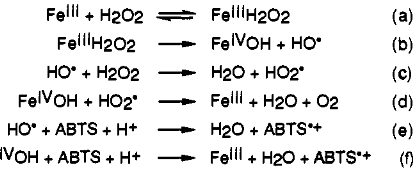
Scheme XIV



In our system, $Fe^{IV}OH$ and $HO^{\bullet}$, formed as primary products, would be trapped by ABTS so that steps (c) and (d) of Scheme XIV would be replaced by (e) and (f). At low pH k_{1y}^{H} is independent of pH, and (k_{1y}^{H}/k_{1y}^{D}) is much the same for Fe^{III} (1.9) and $(\mathbf{1})Fe^{III}(X)_2$ (2.7) and is comparable to $k_{1y}^{H}/k_{1y}^{D} = 3.0$ for the reaction of H_2O_2 with $(\mathbf{2})Fe^{III}(X)_2$. A common mechanism for these reactions is suggested.

In the reactions with *t*-BuOOH the value of k_{1y}^{H} with Fe^{III} is 5-fold greater than is k_{1y}^{H} for the reaction with $(\mathbf{1})Fe^{III}(X)_2$ at low pH. Thus at low pH, porphyrin ligation actually appears to impede the reaction of Fe^{III} with *t*-BuOOH. This may be partially due to the availability of three times as many sites for coordination of hydroperoxide on Fe^{III} as compared to $(\mathbf{1})Fe^{III}(X)_2$. In any case, $(\mathbf{1})Fe^{III}(X)_2$ does not react with *t*-BuOOH through a pathway any more favorable than that for the reaction of Fe^{III} with *t*-BuOOH (Scheme XIII, steps (a), (b), (e), and (f)). Therefore, at low pH homolytic cleavage of the O–O bond of *t*-BuOOH ligated to $(\mathbf{1})Fe^{III}(X)_2$ appears to be the most favorable pathway available for its decomposition.

Acknowledgment. We express our gratitude to the National Institutes of Health for support of this study.

Investigation of Intramolecular Interactions in *n*-Alkanes. Cooperative Energy Increments Associated with GG and GTG′ Sequences

Seiji Tsuzuki,[1a] Lothar Schäfer,*,[1b] Hitoshi Gotō,[1c] Eluvathingal D. Jemmis,[1d] Haruo Hosoya,[1e] Khamis Siam,[1b,f] Kazutoshi Tanabe,[1a] and Eiji Ōsawa*,[1c]

Contribution from the National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan, Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701, Department of Knowledge-Based Information Engineering, Toyohashi University of Technology, Toyohashi 441, Japan, School of Chemistry, University of Hyderabad, Central University P. O., Hyderabad 500134, India, and Department of Chemistry, Faculty of Science, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan. *Received July 16, 1990*

Abstract: Energies of rotational isomers of *n*-alkanes are largely determined by the number of individual gauche bonds (G). However, according to molecular mechanics calculations (MM2), within a group of rotamers with equal number of G bonds, there are characteristic energy variations due to cooperative effects involving sequences of several bonds. For example, the energy is increased by inserting a trans bond (T) between two consecutive G bonds of the same sign (e.g., TGGG < GTGG in *n*-heptane), and special long-range repulsive interactions seem to exist between G and G′, a gauche bond of opposite sign, in a GTG′ sequence (e.g., GTG < GTG′ in *n*-hexane). With use of ab initio MP4SDQ/6-31G*//6-31G* energies and geometries of ethane to *n*-hexane, including all rotamers, a 0.16 kcal/mol stabilizing energy increment is found to be characteristic for GG sequences. The potential source of this increment is found in nonbonded *attractive* interactions between 1,5-CH_3/CH_3, -CH_3/CH_2, and -CH_2/CH_2 groups, which are specific for GG but not for other combinations, such as GT, TT, or GG′. In addition, a 0.12 kcal/mol destabilizing energy increment is found to be associated with GTG′ sequences relative to GTG. It is rationalized by unfavorable nonbonded interactions that can be relaxed in GTG but not in GTG′ due to symmetry constraints. Whereas these cooperative energy increments are small for a single GG or GTG′ sequence, their accumulation in polymers can be considerable. The GG′ equilibrium structure of *n*-pentane belongs to the C_1 point group due to unequal C–C–C–C dihedral angles (±63 and ∓95°). A symmetric GG′ conformer (C_s) is 0.28 kcal/mol above the GG′ energy minimum and is identified as a saddle point. In contrast to a generally accepted rule, the lack of local symmetry in GG′ sequences implies the possible existence of more than 3^n rotamers for alkanes with *n* rotatable bonds. Good agreement is found for the order of MM2 and ab initio conformational energies. The results of this study are also of general interest, because they demonstrate one of the factors that can contribute to errors in conformational energies at the SCF level: Different conformations of a molecule may differ in stabilizing van der Waals interactions whose neglect leads to errors in all energy calculations that do not include dispersion forces.

The success of molecular modeling based on empirical potential energy calculations[2] depends on the ability of the computational techniques to correctly reproduce intra- and intermolecular relative energies. The problem here is the sparsity of accurate conformational energies, experimental or theoretical, by which parameters of empirical potential functions can be determined.[3]

Among small *n*-alkanes, for example, only a few rotamer energies for *n*-butane and *n*-pentane in the vapor phase have been recorded in the literature (Table I). A glance at this table reveals that, in addition to the considerable scatter in the experimental gauche butane energies, there is a serious problem in that the experimental gauche energy decreases significantly in going from *n*-butane (about 870 cal/mol) to *n*-pentane (about 500 cal/mol), whereas ab initio calculations at certain higher levels consistently reproduce about 700 cal/mol for these molecules.[4] Current molecular mechanics force fields neglect these difficulties[5] and

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(1) (a) NCLI. (b) University of Arkansas. (c) Toyohasi University of Technology (correspondence address). (d) University of Hyderabad. (e) Ochanomizu University. (f) Present address: Chemistry Department, Pittsburgh State University, Pittsburgh, KS 66762.

