **1980**, *1*, 181.

(15) Darsey, J. A.; Rao, B. K. *Macromolecules* **1981**, *14*, 1575.

(16) Steele, D. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1077.

(17) Raghavachari, K. *J. Chem. Phys.* **1984**, *81*, 1383.

(18) Van-Catledge, F. A.; Allinger, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 6272.

(19) Moller, C.; Plesser, M. S. *Phys. Rev.* **1934**, *46*, 618. Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1.

0002-7863/88/1510-8029$01.50/0

Table II. Calculated Energies of Butane Conformers

	conformer			
basis set	trans	gauche	A	syn
a. Total Energies (hartrees)				
6-31G*//6-31G*	−157.298 41	−157.296 89	−157.292 62	−157.288 55
6-31G**//6-31G**	−157.313 95	−157.312 44	−157.308 14	−157.304 05
MP3/6-31G*//6-31G*	−157.870 72	−157.869 52	−157.865 07	−157.861 19
MP4/6-31G*//6-31G*	−157.894 55	−157.893 41	−157.888 95	−157.885 08
MP3/6-31G*//MP2/6-31G*	−157.871 27	−157.870 08	−157.865 63	−157.861 75
MP3/6-31+G*//MP2/6-31G*	−157.877 17	−157.875 96	−157.871 75	−157.867 39
6-311G**//MP2/6-31G*	−157.339 47	−157.337 87		
MP3/6-311G**//MP2/6-31G*	−158.012 59	−158.011 61		
6-311G**//6-311G**	−157.339 89	−157.338 37		
MP3/6-311G**//6-311G**	−158.012 18	−158.011 15		
6-31G(df,p)//6-311G**	−157.315 17	−157.313 65		
MP3/6-31G(df,p)//6-311G**	−158.014 90	−158.013 72		
b. Relative Energies (kcal/mol)				
6-31G*//6-31G*	0.00	0.95	3.63	6.19
6-31G**//6-31G**	0.00	0.95	3.65	6.21
MP3/6-31G*//6-31G*	0.00	0.75	3.55	5.99
MP4/6-31G*//6-31G*	0.00	0.72	3.51	5.94
MP3/6-31G*//MP2/6-31G*	0.00	0.75	3.54	5.97
MP3/6-31+G*//MP2/6-31G*	0.00	0.76	3.40	6.14
6-311G**//MP2/6-3G*	0.00	1.00		
MP3/6-311G**//MP2/6-31G*	0.00	0.61		
6-311G**//6-311G**	0.00	0.95		
MP3/6-311G**//6-311G**	0.00	0.65		
6-31G(df,p)//6-311G**	0.00	0.96		
MP3/6-31G(df,p)//6-311G**	0.00	0.74		
c. Thermodynamic Data (kcal/mol)				
ZPE	79.94	80.04	79.97	80.14
ΔZPE	0.00	0.10	0.03	0.20
$\Delta\Delta H$(0 K)	0.00	0.86	3.43	6.34
$H - H_0$	4.38	4.33		
$\Delta(H - H_0)$	0.00	−0.05		
$\Delta\Delta H$(298 K)	0.00	0.81		

The optimizations for trans and gauche were carried out without constraints, and those for A and syn were constrained only with regard to the dihedral angle, which maintained the eclipsed conformation. The energies are compared with those obtained with the 6-31G* basis in Table II, and the geometries are compared in Table III. It can be seen that the addition of polarization functions at the hydrogens had no significant effect on the structures or relative energies. In accord with previous calculations,[17] the trans/syn energy difference was 6.2 kcal/mol, much larger than the value extrapolated from the spectroscopic data.[6]

It is known that these basis sets[20] generally give very good bond angles[21] and bond lengths that are about 1% shorter than the experimental lengths.[22] In order to see if improved bond lengths would lead to a significant change in energy, the effect of electron correlation on the calculated structures was then studied with the Moller–Plesset method through the second order (MP2)[19] with the 6-31G* basis set. The data given in Table III show that again the changes in structural parameters are relatively small.

The effect of electron correlation on the relative energies was obtained with both the 6-31G* and MP2/6-31G* structures. The trans/gauche energy difference dropped to 0.75 kcal/mol, and the trans/syn difference dropped to 5.9 kcal/mol. The use of a larger basis set with diffuse functions added to the carbons had very little effect on the relative energies. It has been suggested that the use of still larger basis sets might reduce the trans/gauche energy difference.[17] In order to examine this possibility, several further calculations were carried out (Table II). The use of the 6-311G** basis set, which is effectively triple-ζ plus polarization functions at carbon and hydrogen, plus correction for electron correlation led to a decrease in the energy difference. However, when the flexibility of the basis set was further increased by using both d and f functions at the carbons, the barrier returned to the value obtained with the 6-31G* basis. We therefore conclude that the energy difference is close to 0.75 kcal/mol and that the 6-31G* basis with MP3 correction for electron correlation should be satisfactory for conformational calculations for alkanes.

Table III. Structures of Butane Conformers

		conformer			
bond	basis	trans	gauche	A	syn
C1–C2	6-31G*	1.5282	1.5296	1.5291	1.5313
	6-31G**	1.5278	1.5292	1.5287	1.5311
	MP2/6-31G*	1.5245	1.5256	1.5255	1.5277
	6-311G**	1.5276	1.5293		
C2–C3	6-31G*	1.5298	1.5330	1.5463	1.5551
	6-31G**	1.5293	1.5327	1.5459	1.5513
	MP2/6-31G*	1.5250	1.5283	1.5413	1.5552
	6-311G**	1.5289	1.5324		
C–C–C	6-31G*	113.09	114.43	113.48	116.98
	6-31G**	113.12	114.49	113.50	117.02
	MP2/6-31G*	112.88	113.78	112.88	116.43
	6-311G**	113.20	114.55		
C′–C–C–C[a]	6-31G*	180.0	65.49	121.93	0.0
	6-31G**	180.0	65.52	121.93	0.0
	MP2/6-31G*	180.0	65.21	121.64	0.0
	6-311G**	180.0	65.44		

[a] The experimental gauche dihedral angles are 72 ± 5° (ED[7]) and 62 ± 1° (Raman[5,6]).

In view of the robust nature of the calculated energy differences found in this study and that of Raghavachari,[17] we are forced to conclude that the high trans/syn difference is correct and that the extrapolation of the experimental measurements led to a barrier

---

[20] 6-31G*: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 203. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1983**, *77*, 3054. 6-31+G*: Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609. Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

[21] DeFrees, D. J.; Raghavachari, K.; Schlegel, H. B.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5576.

[22] Wiberg, K. B. *J. Org. Chem.* **1985**, *50*, 5285.

