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Enthalpy Differences of the *n*-Pentane Conformers

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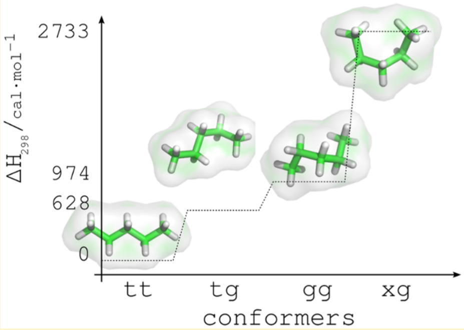
Ⓢ *Supporting Information*



ABSTRACT: The energy and enthalpy differences of alkane conformers in various temperature ranges have been the subject for both experimental and theoretical studies over the last few decades. It was shown previously for the conformers of butane [G. Tasi et al., *J. Chem. Theory Comput.* **2012**, *8*, 479−486] that quantum chemical results can compete with spectroscopic techniques and results obtained even from the most carefully performed experiments could be biased due to the improper statistical model utilized to evaluate the raw experimental data. In the current study, on one hand, the experimental values and their uncertainties for the enthalpy differences for pentane conformers are re-evaluated using the appropriate statistical model. On the other hand, a coupled-cluster-based focal-point analysis has been performed to calculate energy and enthalpy differences for the conformers of pentane. The model chemistry defined in this study includes contributions up to the perturbative quadruple excitations augmented with further small correction terms beyond the Born−Oppenheimer and nonrelativistic approximations. Benchmark quality energy and enthalpy differences for the pentane conformers are given at temperatures 0 and 298.15 K as well as for the various temperature ranges used in the gas-phase experimental measurements. Furthermore, a slight positive shift for the experimental enthalpy differences is also predicted due to an additional Raman active band belonging to the gauche−gauche conformer.

1. INTRODUCTION

The crucial importance that conformational flexibility plays in many areas of natural sciences is difficult to overemphasize. Extensive analysis of the conformational space in terms of both structural and energetic aspects, on one hand, gives a molecular level insight into intramolecular behavior, e.g., folding of protein chains, and may also serve as a basis for the interpretation of various structure-dependent molecular properties. On the other hand, intermolecular interactions are also significantly affected by conformational equilibria. For instance, among many others, solvation effects or protein binding properties depend on molecular structure making conformational analysis vital in studies concerning various chemical, physical, and biological processes. Normal alkanes are known as the simplest basic building blocks in organic chemistry with a high level of conformational flexibility. Consequently, since the pioneering work of Pitzer,[1] an extensive number of papers have been published about their conformational properties. (See refs 2−5 and references therein for a more detailed bibliography.)

Of particular interest are the enthalpy differences among minimum energy structures, i.e., conformers, on the conformational potential energy surface (PES). The smallest *n*-alkane, where rotational isomerism occurs, is *n*-butane with its well-known trans and gauche conformers. For the next species in the homologous series of alkanes, *n*-pentane, there are four unique conformers on the conformational PES:[6−8] tt, tg, gg, and xg, where t, g, and x stand for trans, gauche, and "cross" or "perpendicular" structures with characteristic torsional angles around 180°, ±60°, and ±95°, respectively.

Recently, a number of papers have appeared dealing with the gas-phase thermochemistry of alkane conformers invoking both highly accurate experimental measurements[5] as well as high-level computational methods.[9−12] In the most recent study on *n*-butane[12] by three of the authors of the present paper it was shown that due to the linearized statistical model used generally to evaluate the raw experimental data, the resulting values might be biased. The same study used a carefully selected sequence of high-level *ab initio* quantum chemical calculations in the framework of the focal-point analysis (FPA) principle[13,14] which was applied to obtain energy and enthalpy differences between the two butane conformers. With their exceptionally low estimated uncertainties, ±10 cal/mol, the results obtained for various temperature ranges definitely superseded the experimental values in accuracy leading to the conclusion that, for conformational energy prototypes, state-of-the-art electronic structure computations are indeed capable of yielding more accurate results than precise spectroscopic measurements.

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In this study, our aim is to give the best available theoretical estimates for the enthalpy differences among the conformers of *n*-pentane for various temperature ranges used in the experimental measurements as well as at zero Kelvin and room temperature.

2. METHODS

The composition of the protocol applied here is similar to that used recently to investigate the enthalpy difference of *n*-butane conformers,[12] and it is mostly inspired by the Weizmann-*n*[17−20] and HEAT[21−23] families of thermochemical protocols. These protocols can achieve the sub-kJ/mol accuracy range without relying on empirical corrections. The sound basis for these model chemistries is provided by the coupled-cluster (CC) approach.[24−26] Nonetheless, they are further augmented by various relativistic and post-Born−Oppenheimer contributions as well.[14,15,16−19,21−23] It has been proven that these cutting-edge schemes can compete with experimental techniques.[12,18,20,21−23,27−32] The usual technique of treating the errors arising from the incompleteness of the applied basis sets makes use of extrapolation formulas to estimate the complete basis set (CBS) limit of the various contributions of the total energy. Several extrapolation formulas have been proposed to calculate the basis set limits for correlation energies, and different model chemistries rely on different ones. However, studies have shown that no extrapolation formula can outperform the others for all basis set combinations and for all types of molecules.[33−36] In this work, the correlation contributions were extrapolated using the two-point $1/l_{\max}^3$ formula of Helgaker and associates.[37]

The reference equilibrium structures of the conformers were obtained by performing geometry optimizations with the CC singles, doubles, and perturbative triples [CCSD(T)] method[38] using the cc-pVTZ basis set.[39,40]