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Table I. Vapor-Phase Trans/Gauche Energy Differences (cal/mol) for *n*-Butane and *n*-Pentane Reported in the Literature

	method	year	ref
	n-Butane		
966 (50)[a]	Raman	1974	*b*
497 (220)	ED	1977	*c*
877	far-IR	1979	*d*
889 (29)	Raman	1980	*e*
751 (235)	ED	1983	*f*
≤730	IR	1985	*g*
600–700	MP3/6-311G*//MP2/6-31G	1984	*h*
750	MP3/6-31G*//6-31G*	1988	*i*
690	CISD(Q)DZP//DZP	1990	*j*
	n-Pentane		
560 (100)	Raman	1983	*k*
465 (30)	Raman	1986	*l*
760	MP3/6-31G*//6-31G*	1988	*i*

[a] Parenthesized numbers are the reported experimental error estimates. [b] Verma, A. L.; Murphy, W. F.; Bernstein, H. J. *J. Chem. Phys.* **1974**, *60*, 1540. [c] Bradford, W. S.; Fitzwater, S.; Bartell, L. S. *J. Mol. Struct.* **1977**, *38*, 185. [d] Durig, J. R.; Compton, D. A. C. *J. Phys. Chem.* **1979**, *83*, 265. [e] Compton, D. A. C.; Montrero, S.; Murphy, W. F. *J. Phys. Chem.* **1980**, *84*, 3587. [f] Heenan, R. K.; Bartell, L. S. *J. Chem. Phys.* **1983**, *78*, 1270. [g] Rasanen, M.; Bondybey, V. E. *J. Chem. Phys.* **1985**, *82*, 4718; *Chem. Phys. Lett.* **1984**, *111*, 515. [h] Reference 13. [i] Reference 12. [j] Reference 11. [k] Maissara, M.; Cornut, J. C.; Devaure, J.; Lascombe, J. J. *Spectrosc. Int. J.* **1983**, *2*, 104. [l] Reference 21.

use any one of the experimental values of Table I as the standard value. Therefore, to our knowledge, it has never been guaranteed that a molecular mechanics scheme correctly reproduces relative energies among the rotamers of *n*-alkanes.

A puzzling energetic order is obtained when *n*-heptane rotamers are calculated with use of MM2 (Figure 1).[3,6] Among the low-energy rotamers appearing between TTTT and GGGG (T = trans bond, G = gauche bond),[7] the number of gauche bonds determines the basic order as expected. However, there are significant fluctuations within each group containing equal numbers of gauche bonds.

A consistent but unexpected rule is found in these fluctuations: Whenever successive gauche bonds of the same sign (GG, GGG, etc.) are separated by one or more trans bonds, the total energy increases (e.g., TTGG < TGTG or GTTG, and TGGG < GTGG). These changes are difficult to rationalize because long-range interactions between two gauche segments separated by a trans bond or two are unlikely. Similar considerations apply to TGTG and TGTG′.[8]

The energy variations involved in the trends described above are small, but their accumulation in large systems can be significant. Furthermore, they will be misleading, if they are artifacts of the calculations. Therefore, we decided to search for potential sources of these trends. Because of the continuing problem of choosing the correct experimental gauche energy,[9] this study is based on the results of ab initio calculations.

Computational Methods

It has recently been shown that predictions of absolute heats of formation of molecules with no more than two non-hydrogen atoms to an accuracy better than 2 kcal/mol[10] or of the syn rotational barrier of *n*-butane to within 0.5 kcal/mol[11] require calculations at a level that is currently impracticable for systems that are of interest for this study, i.e., molecules with at least three rotatable bonds.

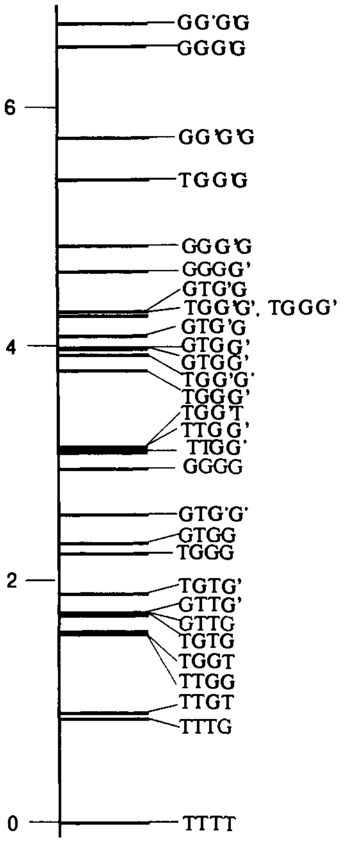

Figure 1. Relative MM2 steric energies of *n*-heptane rotamers (kcal/mol): T = trans, G = gauche(+), G′ = gauche(−), G = dihedral angle about 95°, G′ = dihedral angle about −95°. Rotamers were generated by using the CONFLEX3 program (Ōsawa, E.; Gotō, H. *Proc. Int. Conf. Comput. Appl. Mat. Sci. Eng.-CAMSE '90, Tokyo, 1990*; Doyama, M., Ed.; Elsevier: Amsterdam, in press; see also Gotō, H.; Ōsawa, E. *J. Am. Chem. Soc.* **1989**, *111*, 8950; CONFLEX2, *QCPE 592*). From among more than 3^4 rotamers (see text) for *n*-heptane, only the unique rotamers with steric energies below 6.7 kcal/mol relative to the TTTT global energy minimum were generated and their geometries optimized.

Fortunately, relative conformational energies of simple hydrocarbons can be calculated quite well, when sufficiently large double-ζ-type basis sets are used with polarization functions on carbon and with electron correlation corrections using higher order perturbational methods.[12,13] In this regard, Wiberg and Murcko's recent MP3/6-31G*//6-31G* calculations[12] of small alkanes are most interesting for our present purpose. However, since they did not consider all of the hexane rotamers, we undertook a thorough examination of this molecule and recalculated some of the lower homologues by using an ab initio formalism similar to that of Wiberg.[12]

The Gaussian 82 and 86 packages[14] were used with the 6-31G* basis set on a Cray X-MP supercomputer. Standard default criteria were applied for the SCF convergence and the gradient geometry optimization. Total energies (ΔE^0, footnote *a* of Table II) were corrected for electron

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(4) Zero-point energy corrections (ZPE) to transform ab initio $\Delta\Delta E^0$ values to spectroscopically determined $\Delta\Delta H^0$ values are about 100 cal/mol for *n*-alkanes studied here. Thermal energy corrections, to obtain $\Delta\Delta H^{298}$, are about −30 cal/mol (see Table IV and refs 11 and 12). For measurements in the condensed phase, see, e.g., Hartge, U.; Schrumpf, G. *J. Chem. Res., Synop.* **1981**, 189 and references cited therein.