Table IV. Calculated Energies of Alkanes

compd	conf	3-21G	6-31G*	MP2	MP3
		a. Total Energies (hartrees)			
pentane	trans	195.251 56	196.333 10	196.991 09	197.045 79
	gauche	195.250 32	196.331 50	196.989 96	197.044 58
	g^+g^+	195.249 16	196.330 10	196.989 14	197.043 63
	g^+g^- (60, −60)[a]	195.241 97	196.324 13	196.983 21	197.037 90
	g^+g^- (C_s)	195.245 14	196.326 55	196.985 31	197.040 04
	g^+g^- (C_1)	195.245 69	196.326 92	196.985 83	197.040 48
hexane	trans	234.070 67	235.367 79	236.156 68	236.220 88
	g (3–4)	234.069 43	235.366 12	236.155 56	236.219 66
	g (2–3)	234.069 44	235.366 19	236.155 54	236.219 65
	g^+tg^+	234.068 07	235.364 45	236.154 29	236.218 33
	$g^+g^+g^+$	234.067 05	235.363 29	236.154 03	236.217 84
	ecl (3–4)[b]	234.061 15	235.357 73	236.147 23	236.211 57
2-methylbutane	C_1	195.252 07	196.331 81	196.992 62	197.046 60
	C_s	195.250 95	196.330 35	196.991 33	197.045 29
2,3-dimethylbutane	C_2	234.069 66	235.363 20	236.158 27	236.220 92
	C_{2h}	234.069 71	235.363 06	236.158 38	236.220 98
	TS	234.063 08	235.357 20	236.151 78	236.214 65
2,2-dimethylbutane		234.072 19	235.364 28	236.161 34	236.223 26
	TS	234.063 24	235.355 80	236.152 37	236.214 59
heptane	trans	272.889 77	274.402 49	275.322 27	275.395 97
octane	trans	311.708 88	313.437 18	314.487 86	314.571 06
	g (4–5)	311.707 65	313.435 51	314.486 86	314.569 94
cyclohexane	chair	232.916 73	234.208 00	234.991 66	235.047 82
methylcyclohexane	eq	271.738 11	273.243 61[c]	274.160 57	274.225 51
	ax	271.735 06	273.239 94[c]	274.157 48	274.222 30
		b. Relative Energies (kcal/mol)			
pentane	trans	0.00	0.00	0.00	0.00
	gauche	0.78	1.00	0.71	0.76
	g^+g^+	1.51	1.88	1.22	1.36
	g^+g^- (60, −60)[a]	6.02	5.16	4.94	4.95
	g^+g^- (C_s)	4.03	4.11	3.63	3.61
	g^+g^- (C_1)	3.68	3.88	3.30	3.33
hexane	trans	0.00	0.00	0.00	0.00
	g (3–4)	0.78	1.05	0.70	0.77
	g (2–3)	0.78	1.00	0.72	0.77
	g^+tg^+	1.63	2.10	1.50	1.60
	$g^+g^+g^+$	2.27	2.82	1.66	1.91
	ecl (3–4)[b]	5.97	5.84	5.93	5.84
2-methylbutane	C_1	0.00	0.00	0.00	0.00
	C_s	0.70	0.92	0.81	0.82
2,3-dimethylbutane	C_{2h}	0.00	0.00	0.00	0.00
	C_2	0.03	−0.09	0.07	0.04
	TS	4.13	3.77	4.14	3.97
2,2-dimethylbutane		0.00	0.00	0.00	0.00
	TS	5.62	5.32	5.63	5.44
heptane	trans	0.00	0.00	0.00	0.00
octane	trans	0.00	0.00	0.00	0.00
	g (4–5)	0.77	1.05	0.63	0.70
methylcyclohexane	eq	0.00	0.00	0.00	0.00
	ax	1.91	2.30	1.94	2.01

[a] The dihedral angles were fixed at 60° and −60° to simulate a 1,3-diaxial interaction. [b] A saddle-point geometry. [c] 6-31G-optimized geometries.

that is too small. Raghavachari has come to the same conclusion.[17] In this connection, it is interesting to note that Jaime and Osawa[23] have found that barriers to rotation in crowded alkanes cannot be reproduced with the standard molecular mechanics MM2[1] force field, which is set to give a butane barrier of 4.7 kcal/mol. When the torsional and van der Waals potentials are stiffened, yielding a molecular mechanics butane barrier of 5.2 kcal/mol, other rotational barriers are well modeled.[23] It is clear that the MM2 torsional potential function is incorrect.

The calculated energy differences cannot, of course, be directly compared with the experimental value. They must be corrected for the zero-point energy differences and, in some cases, for the change in enthalpy on going from 0 to 298 K. This latter correction is needed when the ratio of trans to gauche forms is measured directly, as in electron diffraction experiments but should not be included when the difference in energy is determined with spectroscopically determined energy levels. The zero-point energies have been calculated by Raghavachari, and when his vibrational frequencies and the moments of inertia derived from our calculated structures were used, $H_T - H_0$ has been obtained. When these corrections are used, the MP3/6-31G* calculated trans/gauche energy difference becomes 0.86 kcal/mol at 0 K and 0.81 kcal/mol at 298 K. The former is in very good agreement with the spectroscopically derived value (0.89 ± 0.03 kcal/mol). The barrier to rotation becomes 6.34 kcal/mol.

The structural differences between the four rotamers listed in Table III deserve to be noted. The gauche rotamer has longer C–C bonds and a larger C–C–C bond angle than the trans rotamer. In addition, the C–C–C–C dihedral angle in the gauche rotamer is greater than 60°. All of these changes indicate a repulsive steric interaction in this species. The differences in energy between the trans and gauche rotamers due to stretching and bending deformations was estimated by taking the trans values as normal and applying quadratic potential functions to the changes on going to the gauche structure. We used $k_{str} = 5$ mdyn/Å and $k_{bend} = 1$ mdyn/Å, giving a deformation energy of about 0.15 kcal/mol. The distortion in the gauche rotamer must result from nonbonded interactions, and, in view of the small distortion energy, the energies associated with the two opposing

---

[23] Jaime, C.; Osawa, E. *Tetrahedron* **1983**, *39*, 2769.

Table V. Calculated Geometries of Alkanes (6-31G*)

Pentane

	trans	gauche[a]	g^+g^+[b]	g^+g^-[c]	g^+g^-[d]	g^+g^-[e]
C1–C2	1.5284	1.5287	1.5310	1.5313	1.5307	1.5291
C2–C3	1.5297	1.5310	1.5336	1.5371	1.5372	1.5347
C3–C4	1.5297	1.533	1.5338	1.5373	1.5372	1.5415
C4–C5	1.5284	1.5298	1.5313	1.5313	1.5305	1.5309
C1–C2–C3	113.03	112.63	113.14	118.00	116.40	115.78
C2–C3–C4	113.40	114.85	114.84	120.21	117.38	115.86
C3–C4–C5	113.03	114.56	113.17	117.98	116.46	114.80
C1–C2–C3–C4	180.00	177.21	63.77	60.00	78.13	63.23
C2–C3–C4–C5	180.00	68.76	63.40	–60.00	–77.14	–94.61

Hexane

	trans	gauche[f]	gauche[g]	g^+tg^+[h]	$g^+g^+g^+$[i]
C1–C2	1.5284	1.5287	1.5284	1.5299	1.5297
C2–C3	1.5299	1.5313	1.5304	1.5339	1.5343
C3–C4	1.5295	1.5331	1.5309	1.5320	1.5354
C4–C5	1.5299	1.5313	1.5334	1.5339	1.5343
C5–C6	1.5284	1.5287	1.5300	1.5299	1.5297
C1–C2–C3	113.02	112.63	113.10	114.71	114.44
C2–C3–C4	113.34	114.84	112.95	114.42	116.09
C3–C4–C5	113.34	114.84	114.73	114.42	116.09
C4–C5–C6	113.02	112.63	114.59	114.71	114.44
C1–C2–C3–C4	180.0	176.55	179.89	66.77	61.32
C2–C3–C4–C5	180.00	67.78	176.75	180.0	59.54
C3–C4–C5–C6	180.00	176.55	66.70	66.77	61.32

