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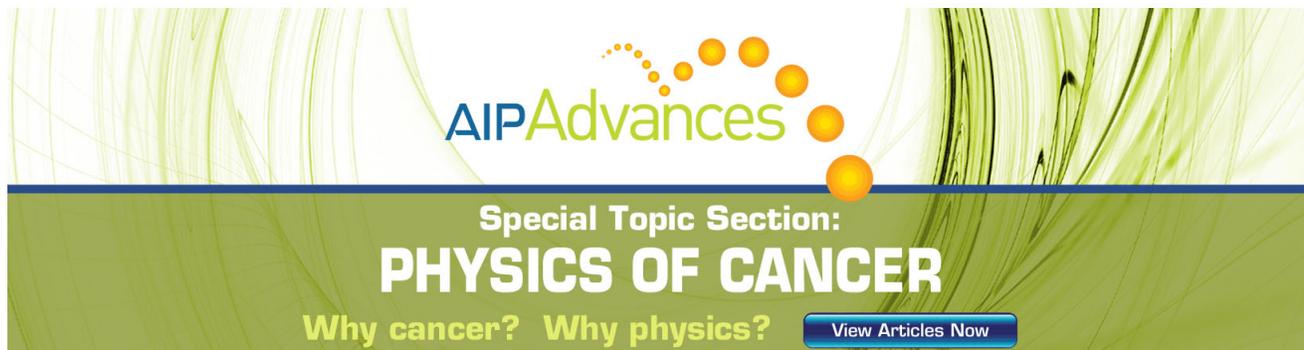
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Enthalpy difference between conformations of normal alkanes: Intramolecular basis set superposition error (BSSE) in the case of *n*-butane and *n*-hexane

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In this paper, an extra error source for high-quality *ab initio* calculation of conformation equilibrium in normal alkanes—intramolecular basis set superposition error (BSSE)—is discussed. Normal butane (*n*-butane) and normal hexane (*n*-hexane) are used as representative examples. Single-point energy difference and BSSE values of *trans* and *gauche* conformations for *n*-butane (and *trans-trans-trans* and *gauche-gauche-gauche* conformations for *n*-hexane) were calculated using popular electron correlation methods: The second-order Moller–Plesset (MP2), the fourth-order Moller–Plesset (MP4), and coupled cluster with single and double substitutions with noniterative triple excitation [CCSD(T)] levels of theory. Extrapolation to the complete basis set is applied. The difference between BSSE-corrected and uncorrected relative energy values ranges from ~ 100 cal/mol (in case of *n*-butane) to more than 1000 cal/mol (in case of *n*-hexane). The influence of basis set type (Pople or Dunning) and size [up to 6-311G(3*df*,3*pd*) and aug-cc-pVQZ] is discussed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2997349]

I. INTRODUCTION

The progress in computer hardware development has led to the possibility of relatively high-level *ab initio* quantum chemistry calculations with an expected error below 1 kcal/mol. However, to achieve such accuracy in relative energy or enthalpy, other factors, primarily zero-point energy (ZPE) correction and thermal correction to enthalpy (ΔH_T), should be considered. Intramolecular basis set superposition error (BSSE) is one of the factors whose magnitude is still not well understood. We still have not attained an answer to the following questions: How large is BSSE value in a single molecule? For what systems do we need to consider intermolecular BSSE?

Recently,¹ the surprising result that *ab initio* calculations on benzene and other planar arenes at the second-order Moller–Plesset (MP2), the third-order Moller–Plesset (MP3), and configuration interaction with singles and doubles (CISD) using standard Pople's basis sets yield nonplanar minima has been reported. According to these calculations, the planar optimized structures turn out to be transition states presenting one (or more) imaginary frequencies, whereas single-determinant-based methods [Hartree–Fock (HF), BLYP, or B3LYP] lead to the expected planar minima.

Asturiol *et al.*² provided evidence that intramolecular BSSE accounts for the existence of nonplanar optimized minima structures predicted by typical electronic structure methods. It has been shown (by taking as fragments the C–H and C–C moieties) that the counterpoise (CP) corrected optimized structures correspond to planar minima with no imaginary frequencies.