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(7) Unstable conformers above the GGGG rotamer of *n*-heptane are discussed below.

(8) These trends are also observed in MM2 calculations of *n*-hexane (vide infra), *n*-octane, and *n*-nonane.

(9) This problem has a long history. See, e.g., Scott. R. A.; Scheraga, H. A. *J. Chem. Phys.* **1966**, *44*, 3054. Stidham, H. D.; Durig, J. R. *Spectrochim. Acta* **1986**, *42A*, 105.

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Table II. Calculated Conformational Energies (kcal/mol) for Some Small *n*-Alkanes

		$\Delta\Delta E^0$		
rotamer[a]	point group	MP4SDQ/ 6-31G*//HF/ 6-31G*[j]	HF/ 4-21G[b,j]	$\Delta\Delta E^{298}$ MM2[j]
		n-Butane		
T	C_{2h}	0.000 (0.00)[c]	0.00 (0.00)[d]	0.000 (0.00)[e]
G	C_2	0.740 (0.74)	0.83 (0.85)	0.864 (0.91)
		n-Pentane		
TT	C_{2v}	0.000 (0.00)	0.00 (0.00)	0.000 (0.00)
TG	C_1	0.740 (0.74)	0.86 (0.85)	0.897 (0.91)
GG	C_2	1.302 (1.32)	1.63 (1.70)	1.623 (1.62)
GG′	C_1	3.289 (3.28)	3.69 (3.70)	3.357 (3.24)
GG′[f]	C_s	3.565		3.579
		n-Hexane		
TTT	C_{2h}	0.000 (0.00)	0.00 (0.00)	0.000 (0.00)
TTG	C_1	0.721 (0.74)	0.86 (0.85)	0.884 (0.91)
TGT	C_2	0.733 (0.74)	0.88 (0.85)	0.934 (0.91)
TGG	C_1	1.299 (1.32)	1.67 (1.70)	1.617 (1.62)
GTG	C_2	1.439 (1.48)	1.71 (1.70)	1.701 (1.82)
GTG′	C_i	1.564[g]	1.81[g]	1.889[g]
GGG	C_2	1.843 (1.90)	2.43 (2.55)	2.302 (2.33)
TGG′	C_1	3.117 (3.28)		3.205 (3.24)
TGG′	C_1	3.211 (3.28)	3.70 (3.70)	3.244 (3.24)
GGG′	C_1	3.872 (3.86)	4.56 (4.55)	3.938 (3.95)
GGG′	C_1	3.902 (3.86)[h]		4.239 (4.15)[h]
GG′G	C_2	5.916 (5.82)	6.73 (6.55)	5.579 (5.57)
GG′G[i]				

[a] Bold-faced gauche (G) bond has a dihedral angle of ca. ±95°. $\Delta\Delta E^0$ values are differences between the total energy (ΔE^0 or ΔE^{298}) of the all-trans form of a given molecule and its other conformers. Reference ΔE^0 values (au): *T*-butane, −157.879 809 6; *TT*-pentane, −197.056 688 3; *TTT*-hexane, −236.233 585 8. [b] References 23b and 25. [c] Calculated by using additivity increments: G = 0.74, GG = −0.16, GG′ = 1.80. For more details, see text. [d] Calculated by using additivity increments: G = 0.85, GG′ = 2.00. [e] Calculated by using additivity increments: G = 0.91, GG = −0.20, GG′ = 1.42. [f] A saddle point. [g] Increment for G does not apply to this rotamer; see text. [h] For GG segment, GG increment is ignored. [i] Not a stationary point; see text. [j] Standard deviation of the energies obtained with the additivity principle described in the text: MP4SDQ|6-31G*//HF/6-31G*, 0.04; HF/4-21G, 0.06; MM2, 0.04.

correlation with the 6-31G* geometries and a simplified Møller–Plesset method of the fourth order (MP4SDQ).[15] Wiberg and Murcko[12] have noted that this level of theory produces results comparable to those obtained by MP3/6-31G(df,p)//6-311G** calculations for *n*-butane. For the purpose of comparison, the 4-21G gradient optimization calculations have also been performed.

Zero-point energy (ZPE) and thermal energy (E_{therm}) corrections were carried out by standard statistical thermodynamics procedures.[16] Harmonic vibrational frequencies, needed for these corrections, were obtained for the 6-31G* geometries by using the normal mode analysis routine in Gaussian 86. A scaling factor (0.9) for the calculated frequencies was optimized with the experimental infrared frequencies of ethane.[17] The scaled force constants reproduced the ethane spectrum with a standard deviation of 25 cm^{-1}.

The MM2 program[6,18] was obtained from QCPE and run on a VAXstation 2000. Final structures from these calculations were reoptimized by using the full-matrix Newton–Raphson algorithm implemented in BIGSTRN3.[19]

In both the ab initio and MM2 calculations, vibrational analyses and the imaginary frequency criterion were used to identify energy minima or maxima.

Table III. Calculated Zero-Point Energy (ZPE), Thermal Energy (E_{therm}), Entropy (S), and Heat Capacity (C_v) of *n*-Alkanes[a]

	ZPE (kcal/mol)	E_{therm} (kcal/mol)	S (cal/mol K)	C_v (cal/mol)
		Ethane		
	45.045	2.215	54.535	10.307
		Propane		
	62.448	2.896	64.453	15.146
		n-Butane		
T	79.725	3.706	72.253	20.162
G	79.818	3.677	73.643	20.086
		n-Pentane		
TT	96.978	4.547	80.037	25.121
TG	97.076	4.510	82.773	25.016
GG	97.217	4.437	80.838	24.940
GG′	97.185	4.475	82.509	24.987
		n-Hexane		
TTT	114.213	5.405	87.827	30.109
TTG	114.312	5.366	90.599	30.042
TGT	114.312	5.368	89.217	30.013
TGG	114.458	5.293	90.133	29.956
GTG	114.419	5.323	89.101	29.975
GTG′	114.393	5.347	89.507	30.013
GGG	114.592	5.225	88.016	29.842
TGG′	114.438	5.310	90.104	29.908
TGG′	114.412	5.331	90.142	29.975
GGG′	114.538	5.279	89.774	29.947
GGG′	114.499	5.287	90.087	29.947
GG′G	114.546	5.277	87.897	29.975

[a] E_{therm}, S, and C_v refer to a temperature of 298.15 K.