Heptane

	trans		trans
C1–C2	1.5283	C4–C5	1.5297
C2–C3	1.5298	C5–C6	1.5298
C3–C4	1.5297	C6–C7	1.5283
C1–C2–C3	113.04	C1–C2–C3–C4	180.00
C2–C3–C4	113.36	C2–C3–C4–C5	180.00
C3–C4–C5	113.33	C3–C4–C5–C6	180.00
C4–C5–C6	113.36	C4–C5–C6–C7	180.00
C5–C6–C7	113.04		

Octane

	trans	gauche[j]		trans	gauche[j]
C1–C2	1.5283	1.5283	C5–C6	1.5297	1.5311
C2–C3	1.5298	1.5302	C6–C7	1.5298	1.5302
C3–C4	1.5297	1.5311	C7–C8	1.5283	1.5283
C4–C5	1.5300	1.5334			
C1–C2–C3	113.04	113.04	C1–C2–C3–C4	180.00	179.80
C2–C3–C4	113.36	112.96	C2–C3–C4–C5	180.00	176.45
C3–C4–C5	113.33	114.82	C3–C4–C5–C6	180.00	67.80
C4–C5–C6	113.33	114.82	C4–C5–C6–C7	180.00	176.45
C5–C6–C7	113.36	112.96	C5–C6–C7–C8	180.00	179.79
C6–C7–C8	113.04	113.04			

2-Methylbutane[k]

	C_1[l]	C_s[m]		C_1[l]	C_s[m]
C1–C2	1.5319	1.5324	C3–C4	1.5297	1.5310
C2–C5	1.5325	1.5324	C2–C3	1.5366	1.5396
C1–C2–C3	110.33	112.65	C1–C2–C5	110.35	110.91
C3–C2–C5	112.49	112.65	C1–C2–C3–C4	187.64	63.19
C2–C3–C4	115.00	116.27	C4–C3–C2–C5	63.94	63.19

2,3-Dimethylbutane H1–C2(C5)(C7)–C3(C6)(C8)–H4

	C_2[n]	C_{2h}[o]	TS[p]		C_2[n]	C_{2h}[o]	TS[p]
C2–C3	1.5484	1.5469	1.5658	C2–C7	1.5337	1.5348	1.5334
C2–C5	1.5335	1.5348	1.5328	C3–C8	1.5337	1.5348	1.5334
C3–C6	1.5335	1.5348	1.5328				
C2–C3–C6	112.06	112.33	110.50	H1–C2–C3–H4	66.91	180.00	124.20
C3–C2–C5	112.06	112.33	110.50	C5–C2–C3–C6	165.39	56.58	108.12
C2–C3–C8	114.23	112.33	115.73	C5–C2–C3–C8	68.53	180.00	125.94
C3–C2–C7	114.23	112.33	115.73	C7–C2–C3–C6	68.53	180.00	124.20
C5–C2–C7	110.10	109.08	110.08	C7–C2–C3–C8	57.55	56.58	0.00
C6–C3–C8	110.10	109.08	110.08				

Table V (Continued)

2,2-Dimethylbutane C1–C2(C5)(C6)–C3–C4

	ground	TS		ground	TS
C1–C2	1.5366	1.5373	C2–C3	1.5459	1.5687
C2–C5	1.5366	1.5373	C3–C4	1.5308	1.5320
C2–C6	1.5366	1.5373			
C1–C2–C3	110.00	110.58	C5–C2–C6	109.64	108.44
C3–C2–C5	110.00	110.58	C1–C2–C3–C4	180.00	0.00
C3–C2–C6	110.00	110.58	C5–C2–C3–C4	60.43	119.94
C2–C3–C4	117.34	118.96	C6–C2–C3–C4	–60.43	–119.94

[a] Gauche "kink" is at C2–C3–C4–C5. [b] Both C–C–C–C dihedral angles are ~60° (~C_2 symmetry). [c] One C–C–C–C dihedral angle is fixed at 60° and the other at -60°. [d] Fully relaxed with approximate C_s symmetry. [e] Fully relaxed with no symmetry. [f] Gauche kink is at C2–C3–C4–C5. [g] Gauche kink is at C3–C4–C5–C6. [h] Two gauche kinks at C1–C2–C3–C4 and C3–C4–C5–C6. Overall C_i symmetry. [i] Three gauche kinks; overall C_2 symmetry. [j] Gauche kink in middle, at C3–C4–C5–C6. Overall C_2 symmetry. [k] The methyl branch is at C_2. [l] The conformer of C_1 symmetry has one gauche interaction. [m] The conformer of C_s symmetry has two gauche interactions. [n] The C_2 symmetry conformer has three gauche interaction. [o] The C_{2h} symmetry conformer has two gauche interactions. [p] The transition state has torsion C7–C2–C3–C8 fixed at 0°.

intramolecular interactions should be about equal. Therefore, the nonbonded repulsion should also be about 0.15 kcal/mol. The total steric interaction is then about 0.3 kcal/mol, or about one-third of the observed energy difference. The syn rotamer, which has the largest steric repulsion between methyl groups, leads to a further large increase in the C–C–C bond angle.

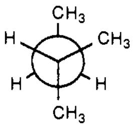
II. Pentane, Hexane, and Octane. To better understand the sources of gauche destabilization in hydrocarbons, a systematic study of some larger cyclic and acyclic systems has been undertaken. Using the 6-31G* basis set and MP3 correction for electron correlation, we have calculated the energies of pentane, hexane, and octane conformers having one gauche interaction. Forms of pentane and hexane with two or three gauche interactions also have been studied. In addition, calculations have been performed on the various minima and transition states of 2-methylbutane and 2,2- and 2,3-dimethylbutane. Finally, cyclohexane and both equatorial and axial methylcyclohexane were studied. The calculated energies of all species are given in Table IV. Geometric parameters for all acyclic compounds are given in Table V, while geometric data for the cyclic compounds are given in Table VI.

Are the gauche methyl–methylene and methylene–methylene interactions energetically the same as a methyl–methyl interaction? The energy difference between the trans and gauche rotamers of *n*-pentane is the same as that for *n*-butane. The zero-point energy and the enthalpy change corrections should be essentially the same for pentane as for butane, leading to a corrected energy change of 0.86 kcal/mol at 0 K. With *n*-hexane, the trans/gauche energy difference is the same for the 2,3-gauche and 3,4-gauche rotamers, and the same difference is found with the octane 4,5-gauche rotamer. All agree with the butane value. This suggests that the use of the butane energy difference with longer chains will correctly reproduce the proportion of the gauche forms.

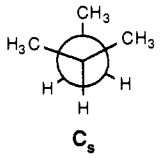
The g^+g^+ pentane conformer, with C_2 symmetry, has a relative energy roughly twice as high as gauche pentane relative to the all-trans form. The same result is seen in g^+tg^+ hexane, which has C_{2h} symmetry. These facts imply that if close Me–Me interactions are avoided, gauche energies will normally be approximately additive in polymethylene chains. The g^+g^- pentane conformer is much more sterically congested as a result of a 1,5 Me–Me interaction, which is analogous to that found in the diaxial form of *cis*-1,3-dimethylcyclohexane. We find both an unsymmetrical form with C–C–C–C dihedral angles of roughly 63° and -95° and an almost symmetrical (C_s) form with dihedral angles of roughly 77° and -78°. The strain in the C_s conformer may be a good model for that in dimethylcyclohexane because a 4-21G optimization of the latter ring system gave the gauche dihedral angles as 78°,[24] almost identical with the value we see in pentane at the 6-31G* level. In an earlier study, Darsey and Rao had found an asymmetrical energy minimum for the g^+g^- conformer with dihedral angles of 64° and -107° and a relative energy of 4.3 kcal/mol using a smaller basis set.[15] Our C_1 conformer has an energy 3.3 kcal/mol above the global minimum at our highest level, MP3/6-31G*, while the C_s rotamer is at 3.6 kcal/mol.