At a given temperature T and a pressure of 1 bar, the enthalpy difference between the conformer $\alpha\beta$ and the most stable trans−trans conformer is defined as

$$\Delta H_T^\circ(\alpha\beta) = H_T^\circ(\alpha\beta) - H_T^\circ(\mathrm{tt}) \tag{1}$$

where $H_T^\circ(\alpha\beta)$ and $H_T^\circ(\mathrm{tt})$ are the enthalpies of conformers $\alpha\beta$ and tt, respectively. The corresponding enthalpies are calculated according to the following equation:

$$H_T^\circ = E + E_{\mathrm{ZPE}} + \frac{RT^2}{\Omega} \times \frac{\partial \Omega}{\partial T} + RT \tag{2}$$

with E as the total energy, E_{ZPE} as the zero-point vibrational energy (ZPE), and Ω, R, and T denoting the molecular partition function, ideal gas constant, and the absolute temperature, respectively. The total energy is decomposed as

$$\begin{aligned} E = {} & E_{\mathrm{HF}} + \Delta E_{\mathrm{MP2}} + \Delta E_{\mathrm{CCSD}} + \Delta E_{(\mathrm{T})} + \Delta E_{\mathrm{HO}} \\ & + \Delta E_{\mathrm{DBOC}} + \Delta E_{\mathrm{SR}} \end{aligned} \tag{3}$$

where (i) E_{HF} is the Hartree−Fock (HF) self-consistent field (SCF) energy calculated with the cc-pV6Z[41] basis set; (ii) ΔE_{MP2} is the correlation energy evaluated by the second-order Møller−Plesset (MP2)[42] method and extrapolated to the CBS limit using the cc-pV5Z and cc-pV6Z basis set results; (iii) ΔE_{CCSD} and $\Delta E_{(\mathrm{T})}$ are correlation contributions defined as $\Delta E_{\mathrm{CCSD}} = E_{\mathrm{CCSD}} - E_{\mathrm{MP2}}$ and $\Delta E_{(\mathrm{T})} = E_{\mathrm{CCSD(T)}} - E_{\mathrm{CCSD}}$, respectively; E_{MP2}, E_{CCSD}, and $E_{\mathrm{CCSD(T)}}$ are total energies obtained, respectively, with the MP2, CCSD,[43] and CCSD-(T)[38] methods and extrapolated to the CBS limit using the cc-pVQZ and cc-pV5Z basis set results; (iv) ΔE_{HO} indicates the higher-order correlation contribution beyond the CCSD(T) method calculated as $\Delta E_{\mathrm{HO}} = E_{\mathrm{CCSDT(Q)}} - E_{\mathrm{CCSD(T)}}$ or for conformers with C_1 symmetry $\Delta E_{\mathrm{HO}} = E_{\mathrm{CCSDT}} - E_{\mathrm{CCSD(T)}}$; here $E_{\mathrm{CCSD(T)}}$, E_{CCSDT}, and $E_{\mathrm{CCSDT(Q)}}$ are total energies determined, respectively, with the CCSD(T), CCSD with triples (CCSDT), and CCSDT including perturbative quadruples [CCSDT(Q)][44,45] methods using the cc-pVDZ basis set; (v) ΔE_{DBOC} is the diagonal Born−Oppenheimer correction[46] (DBOC) calculated at the CCSD/cc-pCVDZ[47] level; and (vi) ΔE_{SR} is the scalar relativistic contribution estimated using the fourth-order Douglas−Kroll−Hess (DKH) Hamiltonian[48−51] in CCSD(T)/aug-cc-pCVDZ-DK calculations.

E_{ZPE} is given by

$$\Delta E_{\mathrm{ZPE}} = G_0 + \sum_i \frac{\omega_i}{2} + \sum_{i \geq j} \frac{x_{ij}}{4} \tag{4}$$

where G_0 is a constant term independent of the vibrational level, ω_i's are the harmonic frequencies, x_{ij}'s are anharmonicity constants, and the summation runs through all vibrational modes.[52] The ZPEs were determined correlating all electrons. For harmonic frequencies the CCSD(T)/cc-pVTZ basis set and analytic second derivative techniques were used.[53,54] The G_0 term and the anharmonicity constants were taken from MP2/cc-pVDZ semiquartic force fields.[22,55] Ω is calculated via the standard formulas of statistical thermodynamics within the ideal gas approximation;[56] for the rotational and vibrational degrees of freedom the rigid rotor-harmonic oscillator (RRHO) approximation is invoked. To correct the errors of the RRHO model for the hindered rotations around the C−C bonds the one-dimensional hindered rotor model (1D-HR) was applied,[57,58] and the energy levels calculated for the hindered rotor were used to correct the ZPE and thermal correction values. At the calculation of the ZPE (eq 4) the contribution of the harmonic frequencies due to methyl-torsions and C−C backbone torsions was replaced by the lowest solution of the corresponding one-dimensional Schrödinger equation, as well as the diagonal elements of the anharmonicity matrix x_{ii} belonging to these motions were dropped while the off-diagonal elements describing the interactions of different normal modes were retained. For the temperature corrections to enthalpies, the partition functions were explicitly calculated for the rotational motion considering the eigenvalues of the rotational Hamiltonian. To solve the one-dimensional Schrödinger equation,

$$-\frac{\hbar^2}{2I_r}\frac{\mathrm{d}^2}{\mathrm{d}\theta^2}\psi + V(\theta)\psi = E\psi \tag{5}$$

the Fourier grid Hamiltonian method of Marston and Balint-Kurti[59,60] was used. I_r and $V(\theta)$ are the reduced moment of inertia and the potential, respectively. The $V(\theta)$'s are obtained in MP2/cc-pVTZ relaxed scans for the rotating tops. To get an analytical form of the potential $V(\theta)$ was expanded in a Fourier series,

$$V(\theta) = c + \sum_k \{a_k \cos(k\theta) + b_k \sin(k\theta)\} \tag{6}$$

where c, a_k's, and b_k's are fitted parameters. I_r was calculated at the equilibrium geometries using Pitzer's approximation.[61,62]

Based on eq 3 the energy difference between the pentane conformers $\alpha\beta$ and tt is calculated as

Table 1. Convergence of the Most Dominant Factors Contributing to the Energy Differences (ΔE) of the *n*-Pentane Conformers[a]

	ΔE(tg)					ΔE(gg)					ΔE(xg)				
X[b]	ΔE_{HF}	δE_{MP2}	δE_{CCSD}	$\delta E_{\mathrm{(T)}}$	$\sum$[c]	ΔE_{HF}	δE_{MP2}	δE_{CCSD}	$\delta E_{\mathrm{(T)}}$	$\sum$[c]	ΔE_{HF}	δE_{MP2}	δE_{CCSD}	$\delta E_{\mathrm{(T)}}$	$\sum$[c]
2	1170	−567	98	−58	644	2340	−1381	285	−128	1117	4318	−1263	147	−134	3069
3	1171	−618	106	−76	584	2338	−1600	301	−176	862	4257	−1419	174	−193	2819
4	1182	−614	109	−77	600	2358	−1565	318	−183	928	4276	−1450	186	−200	2811
5	1182	−614	113	−79	603	2361	−1565	324	−186	934	4278	−1444	192	−202	2824
6	1183	−615			603	2363	−1571			929	4279	−1456			2813
(3,4)[d]		−612	112	−79	604		−1540	330	−188	961		−1473	194	−205	2792
(4,5)[d]		−614	117	−80	606		−1565	330	−190	938		−1438	199	−204	2834
(5,6)[d]		−615			606		−1580			924		−1473			2801
σ_Y[e]	1	1	5	1	8	2	15	0	2	19	1	35	5	1	42