Results

Comparison of the MP4/6-31G*//6-31G* Calculations with Experimental Data. The MP4SDQ/6-31G*//6-31G* energies of ethane, propane, *n*-butane, *n*-pentane, and *n*-hexane are obtained and a part of them summarized in Table II. These energies can be compared with two kinds of experimental data: the trans/gauche energy differences of *n*-butane and *n*-pentane (Table I) and the entropies and heat capacities of ethane to *n*-hexane. For the latter, the calculated potential energies (E^0) were corrected for contributions from zero-point energy (ZPE) and thermal excitation (E_{therm}).[16] The resulting values are given in Tables III and IV.

We obtain 833 cal/mol for $\Delta\Delta H^0$, the difference between the ΔH^0 values of *T*- and *G*-butane, and 804 cal/mol for the corresponding $\Delta\Delta H^{298}$ (Table IV). The experimental values for these quantities have kept changing, as shown in Table I. Simple averaging yields approximately 870 (90)[20] for $\Delta\Delta H^0$ and 600 (130) cal/mol for $\Delta\Delta H^{298}$. Thus, the experimental estimates for the thermal effects are significantly larger than the calculated ones, and only the $\Delta\Delta H^0$ values are close. On the other hand, the $\Delta\Delta H^0$ value between TG and TT forms of *n*-pentane is calculated to be 837 cal/mol (Table IV). This value is much larger than the spectroscopic equivalent (465 (30) cal/mol, Table I).[21] Thus, there is significant disagreement between theory and experiment but also between individual values of the experimentally derived parameters.

Calculated Gibbs free energies of the various rotamers relative to their respective all-trans forms ($\Delta\Delta G^{298}$, Table IV) were used to calculate the standard-state heat capacities and entropies of mixing for conformational equilibria. The results (Table V) are within a few percent of the experimental values. In view of this agreement and since these properties depend critically on the relative conformational energies, we will tentatively assume that the internal consistency of our procedures is sufficient to support

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(15) (a) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244. (b) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1988**, *22*, 377.

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(18) After this work was completed, an improved version of Allinger's MM series (MM3) was announced: Allinger, N. L.; Lii, J.-H.; Yuh, Y. H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.

(19) BIGSTRN3: Nachbar, R. B., Jr.; Mislow, K. *QCPE*, **1986**, *19*, 514. Cf. *QCPE Bull.* **1986**, *6* (3), 96.

(20) Parenthesized numbers are either rms error or the reported experimental error range.

(21) Kanesaka, I.; Snyder, R. G.; Strauss, H. L. *J. Chem. Phys.* **1986**, *84*, 395.

Table IV. Calculated Relative Energies and Rotamer Populations of *n*-Alkanes

	$\Delta\Delta H^{0\,a,b}$ (kcal/mol)	$\Delta\Delta H^{298\,a,c}$ (kcal/mol)	$\Delta\Delta G^{298\,a,c}$ (kcal/mol)	population[c] (%)
		n-Butane		
T	0.000	0.000	0.000	65.9
G	0.833	0.804	0.390	34.1
		n-Pentane		
TT	0.000	0.000	0.000	46.1
TG	0.837	0.800	−0.015	47.2
GG	1.541	1.431	1.192	6.2
GG′	3.496	3.424	2.687	0.5
		n-Hexane		
TTT	0.000	0.000	0.000	30.9
TTG	0.819	0.780	−0.047	33.5
TGT	0.831	0.794	0.380	16.3
TGG	1.544	1.432	0.745	8.8
GTG	1.654	1.562	1.182	4.2
GTG′	1.744	1.686	1.185	4.2
GGG	2.222	2.041	1.985	1.1
TGG′	3.343	3.247	2.569	0.4
TGG′	3.410	3.336	2.646	0.4
GGG′	4.198	4.071	3.491	0.1
GGG′	4.188	4.070	3.396	0.1
GC′G	6.249	6.121	6.100	0.0

[a] $\Delta\Delta H$ ($\Delta\Delta G$) values are differences between the total ΔH(ΔG) values of the all-trans form of a given molecule and its other conformers. [b] 0 K. [c] 298.15 K.

Table V. Entropies and Heat Capacities of Small Alkanes

	heat capacity (cal/mol)		entropy (eu)	
	obsd[a]	calcd	obsd[a]	calcd
ethane	10.59	10.307	54.85	54.535
propane	15.58	15.146	64.51	64.453
n-butane	21.30	20.136	74.12	74.002
n-pentane	26.74	25.060	83.40	83.199
n-hexane	32.21	30.043	92.83	92.532

[a] Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley & Sons: New York, 1969.

our conclusions and that the $\Delta\Delta E^0$ values of Table II are sufficiently accurate for this study.

The gradient optimization method at the double-ζ quality is known to give good equilibrium geometries; further upgrading of theoretical levels does not produce much change.[12,22,23] The 6-31G*-optimized geometries of the rotamers of *n*-butane[13,22] and *n*-pentane[12,22] and five rotamers of *n*-hexane (TTT, TTG, TGT, GTG, and GGG)[12] have been previously reported. Table VI lists 6-31G* geometries of the remaining forms of *n*-hexane and a GG′ saddle point of *n*-pentane.

A Remark on *gauche-n*-Butane. In addition to the well-known structural characteristics of *gauche*-butane (longer C–C bonds than in trans, a large C–C–C bond angle, and a C–C–C–C dihedral angle greater than 60°),[12,23b,24,25] we note here the fact that its methyl group is rotated by 4–6° away from a standard torsional angle of 60°, apparently to reduce the H/H repulsion between the methyl groups in a G′GG′-like arrangement. This H/H interaction is known to produce an unusually high ν_{CH} frequency of 2949 cm^{-1} at one of the methyl hydrogens of *gauche*-butane, compared to that of the corresponding hydrogen atom of *trans*-butane (2936 cm^{-1}).[26] The interacting pair of methyl hydrogen atoms is symmetrically equivalent (C_2). We find that similar deformations occur at nearly every gauche bond in larger homologues, and they are a key to understanding some important aspects of the conformational behavior of alkane rotamers.