The calculated relative energy of the $g^+g^+g^+$ form of *n*-hexane, which has three successive gauche interactions, is interesting in that it is only 0.3 kcal/mol greater than the g^+tg^+ form at the MP3/6-31G* level. This is the only case in which the gauche interactions were not approximately additive. It was unfortunately not practical to investigate this for longer chains because of the long computation times. With hexane, the saddle-point conformation for rotation about the C3–C4 bond was found to have an energy 5.8 kcal/mol higher than the all-trans conformer, a value close to that calculated for butane. Thus, the barriers to rotation, like the gauche/trans energy differences, appear to be relatively constant in unbranched alkanes.

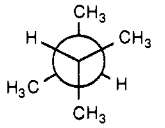
III. Branched Chains. When methyl groups are substituted onto linear alkanes, additional gauche interactions will be found.



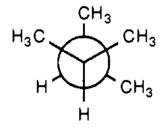
C_1



C_s



C_{2h}



C_2

We were interested in how such substitution affects structures and energies. Vibrational assignments for the branched alkanes are needed if one is to compare calculations with experiment, but the experimental values are not entirely secure.[25] In order to avoid adding to the uncertainty in the energies, we have calculated the vibrational frequencies using the 3-21G basis set, which generally gives very good results when the calculated frequencies are scaled by the factor 0.9.[26] The zero-point energies and enthalpies derived from the calculated frequencies are summarized in Table VII.

The rotamer of 2-methylbutane with C_s symmetry will have two gauche interactions, whereas the other with C_1 symmetry has but one. The calculated energy difference is 0.82, and after correcting for vibrational differences (Table VII) a final answer of 0.92 is obtained, in good agreement with the observed value of 0.81 kcal/mol.[3]

In the case of 2,3-dimethylbutane, one rotamer with C_2 symmetry (often called "gauche") has three gauche interactions, whereas the other with C_{2h} symmetry (often called "trans") has

---

(24) Klimkowski, V. J.; Manning, J. P.; Schafer, L. *J. Comput. Chem.* **1985**, *6*, 570.

(25) Snyder, R. G.; Schachtschneider, J. H. *Spectrochim. Acta* **1965**, *21*, 169.

(26) Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; p 228ff.

Table VI. Calculated Geometries of Cyclohexanes

Cyclohexane

	6-31G*	6-31G		6-31G*	6-31G
C–C	1.5325	1.5353	C1–C2–C3	111.41	111.36
C–H (eq)	1.0870	1.0856	C1–C2–C3–C4	54.90	55.05
C–H (ax)	1.0892	1.0884			

Methyl Cyclohexane (C1 Attached to Methyl Group C7)

	3-21G opt		6-31G opt	
	eq	ax	eq	ax
C1–C2	1.5410	1.5450	1.5383	1.5427
C2–C3	1.5411	1.5416	1.5345	1.5359
C3–C4	1.5408	1.5406	1.5345	1.5346
C1–C7	1.5388	1.5411	1.5318	1.5363
C7–H (unique)	1.0858	1.0823	1.0861	1.0833
C7–H	1.0853	1.0853	1.0851	1.0852
C1–C2–C3	111.47	112.57	112.03	112.97
C2–C3–C4	110.77	110.64	111.44	111.32
C3–C4–C5	110.61	110.69	111.19	111.33
C2–C1–C6	109.68	110.05	110.25	109.99
C2–C1–C7	110.94	111.93	111.54	112.37
C2–C3–H (ax)	109.20	110.15	109.22	110.03
C1–C7–H (unique)	110.27	111.91	110.87	112.53
C1–C2–C3–C4	56.97	55.94	55.32	54.76
C2–C3–C4–C5	56.19	56.87	54.66	54.85
C2–C1–C6–C5	56.64	53.67	54.86	53.08
C3–C2–C1–C7	179.54	71.46	179.36	72.90
C1–C2–C3–H (ax)	63.30	65.18	65.43	66.72

Table VII. 3-21G Zero-Point Energies and Enthalpy Functions for Hydrocarbons[a]

	ZPE	$H - H_0$	total
butane	79.98	4.44	84.42
pentane	97.27	5.23	102.50
hexane	114.53	6.09	120.62
heptane	131.79	6.95	138.74
octane	149.04	7.83	156.87
2-methylbutane, C_1	97.11	5.25	102.36
2-methylbutane, C_s	97.19	5.27	102.46
2,3-dimethylbutane, C_{2h}	114.24	6.22	120.46
2,3-dimethylbutane, C_2	114.28	6.17	120.45
2,3-dimethylbutane, TS	114.39	5.54	119.93
2,2-dimethylbutane	114.08	6.15	120.23
2,2-dimethylbutane, TS	114.23	5.68	119.91
methylcyclohexane, eq	120.17	5.32	125.49
methylcyclohexane, ax	120.36	5.29	125.65

[a] In kcal/mol.

two. The calculated energy difference is 0.04, and the vibrational correction is only 0.01, giving 0.03 kcal/mol, again in good agreement with the experimental value of 0.05 kcal/mol favoring trans.[3]

The H–C–C–H dihedral angle in 2,3-dimethylbutane is constrained to be 180° in the C_{2h} rotamer but may vary in the C_2 isomer. Various force fields give quite different geometries, with the H–C–C–H dihedral angle ranging from 53° to 72°.[27] The MM2 value,[1] 64.4°, is close to our 6-31G* calculated result of 66.9°.

Why do the rotamers have essentially the same energy rather than the difference expected for one gauche interaction? An examination of the structural data for the two rotamers (Table V) provides some information. The C_{2h} rotamer is constrained in two ways. A normal Me–C–Me bond angle (~112°) would lead to a Me–C–C–Me dihedral angle less than 60° and an increased torsional strain. Thus, whereas the C_2 form has a C–C–C–C dihedral angle of 69°, the C_{2h} form has an angle of only 57°, and the Me–C–Me bond angles are ~1° more congested in the C_2 form. The two additional strain components presumably account for the smaller than expected energy difference between the two rotamers. Other workers have explained the unusual relative energies in terms of the ability of the gauche form to relax.[27-29]

The rotational barriers in 2,2- and 2,3-dimethylbutane have been studied experimentally, but there are some uncertainties in the data. The barrier in 2,2-dimethylbutane has been found by NMR to be 4.9 ± 0.5[30] kcal/mol at 92 K and 5.2 ± 0.2[31] kcal/mol at 100 K. Snyder and Schachtschneider estimated V_3 at 4.5 kcal/mol from IR data.[32] For the 2,3-dimethyl isomer, an NMR study gave 4.3 ± 0.2[33] while an older ultrasonic relaxation study gave 3.75 ± 0.2 kcal/mol.[34] Osawa has found that the standard MM2 parameter set gives too low a value for many sterically crowded hydrocarbons, with the barrier for the 2,3 isomer calculated at 3.09 kcal/mol.[23] Clearly, it is of interest to see whether ab initio methods may help to define some of these fundamental values, so we have carried out 6-31G* optimizations on the ground and transition states of 2,2- and 2,3-dimethylbutane. We find that, at the MP3/6-31G* level, the barriers are 3.97 for 2,3-dimethylbutane isomer and 5.44 for 2,2-dimethylbutane. When zero-point energies are added in (Table VII), these barriers become 4.12 and 5.69 kcal/mol, respectively. The former is in good agreement with the available data, but the value obtained for the 2,2 isomer is slightly higher than the solution-phase NMR results.