[a] All values are in cal/mol. [b] The cardinal number of the cc-pV*X*Z basis set. [c] Sum of the individual contributions. If a contribution is not available with the given basis set, then the one obtained with the largest basis set was used in the sum. [d] Extrapolated using the cc-pV(X,X+1)Z basis set. [e] Error of the contribution, i.e., the unsigned difference between the values obtained with basis sets involving the largest and second-largest cardinal numbers.

$$\Delta E(\alpha\beta) = E(\alpha\beta) - E(\mathrm{tt}) = \Delta E_{\mathrm{HF}} + \delta E_{\mathrm{MP2}} + \delta E_{\mathrm{CCSD}} + \delta E_{\mathrm{(T)}} + \delta E_{\mathrm{HO}} + \delta E_{\mathrm{DBOC}} + \delta E_{\mathrm{SR}} \qquad (7)$$

In the above equation δ denotes the difference of the differences, for instance, δE_{MP2} is equal to $\Delta E_{\mathrm{MP2}}(\alpha\beta) - \Delta E_{\mathrm{MP2}}(\mathrm{tt})$.

The CCSDT(Q) calculations were carried out with the MRCC suite of quantum chemical programs[63] interfaced to the CFOUR package.[64] For the DKH calculations, the MOLPRO package[65] was utilized. All other results were obtained with CFOUR.[64] In all calculations restricted HF orbitals were used.

Uncertainties of the final enthalpy differences were estimated in terms of the remaining errors in each calculated contribution. The remaining error σ_Y in an extrapolated contribution ΔE_Y or δE_Y was defined as the unsigned difference between results obtained with $(X-1, X)$- and $(X-2, X-1)$-based extrapolations, where X is the cardinal number of the largest correlation consistent basis set[39,66−68] used to calculate the contribution. Similarly, for a nonextrapolated term the error was defined by subtracting the result obtained with the $(X-1)$ basis set from that calculated using the basis set with the highest cardinal number X. The final uncertainty was calculated as a sum of the individual error contributions, i.e., $\sigma_{\Delta H_T^\circ} = \sum_Y \sigma_Y$.

3. RESULTS AND DISCUSSION

3.1. Best Theoretical Estimates. The most dominant factors contributing to the energy differences are listed in Table 1. The ΔE_{HF} terms converge smoothly and can be regarded as practically converged, within 5 cal/mol, with the quadruple-ζ basis set (4Z). The largest difference between the sextuple-ζ (6Z) and quintuple-ζ (5Z) results is 2 cal/mol. The convergence of the δE_{MP2} term is remarkably fast for ΔE(tg); even the triple-ζ (3Z) result is within 5 cal/mol of the best, extrapolated (5,6)Z estimate. However, this is an exception. The corresponding differences with the triple-ζ basis set are about 20 and 50 cal/mol, respectively, for ΔE(gg) and ΔE(xg). As it can be seen in Table 1 best estimates for the δE_{MP2} contributions still have relatively large error bars except for ΔE(tg). For ΔE(gg) and ΔE(xg) the errors in δE_{MP2} are 15 and 35 cal/mol. The δE_{CCSD} and $\delta E_{\mathrm{(T)}}$ terms show monotonic sequences with increasing basis set size; in all cases the δE_{CCSD} series increase while $\delta E_{\mathrm{(T)}}$ decrease. The extrapolated (Q,5)Z δE_{CCSD} contributions are converged within 5 cal/mol; the errors in the $\delta E_{\mathrm{(T)}}$ terms are even smaller; they are not larger than 2 cal/mol. It is interesting to note that for ΔE(tg) and ΔE(gg) the magnitude of the $\delta E_{\mathrm{(T)}}$ contributions is considerably smaller than that of the corresponding δE_{CCSD} contributions; however, for ΔE(xg) δE_{CCSD} and $\delta E_{\mathrm{(T)}}$ have the same magnitude with opposite sign and they almost cancel out. The effects of δE_{HO} as well as those of δE_{DBOC} and δE_{SR} on the energy differences are fairly small, amounting to −1, −7, and −5 cal/mol for ΔE(tg), ΔE(gg), and ΔE(xg), respectively (see Table S1 in the Supporting Information). Please note, however, that the corresponding uncertainties are not negligible, 13, 17, and 19 cal/mol, respectively, for δE_{HO}(tg), δE_{HO}(gg), and δE_{HO}(xg).

Table 2 shows how ΔE(gg) depends on the level of theory used for obtaining equilibrium structures. The largest variations between the cc-pVTZ and cc-pVQZ results, around 20 cal/mol, occur for ΔE_{HF} and δE_{MP2} while $\delta E_{\mathrm{(T)}}$ values differ by about 6 cal/mol. The δE_{CCSD} values are practically the same. Although there are some variations among the individual components the total CCSD(T) ΔE(gg) values are the same at the cc-pVTZ and cc-pVQZ reference geometries. This makes us believe that the CCSD(T)/cc-pVTZ reference geometries are sufficiently well-converged to obtain reliable energy and presumably

Table 2. Effects of Level of Geometry on the Convergence of Most Dominant Factors Contributing to ΔE(gg)[a]

geometry	X[b]	ΔE_{HF}	δE_{MP2}	δE_{CCSD}	$\delta E_{\mathrm{(T)}}$	$\sum$[c]
cc-pVDZ	2	2194	−1234	256	−114	1102
	3	2221	−1452	266	−159	876
	4	2242	−1404	283	−165	956
	5	2244	−1401	303	−167	966
	6	2246	−1412			969
cc-pVTZ	2	2340	−1381	285	−128	1117
	3	2338	−1600	301	−176	862
	4	2358	−1565	318	−183	928
	5	2361	−1565	324	−186	934
	6	2363	−1571			929
cc-pVQZ	2	2325	−1354	287	−123	1135
	3	2315	−1582	300	−170	862
	4	2335	−1546	317	−177	928
	5	2338	−1546	323	−180	934
	6	2339	−1552			929

[a] All values are in cal/mol. [b] The cardinal number of the cc-pV*X*Z basis set. [c] Sum of the individual contributions.