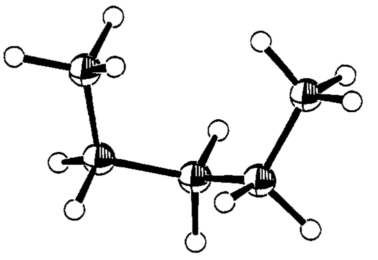
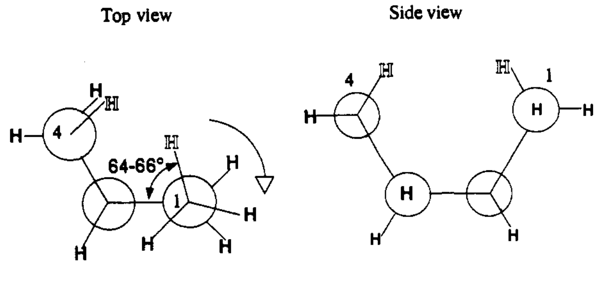


Figure 2. ORTEP drawing of the GG′ rotamer of *n*-pentane, point group C_1.



Gauche butane

Gauche(+)–Gauche(−) Interactions. The GG′ rotamer of pentane has often been considered "forbidden" because of its high strain[27a] (3.3 kcal/mol higher in energy relative to *all-trans*-pentane Table II). However, conformational isomers containing GG′ segments are taken into account in the recent rotational isomeric state analysis of chain polymers[4,28] and in other analyses of larger systems.[29]

The minimum-energy structure of GG′ in pentane (Figure 2) has no symmetry element (C_1) due to its different C–C–C–C dihedral angles (±63 and ∓95°). This feature was previously noticed by both molecular mechanics[9,30] and ab initio calculations.[12,23] Wiberg and Murcko[12] also investigated a GG′ conformer with C_s symmetry.[31] In our calculations, this C_s rotamer has dihedral angles of ±77.5° (Table VI), its energy is 0.28 kcal/mol higher than the C_1 form (Table II), and it has one imaginary vibration at 67i cm^{-1} whose dominant modes are torsional deformations toward enantiomeric C_1 conformers. Thus, this form very likely corresponds to a saddle point of interconversion between enantiomeric C_1 GG′ energy minima.

Because of the asymmetry of the GG′ form, larger molecules containing this segment, XGG′Y, give rise to two distinct energy minima when X and Y are not identical. For example, the hexane molecule with the TGG′ sequence consists of two rotamers, TGG′ and TGG′, where the bond having the abnormally wide (±95°) dihedral angle is printed with a bold face. Thus, 13 unique

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(22) Aljibury, A. L.; Snyder, R. G.; Strauss, H. L.; Raghavachari, K. *J. Chem. Phys.* **1986**, *84*, 6872.

(23) (a) Scarsdale, J. N.; Van Alsenoy, C.; Schäfer, L. *J. Mol. Struct.: THEOCHEM* **1982**, *86*, 277. (b) Schäfer, L.; Siam, K.; Ewbank, J. D.; Ōsawa, E. *Ibid.* **1986**, *139*, 125. Schäfer, L.; Siam, K. *J. Chem. Phys.* **1988**, *88*, 7255.

(24) Allinger, N. L.; Schäfer, L.; Siam, K.; Klimkowski, V. J.; Van Alsenoy, C. *J. Comput. Chem.* **1985**, *6*, 331.

(25) In the 4-21G calculations of ref 24, the C–C–C–C dihedral angle of *n*-butane was constrained for the purpose of that study. When it is refined without constraint, a value of 66.3° results with a T to G energy difference of 0.83 kcal/mol.

(26) Snyder, R. G.; Aljibury, A. L.; Strauss, H. L.; Casal, H. L.; Gough, K. M.; Murphy, W. F. *J. Chem. Phys.* **1984**, *81*, 5352. In Figure 6 of this paper, a dihedral angle involving the congested proton (H–C1–C2–C3) is given a value of ca. 67°. In our calculations, this angle is slightly smaller, 63.9°.

(27) Dale, J. *Stereochemistry and Conformational Analysis*; Verlag Chemie: New York, 1978; (a) p 96; (b) p 100; (c) p 213.

(28) (a) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969. (b) Tevlin, P.; Lafleur, S.; Trainor, L. E. H. *Chem. Phys. Lett.* **1985**, *122*, 581. (c) Riande, E.; Guzman, J.; Saiz, E.; de Abajo, J. *Macromolecules* **1981**, *14*, 608.

(29) Narumi, H.; Hosoya, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1228.

(30) Ōsawa, E. In *Mathematics and Computational Concepts in Chemistry*; Trinajstic, N., Ed.: Ellis Horwood: Chichester, 1986; Chapter 21.

(31) MM3[18] gives a near C_s conformation for the GG′ rotamer of *n*-pentane.

Table VI. Calculated Geometries of the C_s Saddle Point of *n*-Pentane and Some Selected Rotamers of *n*-Hexane (6-31G*)[a]

n-Pentane

	GG′ (C_s)		GG′ (C_s)		GG′ (C_s)
C1–C2	1.531	C1–C2–C3	116.4	C1–C2–C3–C4	77.5
C2–C3	1.537	C2–C3–C4	117.4	C2–C3–C4–C5	−77.5
C3–C4	1.537	C3–C4–C5	116.4		
C4–C5	1.531				

n-Hexane

	TGG	GTG	GTG′	TGG′	TGG′	GGG′	GGG′	GG′G
C1–C2	1.529	1.530	1.530	1.529	1.529	1.530	1.530	1.531
C2–C3	1.531	1.534	1.534	1.532	1.531	1.534	1.536	1.541
C3–C4	1.534	1.532	1.532	1.541	1.535	1.537	1.544	1.537
C4–C5	1.534	1.534	1.534	1.535	1.542	1.541	1.535	1.541
C5–C6	1.530	1.530	1.530	1.529	1.531	1.531	1.529	1.531
C1–C2–C3	112.6	114.5	114.7	112.6	112.5	114.4	113.8	114.8
C2–C3–C4	114.8	114.3	114.4	115.0	116.0	117.6	115.7	117.5
C3–C4–C5	116.3	114.3	114.4	115.9	115.9	116.0	115.2	117.5
C4–C5–C6	114.4	114.5	114.7	115.8	114.8	115.3	115.4	114.8
C1–C2–C3–C4	175.3	66.3	67.5	−179.5	175.2	64.2	72.3	93.4
C2–C3–C4–C5	62.7	172.2	180.0	95.3	63.3	65.2	98.0	−65.8
C3–C4–C5–C6	62.3	66.3	−67.5	−63.0	−95.7	−93.1	−63.9	93.4

[a] Distances in angstroms, angles in degrees. For rotamers not listed here, see refs 12, 13, and 22. [b] The rotamer GTG described in ref 12 (Tables IV and V) is actually GTG′.

conformers are conceivable for *n*-hexane (Table II), instead of the 10 considered before.[9,27b]

The most unfavorable rotamer class of *n*-hexane must be of the type GG′G, since it suffers from the double GG′ strain. Of the two possible conformations, GG′G and GG′G, we were not successful in optimizing the latter form: It changed into GTG during geometry optimization. A total of five forms of hexane with at least one GG′ segment were confirmed to be local energy minima, and their $\Delta\Delta E^0$ values are listed in Table II.