The problem of BSSE inside one molecule has also been discussed in a number of studies.^{3–10}

Sellers and Almlöf³ reported that the superposition error in the CISD correlation energy was large enough to shift the equilibrium geometries of a number of simple diatomic molecules (N₂, O₂, HF, and F₂) by several thousandths of an angstrom. It is also claimed³ that the variations in the gradients and force constants due to intermolecular BSSE (obtained with the basis sets of TZ2P quality and higher) were in general at the 1% level or greater.

Kobko and Dannenberg⁴ reported an optimization of the transition states for several organic reactions (concerted Diels–Alder, 1,2-H-atom shift in ethyl radical, and H-atom transfers from methane and propene to methyl radical) on CP-corrected potential energy surfaces. They have shown that the CP-optimized transition states obtained using small basis sets resemble those obtained using the larger basis sets both in energies and geometries.

Jensen⁵ used a water barrier toward linearity, NH₃ inversion barrier, and ethane rotational barrier to show that changes that normally are considered as a basis set effect are (in part) due to intramolecular BSSE. The reported values of BSSE are a few kilocalories per mole.

Palermo and co-workers^{6,8} have recently published a method to correct intramolecular BSSEs in intramolecular interactions occurring in peptides.⁷

An investigation of a dipeptide (tyrosine–glycine) conformation equilibrium made by Holroyd and van Mourik⁹ has led to a conclusion that large intramolecular BSSE values are responsible for masking the 180° minimum in the MP2 energy profile for rotation around the glycine C_α–N bond. BSSE correction using BSSE values from complexes of phenol and *N*-formylglycine, as well as the application of

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local MP2, or employing large basis sets (aug-cc-pVQZ) and density fitting, has led to a local minimum at 180° .

Sodupe *et al.*¹⁰ showed the importance of BSSE correction for the calculation of the activation energies of Diels–Alder reaction between cyclopropene and butadiene. Both QCISD(*T*) and small basis set calculations are shown to result in large BSSEs, which fortuitously lower the (uncorrected) activation energies. The magnitude of BSSE reaches 9 kcal/mol (for 3–12G basis set).

The local Moller–Plesset second-order method (LMP2) (Refs. 11–13) has been advocated as a method for reducing intramolecular BSSE. Unfortunately, no truly wide analysis in this field has been conducted.

It should be noted that alternative (to standard CP method, see below) solution for BSSE correction exists. Chemical Hamiltonian approach (CHA) of Mayer¹⁴ and Mayer and Valiron¹⁵ is reported to be an *a priori* BSSE-free approach. CP and CHA methods usually provide close results. No information of CHA use for conformation equilibrium problem was found in the literature.

Quantum chemistry of conformation equilibrium is one of the fields where great accuracy (<100 cal/mol) is needed since the energy difference between conformations rarely exceeds 1000–3000 cal/mol.

A few years ago, an inclusion of ZPE and ΔH_T for a conformation study of the simplest hydrocarbons (normal alkanes) has been discussed by Allinger *et al.*¹⁶ (*n*-butane) and Deleuze and co-workers^{17,18} (*n*-pentane). To correctly pinpoint the stationary points of *n*-alkane within the confines of *ab initio* theory in the nonrelativistic Born–Oppenheimer approximation, the convergence of the conformational energy differences toward an asymptotic value when both the number of basis functions and the level of theory used is increased was exploited by means of extrapolations. Inclusion of ZPE, thermal correction, and entropy values (in “rigid rotor-harmonic oscillator” approximation) has greatly influenced the results of the analysis (conformer fractions).¹⁷

This article aims to show the influence of one extra factor—intramolecular BSSE—on the *ab initio* results. We will try to give an answer to the question whether one needs to include BSSE correction to obtain results with an error limit below 100 cal/mol. Conformers of two normal alkanes, *n*-butane (C_4H_{10}) and *n*-hexane (C_6H_{14}), are used as samples.