Table 3. Harmonic, Anharmonic, and Hindered Rotor Contributions to ΔE_{ZPE}[a]

	harmonic[b]			anharmonic[c]			hindered[d]			$\sum$[e]		
basis	tg	gg	xg	tg	gg	xg	tg	gg	xg	tg	gg	xg
cc-pVDZ	71	216	208	−4	−21	−23	−39	−17	−45	28	178	139
cc-pVTZ	87	241	234		−46		−44	−12	−32	39[f]	183	179[f]
σ_Y[g]	16	25	26	4	24	23	5	5	13	25	54	63

[a] All values are in cal/mol. [b] Calculated with the CCSD(T) method; those contributions which belong to internal rotations are removed. [c] Calculated with the MP2 method; diagonal elements of the anharmonicity matrix belonging to internal rotations are deleted (see text). [d] Calculated with the MP2 method; for the list of modes treated as hindered rotations see the Supporting Information. [e] Sum of the individual contributions. [f] Since the anharmonic correction is not available with the cc-pVTZ basis set the cc-pVDZ result is used in the sum. [g] It is the unsigned difference, where available, between the cc-pVTZ and cc-pVDZ data. Otherwise, it is assumed that the error is not larger than the contribution itself.

Table 4. Thermal Correction Values in cal/mol[a]

basis	T (K)	ΔH_T^{therm}(tg)	ΔH_T^{therm}(gg)	ΔH_T^{therm}(xg)
cc-pVDZ	197[b]	−3	−76	−99
	298	−9	−116	−226
	385[c]	−17	−139	−366
	412[d]	−20	−144	−413
cc-pVTZ	197	−5	−82	−110
	298	−15	−126	−242
	385	−27	−150	−382
	412	−30	−155	−428
σ_Y[e]	197	2	6	11
	298	6	10	16
	385	10	11	16
	412	10	11	15

[a] The listed values are corrected for hindered rotations. [b] Midpoint of the temperature range used in ref 5. [c] Midpoint of the temperature range used in ref 85. [d] Midpoint of the temperature range used in ref 86. [e] Error of the contribution, i.e., the unsigned difference between the cc-pVTZ and cc-pVDZ results.

enthalpy differences for the conformers of pentane. In contrast, the cc-pVDZ structures introduced considerable errors, in the worst case about 150 cal/mol, among the individual components. However, we also note that large amount of these deviations cancels out in the total CCSD(T) ΔE(gg) data; for example, the total CCSD(T)/cc-pV6Z energy difference between the cc-pVDZ and cc-pVQZ structures is 40 cal/mol.

The harmonic, anharmonic, and hindered rotor ZPE contributions to the ΔH_0° values are collected in Table 3. It can be seen that the determination of the ZPE contribution is fairly challenging. The associated error bars are fairly sizable when considering the accuracy of the energy terms detailed in Tables 1 or S1 in the Supporting Information. About half of the uncertainty in ΔH_0° comes from the error in the ZPE terms. Unfortunately, the use of larger basis sets in the harmonic or anharmonic calculations at the applied levels of theory is currently not feasible. Nevertheless it is worth mentioning that the description of the tt−tg difference is slightly easier. This is possibly the consequence of the similarities between the tt and tg structures: the "first trans half" of these conformers are the same in contrast to gg and xg where both "halves" differ from the trans conformation. Our best estimates for ΔE_{ZPE}(tg), ΔE_{ZPE}(gg), and ΔE_{ZPE}(xg) are 39 ± 25, 183 ± 54, and 179 ± 63 cal/mol, respectively.

To determine the enthalpy difference at nonzero temperatures the calculation of the molecular partition function, Ω, is also required (eq 2). After calculating Ω for the appropriate conformers, Ω_{tt} and $\Omega_{\alpha\beta}$, the thermal correction to $\Delta H_T^\circ(\alpha\beta)$, $\Delta H_T^{therm}(\alpha\beta)$, can be calculated at temperature T as

$$\Delta H_T^{therm}(\alpha\beta) = RT^2 \frac{\partial \ln(\Omega_{\alpha\beta}/\Omega_{tt})}{\partial T} \tag{8}$$

Thermal corrections along with their errors are listed in Table 4 at various relevant temperatures. As a representative example our best estimates for ΔH_{298}^{therm}(tg), ΔH_{298}^{therm}(gg), and ΔH_{298}^{therm}(xg) are, respectively, −15 ± 6, −126 ± 10, and −242 ± 16 cal/mol.

On the basis of our calculations presented above, our best theoretical estimates for the ΔE, ΔH_0°, and ΔH_{298}° values are ΔE(tg) = 605 ± 21, ΔE(gg) = 917 ± 36, ΔE(xg) = 2796 ± 61, ΔH_0°(tg) = 644 ± 46, ΔH_0°(gg) = 1099 ± 90, ΔH_0°(xg) = 2975 ± 124, ΔH_{298}°(tg) = 628 ± 52, ΔH_{298}°(gg) = 974 ± 100, and ΔH_{298}°(xg) = 2733 ± 140 cal/mol.

3.2. Comparison to Previous Studies.

3.2.1. Computational Studies. Relevant computational studies are summarized in Table 5 and detailed below.

Understandably, early *ab initio* studies[69−72] did not go beyond the Hartree−Fock method. The first investigation, which took account of electron correlation effects on the conformational space of pentane, appeared in 1988[73] and was carried out at the MP3/6-31G(d)//HF/6-31G(d) level of theory. For the energy differences between the pentane conformers, ΔE(tg), ΔE(gg), and ΔE(xg), respectively, 760, 1360, and 3330 cal/mol were reported. Please note that x+g− is improperly designated as g+g−(C_1) in ref 73. Usually, the term g is reserved for the gauche conformation whose torsional angle is about ±60°; however, in this case the first torsional angle is approximately 95°. Furthermore, the conformation (g+g−) which has dihedral angles at about +60 and −60°, respectively, around the C_2−C_3 and C_3−C_4 bonds is not a minimum; it is indeed a transition state.[7,9] Note also that two saddle-points, g+g−(60,-60) and g+g−(C_S), are listed as conformers in Table 4 of ref 73.

Tsuzuki and associates[74] performed MP4(SDQ)/6-31G-(d)//HF/6-31G(d) computations to map the conformational PES of *n*-butane, *n*-pentane, and *n*-hexane. In the case of pentane 740, 1302, and 3289 cal/mol were obtained, respectively, for ΔE(tg), ΔE(gg), and ΔE(xg). ZPE and thermal corrections, determined at the HF/6-31G(d) level of theory, yielded ΔH_0°(tg) = 837, ΔH_0°(gg) = 1541, and ΔH_0°(xg) = 3496 cal/mol, as well as ΔH_{298}°(tg) = 800, ΔH_{298}°(gg) = 1431, and ΔH_{298}°(xg) = 3424 cal/mol.