For larger hydrocarbons, the number of high-energy conformers with G or G′ bonds increases rapidly (see Figure 1). Even though these rotamers are high-energy and will not populate measurably, the premise of simply equating the maximum number of possible rotamers for a molecule having *n* rotatable bonds to 3^n is incorrect.

Gauche(+)–Gauche(+) Interaction. The intriguing features in the order of the MM2 conformational energies of *n*-heptane (Figure 1) are also found in *n*-hexane (Table II): Insertion of a trans bond between two consecutive gauche bonds of the same sign is accompanied by destabilization of about 0.1 kcal/mol. For example, the GTG and TGG forms of *n*-hexane both have two gauche bonds, but the TGG form is more stable than GTG by 0.14 kcal/mol. This effect could be rationalized by assuming either that insertion of a trans bond in a GG sequence is associated with enhancing destabilizing nonbonded interactions or that it leads to the elimination of stabilizing interactions, which are a characteristic of any GG sequence. The following considerations show that evidence can be found for the latter.

The energies of *GG*-pentane and *TGG*-hexane are both 1.30 kcal/mol above those of the respective all-trans TT and TTT forms. This value is 0.14 to 0.18 kcal/mol smaller than the twice the difference between TT and TG in pentane or between TTT and TTG in hexane (Table II). Thus, two consecutive gauche bonds in GG configurations are approximately 0.16 kcal/mol more stable than two gauche bonds that are separated by a trans bond. The same value was obtained by Wiberg and Murcko[12] in their MP3/6-31G*//6-31G* calculations. The postulated 0.16 kcal/mol energy stabilization associated with GG is also in agreement with the 0.4 kcal/mol energy difference between GGG and GTG in hexane (Table II). Since there are two GG sequences in GGG, the net destabilization relative to GTG according to our principle will be 0.74 − (2 × 0.16) = 0.42 kcal/mol. Similar trends can be found in Wiberg and Murcko's study.[12]

In searching for a possible source of the characteristic GG energy increment, we considered the van der Waals interactions in the MM2 force field. Specifically we found that, in contrast to TT, TG, and GG′, the nonbonded C···C, C···H, and H···H interactions between 1,5-CH_3/CH_3, -CH_3/CH_2, and -CH_2/CH_2 groups[32] in local GG segments are predominantly in the strongly attractive region of the van der Waals potential. Table VII summarizes the analysis of group interactions by MM2 force field carried on the HF/6-31G* geometries. Each entry is the sum of C···C, C···H, and H···H van der Waals interaction energies for the atom pairs between methyl or methylene groups in all the conformers studied in this work. As a whole, the sum of 1,4 group interactions is repulsive (positive) except for all-trans cases,[33] whereas that of 1,5 and 1,6 interactions is invariably negative. The 1,5 interactions are generally more negative than the 1,6 type. A close look at the 1,5 component reveals that the GG sequence generally produces about 0.3 kcal/mol of stabilization (see *GG*-pentane and *TGG*- and *GGG*-hexane).[34-36]

In the 4-21G calculation (Table II), the energy difference in *GGG*- and *GTG*-hexane (0.72 kcal/mol) is noticeably larger than calculations at the MP4SDQ/6-31G* level. Since the SCF/4-21G energies do not include dispersion, the attractive nonbonded interactions are incompletely contained in them; i.e., the GG increment is too small (approximately 0.05 kcal/mol, see below).

Thus, the GG framework creates a characteristic environment that is favorable for establishing stabilizing 1,5 interactions. Since GG sequences in different systems have nearly constant geometries, the concomitant energy increment (0.16 kcal/mol), too, is approximately constant.

Even though SCF calculations contain only some of the factors

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(32) The terminology "1,*n* interaction" used throughout this paper means interaction between methyl and/or methylene *groups* but not between atom pairs.

(33) Ōsawa, E.; Collins, J.; Schleyer, P. v. R. *Tetrahedron* **1977**, *33*, 2667. The HF/6-31G* CH_3···CH_3 distance in *trans*-butane (3.92 Å) is close to the two times van der Waals radius of carbon atom (1.94 Å according to MM2)[3], in contrast to the corresponding distance of 3.17 Å in *gauche*-butane.

(34) An exception is GGG′, where the stabilization at its GG part is about two-thirds (−0.2 kcal/mol) of the other GG sequences. In this case, the G′ part clearly affects the other part: The dihedral angles at C2–C3 and C3–C4 bonds increased from 62° (characteristic of GG sequence, see below) to 64–65°, and the C2–C3–C4 valence angle opened up to about 118° (Table VI). These deformations increase the C1···C5 distance to 4.01 Å from the "standard" HF/6-31G* value of 3.87 Å for the C1···C5 distance of *GG*-pentane and reduce attractive forces. A contrasting situation appears in *GG′G*-hexane, where its GG′ sequence produces about the same stabilization as the GG sequence of GGG′. In this case, the large deformation (Table VI) moves the C1···C5 and C2···C6 pairs to the strongly attractive region (3.59 Å).

(35) Another noteworthy attractive interaction seems to exist in *GGG′*-hexane between methyl groups (1,6 type, ca. 0.4 kcal/mol).

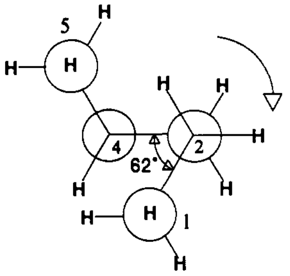
(36) This stabilization of 0.3 kcal/mol compares well with 0.16 kcal/mol of stabilization energy, when corrected to the TG stabilization of 0.12 kcal/mol.