Since we have the calculated energies of isomeric hydrocarbons, it was of interest to see how well the calculated relative energies compare with the experimental values. These data are given in Table VIII. It has been found that very extensive electron correlation is required in order to reproduce the difference in heats of formation of isomers. At the MP3 level, the difference between butane and isobutane and between pentane and neopentane is accurately reproduced, but for none of the other cases is a reasonable result obtained. When the full MP4 treatment is used, the results are better, although still not as accurate as is desirable.

IV. Cyclohexane. A particularly important example of a gauche methyl interaction is found with methylcyclohexane. Here, the axial conformer has two gauche interactions, whereas the equatorial conformer has none. The energy difference also is frequently discussed in terms of 1,3-diaxial interactions. The energy difference in solution (1.75 ± 0.05 kcal/mol) has been well established via NMR spectroscopy.[37] The gas-phase value is believed to be somewhat higher, perhaps 1.9–2.0 kcal/mol.[38]

In order to gain a better understanding of the origin of the energy difference between the two conformers of methylcyclohexane, we have carried out geometry optimizations for both using the 6-31G basis set. The structural data are given in Table VI. The difference in energy was calculated with the 6-31G* basis set and correction for electron correlation (MP3), giving 2.01 kcal/mol. The vibrational frequencies were estimated with the 3-21G basis set, and correcting the calculated energy for the difference in zero-point energy and for the change in ΔH_f on going from 0 to 298 K gave 2.17 kcal/mol, which is ~0.2 kcal/mol higher than the venerable gas–phase experimental data.[38] Considering the importance of this molecule, it is surprising that no one has studied it in the gas phase in the last 40 years.

The difference in energy is greater than twice the gauche interaction in the *n*-alkanes. To what extent is this due to 1,3-diaxial interactions? Such interactions should lead to characteristic changes in geometry at C_1 on the ring for the axial conformer. An examination of the calculated structures (Table VI) shows

---

(27) Osawa, E.; Collins, J. B.; Schleyer, P. v. R. *Tetrahedron* **1977**, *33*, 2667.

(28) Wertz, D. H.; Allinger, N. L. *Tetrahedron* **1974**, *30*, 1579.

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

(30) Bushweller, C. H.; Anderson, W. G. *Tetrahedron Lett.* **1972**, 1811.

(31) Whalon, M. R.; Bushweller, C. H.; Anderson, W. G. *J. Org. Chem.* **1984**, *49*, 1185.

(32) Snyder, R. G.; Schachtschneider, J. H. *Spectrochim. Acta* **1965**, *21*, 169.

(33) Lunazzi, L.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 4573.

(34) Chen, J. H.; Petravskas, A. A. *J. Chem. Phys.* **1959**, *30*, 304.

(35) Wiberg, K. B.; Murcko, M. A. *J. Phys. Chem.* **1987**, *91*, 3616.

(36) Phillips, L.; Wray, V. *J. Chem. Soc., Chem. Commun.* **1973**, 90.

(37) Booth, H.; Everett, J. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 255.

(38) Beckett, C. W.; Pitzer, K. S.; Spitzer, R. *J. Am. Chem. Soc.* **1947**, *69*, 2488.

Table VIII. Calculated Energy Differences ($\Delta\Delta E$) for Hydrocarbons (6-31G*)

compd	RHF	MP2	MP3	MP4(SDTQ)	ΔH_f(0 K)[a]	ZPE
n-butane	157.298 41	157.825 49	157.870 72	157.894 55	−23.6	79.9
i-butane	157.298 96	157.828 21	157.872 81	157.896 97	−25.2	79.6
n-pentane	196.333 10	196.991 09	197.045 79	197.075 74	−27.3	97.3
2-methylbutane	196.331 81	196.992 62	197.046 60	197.077 03	−28.7	97.1
neopentane	196.333 81	196.998 43	197.051 15	197.082 26	−31.3	96.3
n-hexane	235.367 79	236.156 68	236.220 88	236.256 95	−30.9	114.5
2,3-dimethylbutane	235.363 06	236.158 38	236.220 98	236.258 19	−32.9	114.2
2,2-dimethylbutane	235.364 28	236.161 34	236.223 26	236.260 85	−34.7	114.1

compd	RHF	MP2	MP3	MP4(SDTQ)	exp[b]
n-butane	0.00	0.00	0.00	0.00	0.0
i-butane	−0.35	−1.71	−1.31	−1.51	−1.3 ± 0.3
n-pentane	0.00	0.00	0.00	0.00	0.0
2-methylbutane	0.81	−0.96	−0.51	−0.81	−1.2 ± 0.3
neopentane	−0.45	−4.61	−3.36	−4.09	−3.0 ± 0.4
n-hexane	0.00	0.00	0.00	0.00	0.0
2,3-dimethylbutane	2.97	−1.07	−0.06	−0.78	−1.7 ± 0.4
2,2-dimethylbutane	2.20	−2.92	−1.49	−2.45	−3.4 ± 0.4

[a] Reference 41. [b] $\Delta\Delta H_f$ after correcting for differences in ZPE.

that the axial hydrogens on the same side as the axial methyl have somewhat larger bond angles and a somewhat larger dihedral angle than found in the equatorial conformer. Larger distortions are seen in the methyl group where the hydrogen that points toward the axial hydrogens has a shorter C–H bond length and a larger C–C–H bond angle than the methyl in the equatorial form. Thus, the methyl group in the axial form is subject to repulsive interactions, which presumably account for the increase in energy over that expected for two gauche interactions. However, the increase in energy is not large and is on the order of 0.4 kcal/mol.

Although the gauche interaction in the *n*-alkanes is destabilizing, for other types of molecules this is not always true. For example, 1,2-difluoroethane prefers the gauche form, and, after correcting for the dipole-dipole repulsion, there appears to be little difference in energy between *trans*- and *gauche*-1,2-dichloroethane.[35] In all cases, the gauche form shows geometrical parameters (increased bond angles, dihedral angle greater than 60°) that are characteristic of repulsive interactions. It is possible that the "gauche effect" in these cases results from destabilization of the trans form when two strongly electronegative groups are involved.[36] The large trans–gauche energy difference in the *n*-alkanes, which is difficult to explain simply as being due to steric interactions, may then involve a stabilization of the trans form by the alkyl substituents.

To conclude the discussion of the *gauche*-alkyl effect, we shall consider cyclohexane. Assuming that gauche butane is a reasonable model for the gauche tetramethylene fragments, the six gauche interactions in cyclohexane should raise its energy above that of six acyclic methylene groups by ~5.4 kcal/mol. The average value of the CH_2 increment to the enthalpies of formation of pentane through octane is 4.92 ± 0.10 kcal/mol. The enthalpy of formation of a methylene group in cyclohexane is one-sixth of its ΔH_f (−29.50 ± 0.15 kcal/mol[39]), or 4.92 ± 0.03 kcal/mol. The remarkable agreement between these values has previously been noted[40] and fails to show the expected gauche interaction. In addition, the cross-ring C–C distance is calculated (6-31G*) to be only 2.96 Å, a distance that is commonly considered to be repulsive. In *gauche*-butane, which appears to have a small steric interaction between the terminal methyl groups, the C–C distance is 3.14 Å. Thus, the total destabilization might be expected to exceed 6 kcal/mol.