To develop a conformation-dependent molecular mechanics force field Mirkin and Krimm determined scaled HF/6-31G frequencies for the 4 pentane and 10 hexane conformers. For the pentane conformers MP2/6-31G(d) equilibrium structures were also computed. Their MP2/6-31G(d) total energies

Table 5. Energy and Enthalpy Differences (cal/mol) of *n*-Pentane Conformers Reported by Computational Studies

group[a]	ΔE(tg)	ΔE(gg)	ΔE(xg)	ΔH_0°(tg)	ΔH_0°(gg)	ΔH_0°(xg)	ΔH_{298}°(tg)	ΔH_{298}°(gg)	ΔH_{298}°(xg)	ref
A	760	1360	3330							73[b]
	740	1302	3289	837	1541	3496	800	1431	3424	74[c]
	670	1090	3190							75[d]
B	621	1065	2917	676(687)	1423(1118)	3111(3110)	871(645)	1771(1051)	3476(3040)	3[e]
	618	985	2846							77[f]
	614	961	2813							9[g]
C	581	912	2763							10[h]
	582	915	2767	682	1205	3037	640	1052	2911	10[i]
	605 ± 21	917 ± 36	2796 ± 61	644 ± 46	1099 ± 90	2975 ± 124	628 ± 52	974 ± 100	2733 ± 140	this study

[a] Grouping is based on the level of theory used. A: perturbation theory, B: CCSD(T)/double-ζ basis set, and C: CCSD(T)/triple-ζ basis set. [b] MP3/6-31G(d)//HF/6-31G(d). [c] MP4(SDQ)/6-31G(d)//HF/6-31G(d). [d] MP2/6-31G(d). [e] Focal point; results in parentheses are recalculated (B3LYP/6-311++G**) in this study. [f] MP2:CC (see text). [g] W1h-like. [h] CCSD(T)/cc-pVTZ. [i] CCSD(T)-F12b/cc-pVTZ-F12//SCS-MP2/cc-pVTZ.

resulted in 670, 1090, and 3190 cal/mol for ΔE(tg), ΔE(gg), and ΔE(xg), respectively.[75]

Salam and Deleuze[3] also computed the relative energies of pentane conformers. Reference structures were obtained at the B3LYP/6-311++G(p,d) level of theory. A focal point approach used to assess the energy differences was composed of HF/cc-pVQZ, MP3/cc-pVTZ, and CCSD(T)/aug-cc-pVDZ single-point energies, and 621, 1065, and 2917 cal/mol were obtained, respectively, for ΔE(tg), ΔE(gg), and ΔE(xg). Again, please note that x+g− is improperly designated as g+g− by the authors. To calculate molar fractions at various temperatures Salam and Deleuze also invoked the RRHO approximation with B3LYP/6-311++G(d,p) geometries and frequencies. Based on their data summarized in Table 5 of ref 3 one can derive 676, 1423, and 3111 cal/mol for ΔH_0°(tg), ΔH_0°(gg), and ΔH_0°(xg), respectively, and 871, 1771, and 3476 cal/mol, respectively, for ΔH_{298}°(tg), ΔH_{298}°(gg), and ΔH_{298}°(xg).

To refine the torsional potentials of alkanes in the CHARMM force field[76] Klauda and associates[77] investigated the PES of several normal alkanes by means of an *ab initio* composite method dubbed Hybrid Methods for Interaction Energies (HM-IE).[78] Briefly, the equilibrium structures were optimized in MP2/cc-pVDZ calculations, and the relative energies were estimated by combining CCSD(T)/cc-pVDZ and MP2/cc-pVQZ computations denoted as MP2:CC in their paper. In this manner they aimed to approximate the CCSD(T)/cc-pVQZ energy differences among the conformers, and 622, 985, and 2846 cal/mol were obtained, respectively, for ΔE(tg), ΔE(gg), and ΔE(xg). For ΔE(tg) the best MP2:CC estimate is reported as 618 cal/mol in ref 77 combining CCSD(T)/cc-pVDZ and MP2/cc-pV5Z calculations.

To date, regarding the energy differences between the conformers of pentane, most advanced studies were published by the Martin group.[9,10] In order to assess the performance of various density functional methods for conformational energy differences they set up a benchmark *ab initio* database consisted of *n*-butane, *n*-pentane, and *n*-hexane conformer energies. In case of pentane using a W1h-like model chemistry, CCSD/cc-pV(T,Q)Z and CCSD(T)/cc-pV(D,T)Z extrapolated energies, 614, 961, and 2813 cal/mol were obtained, respectively, for ΔE(tg), ΔE(gg), and ΔE(xg).[9] In a follow-up study[10] they mapped the PES of pentane at the CCSD(T)-F12b/cc-pVTZ-F12//SCS-MP2/cc-pVTZ level of theory. The CCSD(T)/cc-pVTZ and CCSD(T)-F12b/cc-pVTZ-F12//SCS-MP2/cc-pVTZ methods yielded ΔE(tg) = 581, ΔE(gg) = 912, ΔE(xg) = 2763, and ΔE(tg) = 582, ΔE(gg) = 915, ΔE(xg) = 2767 cal/mol, respectively. When adding SCS-MP2/cc-pVTZ ZPE and thermal corrections from the Supporting Information of ref 10 one can arrive at ΔH_0°(tg) = 682, ΔH_0°(gg) = 1205, ΔH_0°(xg) = 3037, ΔH_{298}°(tg) = 640, ΔH_{298}°(gg) = 1052, and ΔH_{298}°(xg) = 2911 cal/mol.

It can be recognized that previous results may be easily grouped according to the level at which the electron correlation problem was treated. Earlier investigators only could afford Møller−Plesset perturbation theory truncated at second-, third-, or fourth-order (the first three rows in Table 5, group A). The second group, B, includes composite approaches which involved the CCSD(T) method in conjunction with rather small double-ζ quality basis sets (rows 4 to 6 in Table 5). Although the W1h-like values of the Martin group[9] include fairly large basis sets for CCSD, cc-pVTZ, and cc-pVQZ, the use of the cc-pVDZ basis set in the CCSD(T)/cc-pV(D,T)Z extrapolation together with the MP2/cc-pVTZ reference geometries produces data similar to those of Klauda and associates.[77] Martin's latest contribution to the topic[10] constitutes the third group, C, including CCSD(T) and CCSD(T)-F12b data with medium size triple-ζ quality basis sets.