Table VII. CH_3/CH_3, CH_3/CH_2, and CH_2/CH_2 Interactions in Lower *n*-Alkanes According to MM2 Analysis on the HF/6-31G* Geometries (kcal/mol)[a]

	1,4				1,5			1,6
	C1/C4	C2/C5	C3/C6	(sum)	C1/C5	C2/C6	(sum)	C1/C6
				n-Butane				
T	−0.229			(−0.229)				
G	0.274			(0.274)				
				n-Pentane				
TT	−0.203	−0.203		(−0.406)	−0.071		(−0.071)	
TG	−0.173	0.373		(0.201)	−0.130		(−0.130)	
GG	0.386	0.386		(0.772)	−0.351		(−0.351)	
GG′	0.153	1.287		(1.440)	−0.160		(−0.160)	
				n-Hexane				
TTT	−0.203	−0.179	−0.203	(−0.585)	−0.065	−0.065	(−0.130)	−0.018
TTG	−0.204	−0.151	0.367	(0.012)	−0.055	−0.112	(−0.167)	−0.052
TGT	−0.167	0.459	−0.167	(0.124)	−0.121	−0.121	(−0.241)	−0.024
TGG	−0.162	0.467	0.381	(0.685)	−0.102	−0.310	(−0.412)	−0.094
GTG	0.329	−0.081	0.329	(0.577)	−0.098	−0.098	(−0.196)	−0.093
GTG′	0.442	−0.141	0.442	(0.743)	−0.117	−0.117	(−0.234)	−0.044
GGG	0.370	0.524	0.370	(1.265)	−0.322	−0.322	(−0.643)	−0.092
TGG′	−0.179	1.344	0.153	(1.319)	−0.072	−0.094	(−0.167)	−0.144
TGG′	−0.152	0.215	1.335	(1.398)	−0.100	−0.124	(−0.224)	−0.092
GGG′	0.306	0.213	1.144	(1.663)	−0.193	0.040	(−0.153)	−0.393
GGG′	0.589	1.529	0.190	(2.308)	−0.106	−0.185	(−0.291)	−0.153
GCG′	1.184	0.199	1.184	(2.567)	−0.219	−0.219	(−0.438)	−0.116

[a] Summation of C···C, C···H, and H···H van der Waals energy terms between methyl and/or methylene groups in 1,4, 1,5, and 1,6 relationships. 1,4 interactions include torsional energies. C1, C2···C6 represent methyl or methylene group.

responsible for attractive nonbonded interactions, the effects are sufficient to illustrate the special status of GG segments. This is seen from the C–C–C–C dihedral angles, τ, in GG segments (see drawing below), which are typically smaller ($\tau = 62°$) than in isolated G units ($\tau = 65–69°$; Table VI and refs 12, 13, 23b, and 25). The effect is even more noticeable in the GGG form of *n*-hexane, where $\tau = 60°$.[12,23b] Since small values of τ increase repulsive 1,4 interactions, compensating factors must exist in the equilibrium structures.



GG rotamer of n-pentane

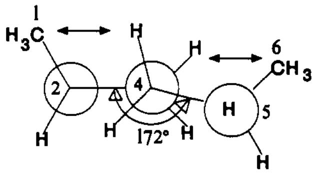
Further supporting evidence is found in some interatomic distance trends. The C1···C5 distance in the 6-31G*-optimized *GG*-pentane, 3.87 Å, is almost exactly twice the van der Waals radius of carbon.[33] Similarly, the C2···C6 distance in *TGG*-hexane and the C1···C5 distance in *GGG*-hexane are also in this range: 3.89 and 3.85 Å, respectively. In addition, in these structures, the 1,5 interactions involving the closest C···H and H···H pairs are strongly attractive.[37]

It is also interesting to note that the GG sequence plays an important role in the formation of cyclic and helical molecules, which are abundant in nature.[38,39] This sequence bends a chain by a right angle and often appears in the corners of a ring structure. For example, regular diamond lattice conformations of cycloalkanes have four GG corners.[27c] Directly connecting more than two gauche bonds of the same sign gives a helix conformation.

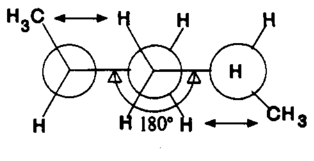
Characteristic Aspects of the GTG′ Sequence. Another interesting trend in the energy order of *n*-alkanes concerns a difference of 0.1 kcal/mol between GTG′ and GTG segments. The GTG form of *n*-hexane is normal in the sense that its energy relative to TTT is nearly exactly twice that of TTG or TGT (Table II). In contrast to this, an additional increment of 0.12 kcal/mol is characteristic for GTG′ (Table II).

In this context, we refer again to the methyl rotation in *gauche*-butane discussed above. In that case, a rotation of 4–6° away from a standard 60° torsional angle was effective in reducing a characteristic H···H repulsive interaction between methyl groups. A similar effect is found for the GTG form of *n*-hexane.

In the equilibrium structure of GTG (see Table VI and the drawing below), the C2–C3–C4–C5 torsional angle is 172°; i.e., it deviates from the ideal 180° trans configuration. This deviation is effective in reducing repulsive nonbonded interactions between H atoms at C1 and C4, and at C6 and C3. It is about twice as large (8°) as the corresponding deviation found for the *gauche*-butane methyl group, since two H···H interaction pairs are involved.



GTG



GTG′

In contrast to GTG (see the drawing above), a similar adjustment of the C2–C3–C4–C5 torsional angle in GTG′ is not effective in providing relief from the H···H steric repulsions due to the inversion symmetry (point group C_i) of this rotamer. As a consequence, in GTG′, the closest H···H distances at C1 and C4 are 2.34 Å, noticeably shorter than in GTG (2.40 Å). Group interaction analysis (Table VII) supports this view: The energy difference between GTG and GTG′ arises from 1,4 interactions.[40]

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(37) According to MM2,[3] the sum of van der Waals radii for C···H and H···H nonbonded pairs are ca. 3.4 and 3.0 Å, respectively. In the 6-31G*-optimized *TGG*-hexane, the closest 1,5-C···H and H···H distances are 3.45 and 2.98 Å, respectively, in close agreement with the maximally attractive distances.

(38) Semlyen, J. A. *Chem. Brit.* **1982**, *18*, 704; *Pure Appl. Chem.* **1981**, *53*, 1797.

(39) Gotō, H.; Ōsawa, E. Manuscript in preparation.