However, this simple comparison may be misleading. First, a collection of *n*-alkane molecules at room temperature contains significant portions of gauche conformers, raising the average energy above that for the all-trans chains. In order to obtain the energy of a methylene group in an all-trans chain, data at 0 K may be used. Second, the energy comparisons should be made at the hypothetical vibrationless states at 0 K. The vibrational frequencies will be quite different for rings and chains, leading to differences in zero-point energies. Similarly, the difference in frequencies (particularly the low torsional frequencies in the chains) and the differences in moments of inertia will lead to differences in heat capacities and a different rate of change of ΔH_f with temperature. None of these factors are germane to the problem and should first be eliminated.

The enthalpies of formation for the *n*-alkanes in the ideal gas state at 0 *k*[41] should correspond to the all-trans forms. Adding the zero-point energies gives an average difference per methylene group of 13.6 ± 0.2 kcal/mol. One-sixth of the corresponding value of cyclohexane is 13.85 ± 0.05 kcal/mol. The difference is 0.25 kcal/mol favoring the *n*-alkanes, but the uncertainty in the value is approximately equally large.

Another way in which to examine the question is to compare the calculated energy of a cyclohexane methylene group (i.e., one-sixth of the total energy) with the energy increment from butane to pentane or pentane to hexane. The difference using the MP3/6-31G* data is 0.28 kcal/mol, with the methylene of an *n*-alkane being the more stable. This is in remarkable agreement with the value derived from the thermochemical data. It is clear that cyclohexane has only about one-third of the expected gauche interaction.

One possible explanation would propose some form of cyclic stabilization in cyclohexane, which would be absent in the *n*-alkanes. A mechanism for such an interaction has been proposed by Dewar.[42] Although much, if not all, of the difference in strain energy between cyclopropane and cyclobutane may be explained by a consideration of the differences in intramolecular interactions and C–H bond strengths in these compounds,[43] Dewar's mechanism may provide a small stabilizing interaction in the case of cyclohexane. One might at first think that such an interaction would be destabilizing for cyclohexane because it would be a 12-electron system. However, it is not planar and might best be thought of as two three-carbon ensembles, each occupying a different plane and having six electrons. It is recognized that this is highly speculative and is introduced to encourage more active consideration of the nature of saturated cyclic compounds.

It is clearly not possible to carry out detailed ab initio calculations for all interesting hydrocarbons, and this realization has led to many efforts to develop suitable parameters for reproducing

---

(39) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, 1970.

(40) Fliszar, S. *Charge Distributions and Chemical Effects*; Springer-Verlag: New York, 1983.

(41) *Selected Values of Properties of Hydrocarbons and Related Compounds*; API Research Project No. 44; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1974.

(42) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669.

(43) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312. See, However: Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467.

Table IX. 3-21G Vibrational Frequencies[a]

n-Butane (Trans)								
Ag	455.9	883.9	1092.4	1277.2	1515.6	1574.8	1655.6	1675.1
Ag	3187.6	3195.8	3250.4					
Au	128.4	238.0	801.1	1077.0	1428.9	1674.0	3227.2	3261.8
Bg	273.4	900.2	1331.8	1471.7	1672.5	3210.2	3249.4	
Bu	283.6	1021.3	1106.6	1470.8	1573.1	1661.0	1677.7	3190.4
Bu	3198.2	3251.6						
n-Pentane (Trans)								
A'	194.0	421.1	433.3	934.4	957.6	1066.2	1090.7	1155.3
A'	1264.6	1442.4	1507.2	1517.3	1572.9	1574.9	1653.1	1655.7
A'	1665.8	1674.5	1678.1	3183.5	3190.0	3192.9	3193.7	3199.8
A'	3250.9	3251.4						
A''	115.8	120.0	255.5	263.5	794.1	841.7	964.0	1111.5
A''	1327.9	1403.4	1467.3	1472.4	1672.9	1673.8	3203.9	3217.5
A''	3233.8	3253.8	3261.4					
n-Hexane (Trans)								
Ag	320.6	389.7	977.7	1030.3	1101.9	1256.9	1486.7	1517.4
Ag	1574.5	1652.4	1660.3	1675.7	3183.1	3191.6	3196.1	3251.2
Au	79.1	107.4	264.6	791.4	892.7	1133.7	1386.0	1478.5
Au	1673.1	3210.0	3238.3	3260.7				
Bg	159.5	253.2	815.2	1011.2	1325.2	1448.0	1471.3	1673.4
Bg	3201.1	3223.8	3255.8					
Bu	142.6	506.2	923.5	1082.4	1175.9	1422.5	1518.9	1573.2
Bu	1652.6	1667.5	1677.8	3184.4	3192.5	3199.3	3251.2	
n-Heptane (Trans)								
A	81.8	107.8	150.6	259.1	317.0	454.4	803.2	939.0
A	971.0	1034.6	1097.6	1149.1	1251.7	1373.1	1464.1	1467.8
A	1474.9	1522.0	1574.1	1651.5	1656.6	1669.2	1673.3	1677.6
A	3183.3	3187.0	3193.4	3199.5	3205.4	3228.4	3250.9	3256.3
B	67.6	155.3	261.3	267.0	518.3	790.5	850.7	924.0
B	1046.5	1059.4	1100.3	1190.2	1323.5	1408.1	1431.4	1480.5
B	1506.8	1517.6	1573.9	1650.7	1661.8	1673.4	1676.0	3181.8
B	3191.4	3195.8	3200.1	3216.2	3241.7	3250.8	3260.0	
n-Octane (Trans)								
Ag	211.6	287.5	512.8	945.6	1058.2	1083.7	1102.7	1247.7
Ag	1451.8	1513.1	1520.5	1573.9	1650.4	1655.0	1664.1	1676.4
Ag	3182.9	3185.4	3192.3	3196.9	3250.8			
Au	50.7	74.4	171.1	258.7	789.7	826.3	977.1	1159.9
Au	1363.5	1457.6	1479.9	1673.4	3202.8	3221.4	3245.1	3259.9
Bg	118.0	146.5	261.7	797.2	889.2	1072.8	1322.2	1416.2
Bg	1465.1	1481.2	1673.3	3200.3	3210.8	3232.5	3257.1	
Bu	84.4	368.3	501.7	942.1	1032.0	1098.4	1200.9	1397.5
Bu	1493.5	1522.6	1574.1	1649.9	1657.7	1670.3	1677.4	3181.5
Bu	3188.9	3192.9	3199.7	3250.8				
2-Methylbutane (C_1 Form)								
	101.8	230.5	250.1	284.8	290.5	397.6	446.3	490.6
	809.2	875.2	959.1	1025.3	1049.1	1071.6	1106.9	1129.0
	1271.1	1305.6	1326.7	1435.1	1467.5	1503.9	1513.7	1562.8
	1573.3	1583.5	1651.5	1662.1	1667.8	1673.2	1675.0	1679.7
	1687.8	3183.9	3187.6	3191.5	3194.7	3197.5	3219.3	3239.9
	3246.8	3248.1	3252.0	3260.6	3271.5			
2-Methylbutane (C_s Form)								
A''	92.7	221.0	287.3	397.9	862.3	1023.1	1051.3	1114.2
A''	1299.1	1438.7	1507.8	1563.4	1659.7	1665.6	1684.5	3189.7
A''	3217.1	3242.8	3253.3	3274.2				
A'	273.4	300.2	402.4	571.3	783.1	949.2	1053.6	1145.2
A'	1272.4	1320.0	1469.8	1534.8	1570.2	1584.7	1654.4	1677.0
A'	1681.4	1684.5	3183.0	3191.8	3199.0	3208.1	3247.0	3251.6
A'	3266.0							
2,3-Dimethylbutane (C_{2h} Form)								
Ag	259.9	421.5	533.2	806.9	1007.7	1306.4	1334.4	1506.8
Ag	1587.4	1674.0	1701.4	3183.0	3197.4	3249.9	3281.5	
Au	60.7	222.3	336.0	1031.0	1056.1	1154.1	1473.4	1567.7
Au	1655.9	1683.1	3190.0	3239.3	3280.4			
Bg	223.7	462.2	1023.2	1042.1	1263.2	1486.8	1560.0	1662.9
Bg	1664.4	3189.0	3239.4	3262.0				
Bu	241.8	377.3	446.7	905.5	1121.9	1294.4	1449.7	1579.5
Bu	1675.7	1684.2	3190.8	3199.9	3253.2	3266.8		
2,3-Dimethylbutane (C_2 Form)								
A	68.5	262.0	286.3	313.4	369.1	509.8	763.1	1008.7
A	1024.7	1053.4	1147.5	1288.8	1333.0	1464.0	1511.2	1560.9
A	1589.1	1663.5	1675.3	1681.3	1684.2	3189.0	3194.3	3207.6
A	3244.6	3250.0	3264.7	3271.3				