It can be observed that MP theory predicts the tt-conformer substantially more stable relative to the other conformers than CC theory does. ΔH_0°(tg) values in group A are larger by about 50−150 cal/mol than those which can be found in group B. In the case of ΔH_0°(gg) the situation is even worse; only MP2 calculations, probably due to fortuitous error cancellation, yield a value around 1100 cal/mol, and the MP3 and MP4 methods underestimate the stability of the gg-conformer by about 300−350 cal/mol relative to group B values. It is clear that the most troublesome case for MP methods is the xg-conformer. Its relative stability is underestimated by about 300−500 cal/mol when comparing to the data that can be seen in group B. The oscillating behavior of the MP2, MP3, and MP4 values is also notable.

We noted, when considering the energetic stability of the gg-conformer in group B, that the work of Salam and Deleuze[3] somewhat diverged from that of refs 9 and 77. Furthermore, their enthalpy differences increased with increasing temperature; this behavior is not in line with the facts. Therefore, we investigated these issues further and tried to recreate their data. However, we were not be able to reproduce their numbers. Although we obtained the same geometries as reported in their Table I at the B3LYP/6-311++G(d,p) level of theory and the same ΔE(tg) and ΔE(xg) values (see the Supporting Information), our ΔE(gg) value, 1660 cal/mol, considerably differs from theirs, 1553 cal/mol. The ΔE_{ZPE}(gg) data of Salam and Deleuze, 358 cal/mol, deviates even further from our value, 53 cal/mol. Finally, their thermal corrections seem to be also incorrect: 195, 347, and 365 cal/mol for $\Delta H_{298}^{therm}(\text{tg})$, $\Delta H_{298}^{therm}(\text{gg})$, and $\Delta H_{298}^{therm}(\text{xg})$, respectively. Our repeated calculations yielded, in qualitative agreement with the other values, −43, −67, and −70 cal/mol, respectively, for the above quantities, and the revised values, given in parentheses in Table 5, are in better agreement with the more accurate studies. One apparent mistake is that although they calculated ΔH_0° on the basis of the focal-point energies ΔH_{298}° was calculated with B3LYP/6-311++G** energies. Consequently the 0 and 298 K values are incompatible. At least this seems to be the case for tg and xg. Meanwhile, for gg there is probably another error in their calculation because $\Delta G_{298}(\text{gg})$ deviates by nearly 500 cal/mol from our value. Of course, these problems also render their mole fraction values erroneous.

When comparing the reported results to our data it is clear that a balanced description of the conformer's energetic landscape is not expected from previous protocols. For example, just to mention the two most advanced studies, (i) the W1h-like protocol of Martin and co-workers yields excellent results for $\Delta E(\text{tg})$ and $\Delta E(\text{xg})$ but underestimates the stability of the gg conformer by 44 cal/mol, and (ii) the triple-ζ CCSD(T)-F12b data for $\Delta E(\text{gg})$ agrees well with ours but the $\Delta E(\text{tg})$ and $\Delta E(\text{xg})$ values are off by 23 and 29 cal/mol, respectively. The present study also demonstrates how difficult it us to find an unbiased theoretical level that treats the conformers of pentane on an equal footing. Our results show that it is easier to reach convergence for $\Delta E(\text{tg})$ than for $\Delta E(\text{gg})$ or $\Delta E(\text{xg})$. A possible reason for this that the calculation of $\Delta E(\text{tg})$ requires the uniform description of the lesser-packed tt and tg conformers, and furthermore, tg is more similar to tt than gg or xg as mentioned in connection with the ZPE terms. Nevertheless, this study presents the most advanced and accurate protocol and provides the best theoretical values to date with conservative error bars for the energy and enthalpy differences of pentane conformers.

3.2.2. Experimental Studies. The accurate determination of the temperature-dependent enthalpy differences between the conformers of *n*-pentane, i.e, that of $\Delta H_T^\circ(\text{tg})$, $\Delta H_T^\circ(\text{gg})$, and $\Delta H_T^\circ(\text{xg})$, has been the focus of numerous experimental studies during the last seven decades. Most of the studies were performed in liquid-phase and in solutions,[79−84] but some results obtained for gas-phase can also be found.[5,85,86] The rather scarce experimental gas-phase values for the enthalpy differences are listed in Table 6.

The majority of the studies[5,79,80,82,83,86] concerning the conformational space utilize infrared or Raman vibrational spectroscopy and are based upon the relation between the ratio of vibrational band intensities belonging to the conformers, $I(\alpha\beta)$ and $I(\text{tt})$, and their free energy difference, $\Delta G(\alpha\beta) = G(\alpha\beta) - G(\text{tt})$. The intensity of the conformer's vibrational band is proportional to the number of the given conformers present: $I(\alpha\beta) = f_\alpha\beta n_\alpha\beta$, where $f_\alpha\beta$ depends on the experimental conditions, the probability of the transition, and the statistical weight of the conformer. Therefore,

$$\frac{I(\alpha\beta)}{I(\text{tt})} = \frac{f_{\alpha\beta}n_{\alpha\beta}}{f_{\text{tt}}n_{\text{tt}}} = f'_{\alpha\beta}\frac{n_{\alpha\beta}}{n_{\text{tt}}} = f'_{\alpha\beta}K \tag{9}$$

where K is the equilibrium constant for the tt ⇌ $\alpha\beta$ process. Thus,

$$\frac{I(\alpha\beta)}{I(\text{tt})} = f'_{\alpha\beta}\cdot \mathrm{e}^{-\Delta G(\alpha\beta)/RT} = f'_{\alpha\beta}\cdot \mathrm{e}^{\Delta S(\alpha\beta)/R}\cdot \mathrm{e}^{-\Delta H(\alpha\beta)/RT}$$
$$= \mathrm{e}^{-(\Delta H(\alpha\beta)/\mathrm{RT})+b_{\alpha\beta}} \tag{10}$$

and finally,

$$\ln\frac{I(\alpha\beta)}{I(\text{tt})} = -\frac{\Delta H(\alpha\beta)}{R}\cdot\frac{1}{T} + b_{\alpha\beta} \tag{11}$$

with $b_{\alpha\beta} = \ln f'_{\alpha\beta} + \Delta S(\alpha\beta)/R$ and $\Delta S(\alpha\beta)$ as the entropy difference between conformer $\alpha\beta$ and tt. Measuring the temperature dependence of the spectrum one can perform a least-squares (LS) fit of a straight line on the logarithm of the ratio of intensities against the inverse temperature (eq 11), and the slope of the fitted line can be used to determine the enthalpy difference, $\Delta H(\alpha\beta)$.