(40) The energy difference of 0.22 kcal/mol in the 1,4 interaction of GTG and GTG′ pertains only to the sum of van der Waals and torsional terms; hence, it does not necessarily correspond to the difference in the total energies (0.12 kcal/mol).

Thus, because of the unique symmetry, the gauche segment of GTG′ is less well relaxed than that of GTG at the expense of about 0.1 kcal/mol.

Discussion

Additivity Rule. The material presented above has shown that subtle trends in the conformational energies of *n*-alkanes can be rationalized by invoking some characteristic long-range nonbonded interactions. In order to explore the possible importance of additional effects, a simple additivity test was performed.

For this test, three energy components were defined, representing the G, GG, and GG′ local alkane segments, respectively. With use of these components, the relative energies of the rotamers considered in this study were then approximated as simple sums: First the total gauche energy was obtained from the total number of individual gauche bonds. Subsequently the result was corrected for GG and GG′ contributions.

The resulting values are listed in parentheses in Table II. They well reproduce the energies calculated by the MP4SDQ/6-31G* formalism with a standard deviation of 0.04 kcal/mol. The largest deviations are observed for the gauche triads, particularly for the highly strained GG′G. The magnitude of the error in this case (0.1 kcal/mol) potentially indicates additional cooperative effects.

Thus, the butane gauche energy is *basically* additive for longer chains as proposed by Wiberg and Murcko,[12] but subtle cooperative phenomena in longer chains must also be considered. The GG component, for example, is significant. When it was omitted in the additivity procedure, the standard deviation increased to 0.12 kcal/mol.

In contrast to this, the SCF/4-21G conformational energies can be reproduced closely without a specific GG increment. Considering only G and GG′ increments allows reproducing the SCF/4-21G energies with a standard deviation of 0.06 kcal/mol (Table II). Thus, the 4-21G energies are also approximately additive, but the GG increment at this level is clearly smaller (approximately 0.05 kcal/mol) than that found for MP4SDQ. This is in agreement with the suggestion that dispersion forces are among the factors that are significant for this term.

Comparison of the ab Initio and Molecular Mechanics Results. MM2 conformational energies ($\Delta\Delta E^{298}$) of *n*-butane to *n*-hexane are included in Table II. Unfortunately, the exact physical meaning of these values is difficult to ascertain, since MM2 parameters were refined with spectroscopic conformational energies (e.g., the butane gauche energy), as well as with conformational energies derived from NMR measurements at ambient temperatures (e.g., the axial–equatorial energy differences of monosubstituted cyclohexanes). The former corresponds to $\Delta\Delta H^0$, the latter to $\Delta\Delta H^{298}$. From Table IV, it is seen that the MP4SDQ/6-31G* $\Delta\Delta H^0$ and $\Delta\Delta H^{298}$ values are in better agreement with MM2 than $\Delta\Delta E^0$. However, considerable differences in magnitudes remain.

In spite of these differences, the order of the energies and the direction of subtle trends among rotamers with equal numbers of gauche bonds are the same in the correlated ab initio and MM2 results. Inspection of Table III suggests that the good correspondence is due to the fact that differences in zero-point energies (ZPE) and thermal energies (E_{therm}) are nearly invariant among the various rotamers. The latent stabilization inherent in the GG sequence was also indicated by Allinger[18] and Farcasiu[41] on the basis of recent MM3 and MM2 calculations, respectively.

The additivity principle described above for the MP4SDQ/6-31G* energies was also applied to the MM2 energies, yielding values (Table II) with the same standard deviation as the former.[42] Not only the deviation value, but also the incremental values are similar among MP4SDQ/6-31G* and MM2 conformational energies.

The consistency of the correlated ab initio and MM2 conformational energy trends confirms the utility of molecular mechanics procedures in conformational analyses. It also supports the view[21,43,44] that ab initio calculations are useful in refining molecular mechanics parameters.

Conclusions

The conformational energies of *n*-alkanes are largely determined by the number of individual gauche bonds. However, on the basis of the analysis given above, it is also possible to identify cooperative energy effects that involve sequences of several bonds. They are manifested by subtle trends in the energies of groups of rotamers that have equal numbers of gauche bonds.

Specifically we have identified an energy increment of 0.16 kcal/mol that is characteristically associated with a GG sequence. This increment can be rationalized in terms of nonbonded attractive interactions that are working between methyl or methylene groups in a 1,5 relationship. These interactions are exclusively found in GG but not in TT, TG, or GG′.

In addition, special symmetry constraints can be postulated for a GTG′ sequence that, in contrast to GTG, prevent it from relaxing some characteristic destabilizing nonbonded interactions in the *gauche*-butane unit. These interactions can be used to rationalize an energy increase of 0.12 kcal/mol that is characteristic for GTG′ compared with GTG.

It is contended that these cooperative effects, albeit small and nearly negligible for single unit, can accumulate significantly in polymers. It is also interesting to note that the energetic order obtained for conformers of small *n*-alkanes is constant at different levels of computation, ab initio MP4SDQ/6-31G*, SCF/4-21G,[23b] and molecular mechanics MM2.

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Registry No. *n*-Butane, 106-97-8; *n*-pentane, 109-66-0; *n*-hexane, 110-54-3.

Supplementary Material Available: Calculated and assigned vibrational frequencies of ethane to *n*-hexane on the HF/6-31G* level (Table VIII for all-trans conformers, Table IX for other conformers) (10 pages). Ordering information is given on any current masthead page.

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(41) Farcasiu, D.; Walter, P.; Sheils, K. *J. Comput. Chem.* **1989**, *10*, 520.

(42) It was possible to increase the accuracy by considering additional increments, for example, for TG, TG, and GG, but the matter was not pursued any further, since it is very likely that the additivity principle will soon fail for branched and more congested alkanes where secondary steric effects (Ōsawa, E.; Shirahama, H.; Matsumoto, T. *J. Am. Chem. Soc.* **1979**, *101*, 4824; Jaime, C.; Ōsawa, E. *J. Mol. Struct.* **1985**, *126*, 363) should engender an increasing number of variations in the basic deformation patterns categorized above. This will make the additivity rule extremely complex and thus less useful.

(43) Hirano, T.; Ōsawa, E. *Croat. Chem. Acta* **1984**, *57*, 1633.

(44) Momany, F. A.; Klimkowski, V. J.; Schäfer, L. *J. Comput. Chem.* **1990**, *11*, 654.