Table IX (Continued)

B	224.1	260.7	291.3	430.9	577.3	912.2	1020.4	1049.2
B	1141.0	1264.4	1311.7	1470.2	1529.4	1566.0	1576.3	1658.6
B	1661.8	1682.4	1687.9	3186.4	3192.5	3198.3	3244.4	3250.6
B	3253.1	3271.6						
2,3-Dimethylbutane (Saddle Point)								
A	−98.3	268.9	290.1	305.7	365.3	525.7	780.9	1006.4
A	1021.6	1050.9	1160.7	1313.6	1321.3	1486.7	1518.6	1566.5
A	1589.3	1663.2	1664.9	1675.9	1690.4	3183.4	3195.4	3203.6
A	3241.8	3245.4	3255.2	3261.7				
B	278.7	333.0	340.9	440.7	512.1	916.7	1026.5	1046.1
B	1161.1	1261.7	1307.4	1462.6	1522.9	1560.5	1577.5	1657.2
B	1669.5	1675.1	1691.1	3183.2	3194.2	3200.9	3240.5	3242.5
B	3251.9	3277.0						
2,2-Dimethylbutane								
A″	85.8	227.5	281.2	320.3	370.7	446.4	866.1	1004.1
A″	1074.1	1117.3	1226.2	1364.2	1472.6	1564.2	1655.0	1658.9
A″	1674.9	1688.3	3187.2	3209.8	3238.1	3243.3	3257.9	3278.5
A′	277.6	301.9	387.6	430.4	516.7	736.8	929.0	1005.4
A′	1066.3	1128.3	1210.4	1353.0	1397.3	1510.4	1562.3	1574.1
A′	1592.8	1651.8	1662.7	1677.5	1683.8	1691.6	3180.1	3183.8
A′	3195.5	3206.1	3240.2	3251.0	3253.0	3269.2		
2,2-Dimethylbutane (Saddle Point)								
A″	268.7	303.6	350.4	387.2	441.3	839.2	998.2	−139.4
A″	1073.0	1138.8	1220.8	1361.9	1481.4	1562.0	1656.5	1659.9
A″	1672.7	1695.5	3180.6	3220.1	3238.5	3244.4	3266.8	3285.6
A′	318.2	355.6	364.8	444.7	510.5	729.3	923.4	1005.6
A′	1067.9	1147.1	1204.6	1352.5	1382.9	1515.9	1563.6	1576.2
A′	1594.9	1657.9	1667.2	1676.3	1679.1	1694.2	3184.2	3193.9
A′	3196.3	3206.5	3241.7	3244.3	3253.1	3258.2		
Methylcyclohexane (Equatorial)								
A′	165.8	351.3	437.0	472.2	587.2	813.8	879.8	943.5
A′	1026.5	1089.7	1106.7	1183.5	1298.5	1405.2	1424.6	1476.6
A′	1507.9	1531.1	1573.8	1650.4	1660.5	1668.2	1671.6	3179.0
A′	3185.2	3188.2	3191.2	3192.3	3225.2	3227.9	3240.6	3248.7
A″	240.9	265.6	333.4	483.9	866.3	919.0	1014.9	1058.2
A″	1136.8	1201.8	1234.1	1343.7	1420.8	1484.2	1502.4	1507.2
A″	1517.8	1646.5	1651.7	1670.7	3181.3	3188.7	3221.3	3230.3
A″	3243.5							
Methylcyclohexane (Axial)								
A′	175.3	336.1	419.3	516.8	658.0	780.5	866.5	930.8
A′	1011.9	1080.2	1117.6	1174.8	1287.0	1405.6	1423.3	1487.8
A′	1525.3	1532.5	1573.6	1649.8	1658.1	1672.0	1678.3	3180.9
A′	3186.9	3192.5	3199.2	3210.0	3224.0	3227.4	3247.6	3275.6
A″	214.7	254.7	397.9	486.9	862.0	891.5	1032.3	1061.4
A″	1123.1	1203.5	1264.1	1312.3	1420.5	1470.2	1503.2	1514.5
A″	1530.0	1649.0	1655.0	1680.1	3184.4	3202.1	3220.9	3237.9
A″	3243.9							

[a] All frequencies have been scaled by the factor 0.90.

the experimental data via molecular mechanics. Although considerable success has been achieved,[1] there are a number of cases in which agreement is less than satisfactory using the standard parameters that are built into programs such as MM2.[23] It is likely that many, if not most, of the deviations may be eliminated by suitable reparameterization, making use of newer experimental information, as well as the results of theoretical calculations such as those reported herein. However, before such efforts are made, it is essential to have better data on nonbonded interactions. They are known to be markedly anisotropic,[44] and we have recently presented a form of the nonbonded potential function for the H- - -H interaction, which takes the anisotropy into account.[45] Efforts are being made to develop suitable potentials for H- - -C and C- - -C interactions.

It can be seen that the molecular orbital calculations, when electron correlation and zero-point energies are taken into account, are able to reproduce the experimental data on the conformations of saturated hydrocarbons and to give some insight into the factors that control energies. The question of the origin of the gauche effect will receive further study.

Calculations

The calculations were carried out with GAUSSIAN-82[46] with the standard basis sets.[20] Initial geometry optimizations were effected by a MicroVAX computer, which was purchased with the aid of a National Science Foundation instrument grant. Most of the 6-31G* optimizations were carried out with a VAX-8600 at the Fairfield University Computer Center, and the larger basis set calculations, post-HF, and vibrational frequency calculations were carried out at the Pittsburgh Supercomputer Center with the aid of a grant from the National Science Foundation Office of Advanced Scientific Computing.

To calculate the enthalpy for each species, $H_{298} - H_0$, the moment of inertia, geometries, and 3-21G frequencies were used in the standard way.[47,48] When the vibrational contribution was calculated, however,

---

(44) Price, S. L.; Stone, A. J. *Mol. Phys.* **1980**, *40*, 805.

(45) Wiberg, K. B.; Murcko, M. A. *J. Comput. Chem.* **1987**, *8*, 1124.

(46) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A., Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA.

(47) Janz, G. J. *Thermodynamic Properties of Organic Compounds: Estimation Methods, Principles and Practice*, revised ed.; Academic: New York, 1967.