Table 6. Gas-Phase Enthalpy Differences of *n*-Pentane Conformers Reported by Experimental Studies[a]

	temperature range (K)	experiment	this study[b]
$\Delta H^\circ(\text{tg})$	143−250	618 ± 5)[c]	638 ± 47
	337−433	560 ± 100[d]	617 ± 55
	316−508	465 ± 68[e]	613 ± 55
$\Delta H^\circ(\text{gg})$	143−250	953 ± 15[c]	1017 ± 97

[a] All values are in cal/mol. [b] Calculated at the midpoint of the temperature range. [c] Reference 5; reevaluated here, see Table 7. [d] Reference 85. [e] Reference 86. Please note the uncertainty is given as a 95% confidence interval recalculated here; in the original paper ±30 cal/mol was reported, probably as the standard deviation.

The above analysis assumes the presence of well-separated, characteristic vibrational bands for the conformers. To that end, Snyder[81] calculated 401, 338, and 389 cm^{-1} for the tt, tg, and gg conformers, respectively, while the appropriate frequencies observed were 401, 336, and 384 cm^{-1}. Shimanouchi and co-workers[82,87] calculated 404 cm^{-1} for tt and measured 403 cm^{-1}; for tg the calculated and observed frequencies were the same, namely, 337 cm^{-1}; in the case of gg 385 cm^{-1} was calculated and 384 cm^{-1} was detected.

The first gas-phase enthalpy difference, $\Delta H_T^\circ(\text{tg}) = 560 \pm 100$ cal/mol for the 337−433 K temperature range, was reported by Maissara and associates in 1983.[85] Their value is based on the relative intensity of the Raman bands at 336 cm^{-1} (tg) and 401 cm^{-1} (tt).

Kanesaka and co-workers reported $\Delta H_T^\circ(\text{tg}) = 465 \pm 30$ cal/mol for the 316−508 K temperature range. To evaluate the enthalpy difference from the experimental data the intensity ratio of the 331 cm^{-1} (tg) and 399 cm^{-1} (tt) Raman bands was plotted as a function of the inverse temperature. Their work is directly comparable to that of Maissara and associates because their temperature range include that of ref 85 and the midpoints, 385 and 412 K, are also nearby. Although the uncertainties overlap the difference between the mean values is fairly striking. Our theoretical value, $\Delta H_T^\circ(\text{tg}) = 613 \pm 55$ cal/mol, does not support the data of Kanesaka et al.; instead it backs that of Maissara et al.[85] Nonetheless, Kanesaka and his colleagues noted that they would have obtained a value consistent with that of ref 85, if they had included the data obtained at low temperature and with 3 cm^{-1} spectral slit width.

The most accurate experimental value for $\Delta H^\circ(\text{tg})$, 618 ± 6 cal/mol, was reported by Balabin[5] for the 143−250 K temperature range. Because the temperature range used by Balabin and the previous two studies is disjointed, the results

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are not directly comparable. Although this statement is indisputable, usually it escapes the investigators' attention. The only available experimental data for $\Delta H^\circ(\mathrm{gg})$, 940 ± 20 cal/mol, was also measured in ref 5. The characteristic vibrational bands were 399, 329, and 267 cm^{-1}, respectively, for the tt, tg, and gg conformers, and the linearized form, eq 11, was used to determine the enthalpy differences of the conformers. It has been shown,[12,88] however, that linearization biases the estimated parameters and their standard errors. This bias can be corrected with appropriate weighting or using the original nonlinear function. Therefore, in general the treatment of the raw experimental data needs some improvement to get more reliable results. Therefore, the data of ref 5 have been reevaluated using various regression models,[88] ordinary linearized least-squares (OLLS), weighted linearized least-squares (WLLS), and ordinary nonlinear least-squares (ONLS) methods, to further improve the results. Table 7 contains the various estimated enthalpy difference values and their 95% confidence intervals. In the case of the tg conformer the OLLS method gives exactly the same value (618 ± 6 cal/mol) reported by Balabin. The WLLS and ONLS methods give the same number for the enthalpy difference but with a slightly lower error (618 ± 5 cal/mol). For the gg conformer, the estimated enthalpy difference matches the one reported by Balabin (943 ± 24 cal/mol compared to 940 ± 20 cal/mol). However, the WLLS and ONLS results (958 ± 13 cal/mol and 953 ± 15 cal/mol, respectively) are different from the reported value. The different values of the WLLS and ONLS fits suggest a higher experimental value for $\Delta H^\circ_T(\mathrm{gg})$. It can be concluded that, for the temperature interval 143–250 K, the best estimates for the experimental enthalpy differences for tg and gg *n*-pentane conformers are 618 ± 5 cal/mol and 953 ± 15 cal/mol, respectively, obtained by ONLS fits using the correct nonlinear function. Our theoretical protocol yielded 638 ± 47 and 1017 ± 97 cal/mol for $\Delta H^\circ_T(\mathrm{tg})$ and $\Delta H^\circ_T(\mathrm{gg})$, respectively (Table 7). It can be observed that our $\Delta H^\circ_T(\mathrm{tg})$ value agrees well with that of the experiment; however, for $\Delta H^\circ_T(\mathrm{gg})$ there exists some discrepancy between the mean data, though the confidence intervals overlap. Although spectral deconvolution was applied in ref 5, a small peak belonging to the gg conformer at around 380 cm^{-1} may have gone unnoticed. Kanesaka and associates considered the signal of the gg conformer at 380 cm^{-1} and its possible contribution to the intensity of the tt isomer at 399 cm^{-1}.[86] They noted that when they neglected this contribution, $\Delta H^\circ_T(\mathrm{tg})$ = 429 ± 28 cal/mol was obtained, but they arrived at $\Delta H^\circ_T(\mathrm{tg})$ = 465 ± 30 cal/mol taking account of it. In brief, the presence of the gg conformer had an effect of about 35 cal/mol on the value of $\Delta H^\circ_T(\mathrm{tg})$. Our calculations (see Supporting Information), beside the Raman active gg band at around 270 cm^{-1}, also support the existence of another Raman active gg band at around 380 cm^{-1}, although the activity of the latter is about one-fifth of the former. Theoretically, a similar effect, a positive shift, can be expected also for the measured $\Delta H^\circ_T(\mathrm{gg})$. Let us suppose that the gg conformation gives an $I'(\mathrm{gg})$ contribution at 380 cm^{-1} to the intensity of the tt band. Then the following can be deduced:

Table 7. Experimental Enthalpy Differences for Pentane Conformers in Gas-Phase Using Various Least-Squares Methods[a]

conformer	parameter estimation[b]	enthalpy difference
tg	OLLS	618 ± 6
	WLLS	618 ± 5
	ONLS	618 ± 5
gg	OLLS	943 ± 24
	WLLS	958 ± 13
	ONLS	953 ± 15

[a] All values are in cal/mol. [b] OLLS: ordinary linearized least-squares fit; WLLS: weighted linearized least-squares fit; ONLS: ordinary nonlinear least-squares fit.

$$\ln\frac{I(\mathrm{gg})}{I'(\mathrm{tt})} = -\frac{\Delta H^m(\mathrm{gg})}{R}\cdot\frac{1}{T} + b^m_{gg} \tag{12}$$

where $I'(\mathrm{tt}) = I(\mathrm{tt}) + I'(\mathrm{gg})$ is the intensity measured including the contribution of conformer gg and $\Delta H^m(\mathrm{gg})$ = 953 cal/mol and $b^m_{gg} = -0.69$ are the corresponding values provided by the fit. Based on the intensity of the gg conformer at 267 cm^{-1}, $I(\mathrm{gg})$, and at 380 cm^{-1}, $I'(\mathrm{gg})$, the following system of equations can be written:

$$\ln\frac{I(\mathrm{gg})}{I(\mathrm{tt})} = -\frac{\Delta H(\mathrm{gg})}{R}\cdot\frac{1}{T} + b_{gg} \tag{13}$$

$$\ln\frac{I'(\mathrm{gg})}{I(\mathrm{tt})} = -\frac{\Delta H(\mathrm{gg})}{R}\cdot\frac{1}{T} + b'_{gg} \tag{14}$$

where $\Delta H(\mathrm{gg})$ is the true enthalpy difference. Thus,

$$b'_{gg} = b_{gg} + \ln\frac{I'(\mathrm{gg})}{I(\mathrm{gg})} \tag{15}$$

and

$$\ln\frac{I(\mathrm{gg})}{I'(\mathrm{tt})} = \ln\frac{I(\mathrm{gg})}{I(\mathrm{tt}) + I'(\mathrm{gg})} = \ln\frac{I(\mathrm{gg})}{I(\mathrm{tt})(1 + \mathrm{e}^{-(\Delta H(\mathrm{gg})/\mathrm{RT}) + b'_{gg}})} \qquad (16)$$
$$= \ln\frac{I(\mathrm{gg})}{I(\mathrm{tt})} - \ln(1 + \mathrm{e}^{-(\Delta H(\mathrm{gg})/\mathrm{RT}) + b'_{gg}}) \qquad (17)$$
$$(16)$$

also follow. Consequently, the experimentally measured ratio, $I(\mathrm{gg})/I'(\mathrm{tt})$, can be corrected according to eq 18.

$$\ln\frac{I(\mathrm{gg})}{I(\mathrm{tt})} = \ln\frac{I(\mathrm{gg})}{I'(\mathrm{tt})} + \ln(1 + \mathrm{e}^{-(\Delta H(\mathrm{gg})/\mathrm{RT}) + b'_{gg}}) = -\frac{\Delta H(\mathrm{gg})}{R}\cdot\frac{1}{T} + b_{gg} \tag{18}$$

Because, according to eq 15, b'_{gg} depends on b_{gg}, eq 18 must be solved iteratively, and one also needs an initial value for b_{gg}. The experimental b^m_{gg} was used as the initial guess for b_{gg}, and because the ratio $I'(\mathrm{gg})/I(\mathrm{gg})$ is not available from the experiment, it was estimated from B3LYP[89]/aug-cc-pVQZ static Raman activity calculations using the Gaussian suite of programs.[90] The B3LYP functional was selected because it yielded reasonable estimates for experimental Raman data in benchmark studies.[91−94]

It also follows that, once b'_{gg} and $\Delta H(\mathrm{gg})$ are obtained, the experimentally measured ratio, $I(\mathrm{tg})/I'(\mathrm{tt})$, can be corrected according to the formula below,

$$\ln\frac{I(\mathrm{tg})}{I(\mathrm{tt})} = \ln\frac{I(\mathrm{tg})}{I'(\mathrm{tt})} + \ln(1 + \mathrm{e}^{-\Delta H(\mathrm{gg})/\mathrm{RT} + b'_{gg}}) = -\frac{\Delta H(\mathrm{tg})}{R}\cdot\frac{1}{T} + b_{tg} \tag{19}$$

To test the above hypothesis we applied eq 18 to the experimental data of ref 5 and after four iterations $\Delta H(\text{gg})$ = 961 ± 15 cal/mol was obtained along with $b_{gg} = -0.66$ and $b'_{gg} = -2.29$. Using these values in eq 19, 626 ± 5 cal/mol can be calculated for $\Delta H(\text{tg})$. As expected, considering the possible effect of the gg conformer on the intensity data of the tt conformer, the relative enthalpy differences increase and, as a consequence, shift even closer to our ab initio predictions. Further experimental and/or theoretical investigations of the conformational PES of pentane can supply additional information about the importance of this issue.

4. CONCLUDING REMARKS

This study presents benchmark theoretical values for the energy and enthalpy differences of the pentane conformers, namely, $\Delta E(\text{tg}) = 605 \pm 21$, $\Delta E(\text{gg}) = 917 \pm 36$, and $\Delta E(\text{xg}) = 2796 \pm 61$, as well as $\Delta H_0^\circ(\text{tg}) = 644 \pm 46$, $\Delta H_0^\circ(\text{gg}) = 1099 \pm 90$, $\Delta H_0^\circ(\text{xg}) = 2975 \pm 124$, $\Delta H_{298}^\circ(\text{tg}) = 628 \pm 52$, $\Delta H_{298}^\circ(\text{gg}) = 974 \pm 100$, $\Delta H_{298}^\circ(\text{xg})$, = 2733 ± 140 cal/mol. The values for the xg conformer are of particular importance because the experimental investigation of this state's occupancy has yet to be performed. The bias introduced during the least-squares regression of the raw experimental data in ref 5 was also accounted for in this work. The theoretical $\Delta H_T^\circ(\text{tg}) = 638 \pm 22$ and $\Delta H_T^\circ(\text{gg}) = 1017 \pm 97$ cal/mol data are in accord with those of the most accurate experiment conducted for the 143−250 K temperature range.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.6b00280.

CCSD(T)/cc-pVTZ geometries and frequencies, HF, MP2, CCSD, and CCSD(T) total energies, hindered rotor energy levels, ΔE_{HO} contributions, and Raman scattering activities for the gg conformer as well as the recalculated data of Table 5 of ref 3 (ZIP)

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Notes

The authors declare no competing financial interest.

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