(48) Boyd, R. H.; Breitling, S. M.; Mansfield, M. *AIChE J.* **1973**, *19*, 1016.

the frequencies corresponding to methyl rotation were treated separately, using Pitzer's tables.[49]

Acknowledgment. This investigation was supported by the Office of Basic Energy Sciences, Department of Energy, and National Science Foundation. M.A.M. acknowledges a Connecticut High Technology Scholarship. We thank Fairfield University for a grant of computer time.

Registry No. Butane, 106-97-8; pentane, 109-66-0; hexane, 110-54-3; 2-methylbutane, 78-78-4; 2,3-dimethylbutane, 79-29-8; methylcyclohexane, 108-87-2; octane, 111-65-9; 2,2-dimethylbutane, 75-83-2; cyclohexane, 110-82-7; heptane, 142-82-5.

---

(49) Pitzer, K. S.; Gwinn, W. D. *J. Chem. Phys.* **1942**, *10*, 428.

Application of Modern ^{3}H NMR Techniques to Analysis of Complex Isotopic Products from a Hydrogenation Reaction

Philip G. Williams,* Hiromi Morimoto, and David E. Wemmer

Contribution from the National Tritium Labeling Facility and Chemical Biodynamics Division, Lawrence Berkeley Laboratory 75-123, University of California, Berkeley, California 94720.
Received February 22, 1988

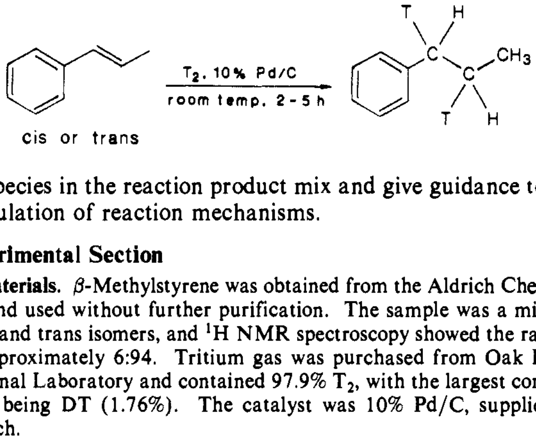
Abstract: A number of modern multiple pulse NMR techniques have been applied to tritium for the first time, demonstrating the power of this approach for analysis of complex isotopic mixtures. In particular, double quantum filtering, DEPT, and tritium homodecoupled BB-proton-decoupled one-dimensional spectra have been obtained. In addition, phase sensitive tritium COSY, tritium–proton correlation, and tritium *J*-resolved two-dimensional experiments are reported. These experiments yield a great deal of information about the isotopic distribution in the subject molecule—*n*-propylbenzene—produced by the catalytic tritiation of β-methylstyrene. Analysis of these NMR data has allowed us to reach some mechanistic conclusions about hydrogenation reactions.

High-resolution tritium NMR spectroscopy has been used routinely for almost 25 years in several laboratories around the world. Since the first observation of a high-resolution spectrum,[1] almost half the published work has originated from the Amersham/University of Surrey collaboration between Evans, Warrell, Elvidge, Jones, and their many co-workers.[2]

Although ^{3}H NMR analysis has been applied to analysis of heterogeneous and homogeneous catalysis,[3,4] determination of product purity,[5] and protein–ligand binding studies,[6] almost all experiments have involved only "onepulse" NMR spectroscopy. In the very recent past a few more adventurous experiments were conducted, including ^{3}H *J*-resolved,[7] ^{3}H–^{3}H COSY,[7,8] and several types of ^{3}H–^{1}H correlation experiments.[8]

As a further illustration and development of the usefulness of multipulse ^{3}H NMR we have conducted a series of NMR experiments on a sample of *n*-propylbenzene prepared by the catalytic tritiation of β-methylstyrene. A double quantum filter has been applied to one-dimensional spectra in order to directly observe the labeled molecules containing spin systems with greater than one tritium atom. *J*-resolved, ^{3}H–^{1}H correlation and phase-sensitive ^{3}H–^{3}H COSY spectra have also been obtained. Selective ^{3}H homodecoupling and ^{3}H–^{1}H DEPT spectra are reported for the first time. All these methods yield extensive information about the species in the reaction product mix and give guidance to the formulation of reaction mechanisms.

Scheme I



Experimental Section

Materials. β-Methylstyrene was obtained from the Aldrich Chemical Co. and used without further purification. The sample was a mixture of cis and trans isomers, and ^{1}H NMR spectroscopy showed the ratio to be approximately 6:94. Tritium gas was purchased from Oak Ridge National Laboratory and contained 97.9% T_2, with the largest contaminant being DT (1.76%). The catalyst was 10% Pd/C, supplied by Aldrich.

Catalytic Tritiation. β-Methylstyrene (1 mL) and catalyst (100 mg) were exhaustively degassed in a microhydrogenation apparatus by the application of several freeze–pump–thaw cycles. Tritium gas was admitted to a pressure of 86.7 kPa, and the substrate was thawed. Excess pressure (>101.3 kPa) was vented to the vacuum system, and the catalyst was added to the substrate. The reaction mixture was then stirred and kept at room temperature, and the uptake of gas was monitored. After 1 h the substrate was frozen (liquid N_2) and the residual T_2 pumped away. The flask was extensively flushed with N_2, and methanol (2 mL, ×2) was added to the mixture to remove any labile or dissolved tritium. After the volume was reduced (i.e., pumping the methanol away) the flask was removed from the vacuum line and the solution filtered. An aliquot of the filtrate was dissolved in C_6D_6 for NMR study.

A second preparation (500-μL substrate) varied in the following ways. When the reaction pressure had dropped to 12–20 kPa the flask was refilled with H_2 and the reaction allowed to proceed. This routine was repeated until uptake of H_2 ceased. No methanol was added during the subsequent workup procedure since there are no labile hydrogens on the expected product, but dissolved T_2 was removed by repeated N_2 flushing and several freeze–pump–thaw cycles. This also alleviated the large methanol peaks from the proton NMR spectra of this product. Deuteriochloroform was added to the reaction product to flush it through the filtration apparatus, and storage in this medium had dire consequences for the radiochemical purity of this sample. The solution became deeply

---

(1) Tiers, G. V. D.; Brown, C. A.; Jackson, R. A.; Lahr, T. N. *J. Am. Chem. Soc.* **1964**, *86*, 2526–2527.

(2) Evans, E. A.; Warrell, D. C.; Elvidge, J. A.; Jones, J. R., Eds. *Handbook of Tritium NMR Spectroscopy and Applications*; Wiley: Chichester, 1985.

(3) Garnett, J. L.; Long, M. A.; Odell, A. L. *Chem. Aust.* **1980**, *47*, 215–220.

(4) Odell, A. L. *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic: New York, 1983, Vol. 2, pp 27–48.

(5) Kaspersen, F. M.; Funke, C. W.; Wagenaars, G. N. *Synthesis and Applications of Isotopically Labeled Compounds 1985, Proceedings of the Second International Symposium*, Muccino, R. R., Ed.; Elsevier: Amsterdam, 1986; pp 355–360.

(6) Evans, J. N. S.; Burton, G.; Fagerness, P. E.; Mackenzie, N. E.; Scott, A. I. *Biochemistry* **1986**, *25*, 905–912.

(7) Sergent, L. R.; Beaucourt, J. P. *Tetrahedron Lett.* **1985**, *26*, 5291–5292.

(8) Funke, C. W.; Wagenaars, G. N.; Kaspersen, F. M. *Magn. Reson. Chem.* **1986**, *24*, 434–437.

0002-7863/88/1510-8038$01.50/0