II. COMPUTATIONAL

All calculations were performed with the GAMESS (Ref. 19) and PC GAMESS (Ref. 20) quantum chemistry packages. The basis sets implemented in the programs were used. Single-point energy calculations were carried out using very tight self-consistent field (SCF) convergence criteria. Electron correlation was accounted for at the MP2, fourth-order Moller–Plesset (MP4),^{21,22} and the CCSD(*T*) (Ref. 23) theory levels. The CHEM3D ULTRA 10.0 modeling suite was used for data visualization. Extraction of necessary data from standard output files was done by a set of self-written programs (C++). The MATLAB computing environment was used for data analysis.

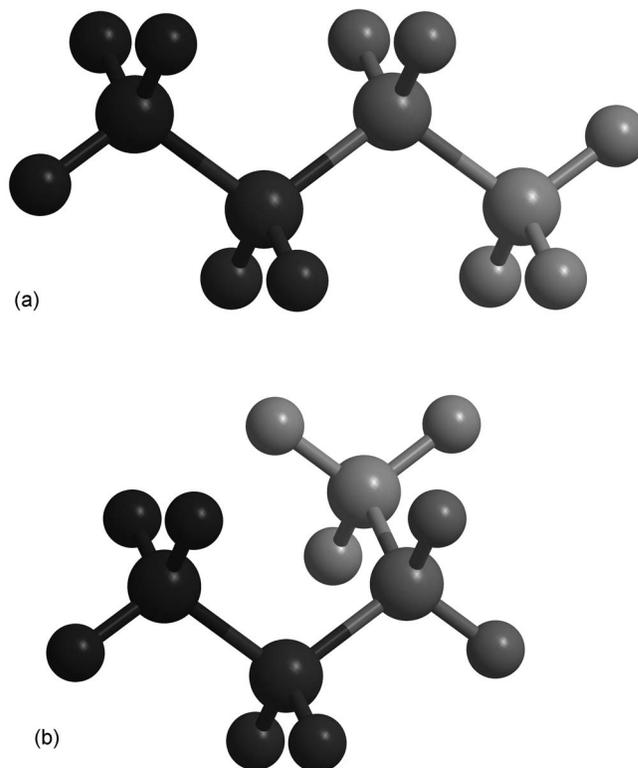


FIG. 1. *Trans* (a) and *gauche* (b) conformations of normal butane (C_4H_{10}). Division into CH_3 and $-CH_2$ subunits for CP correction is shown by different colors.

The geometries of *n*-butane and *n*-hexane conformers were optimized (without CP correction) at the MP2/6-31G(*d*) level with tight optimization criteria.

Normal butane conformer with a torsion angle of 180° was regarded as *trans* or *t*; a conformer with a torsion angle of approximately 60° was termed *gauche* or *g*. *n*-hexane conformers were regarded as *trans-trans-trans* [$180^\circ-180^\circ-180^\circ$] (*ttt*) and *gauche(+)-gauche(+)-gauche(+)* [$60^\circ-60^\circ-60^\circ$] ($g^+g^+g^+$). See Refs. 17, 24, and 25 for more information. The geometries of all conformers are presented in Ref. 35.

The energy difference was reported relative to *trans* ($E_g - E_t$) and *trans-trans-trans* conformation ($E_{g^+g^+g^+} - E_{ttt}$) of *n*-butane and *n*-hexane, respectively. Calories per mole (cal/mol) was used as the default energy unit. Conversion factor to Systeme International unit: 1 cal/mol = 4.184 J/mol. Standard deviation ($\pm\sigma$) is a default uncertainty value.

The procedure of intramolecular CP correction is the same as in Ref. 2: The molecule is divided into N parts ($N=4$ for C_4H_{10} and $N=6$ for C_6H_{14}), which are considered as separate systems (“monomers in dimer”). Two single-point energies are calculated: standard energy E (without CP correction) and corrected energy E_{corr} (with CP correction). The difference between them is the intramolecular BSSE. The value of BSSE depends on *n*-alkane conformation [BSSE = $f(\mathbf{R})$, where \mathbf{R} is the vector of nucleus positions]. It means that the difference between corrected and uncorrected conformer energies is not the same: $\Delta E_{\text{corr}} \neq \Delta E$; $\Delta E_{\text{corr}} = \Delta E + \Delta \text{BSSE}$. So, ΔE_{corr} is a “real” prediction of conforma-

TABLE I. Corrected energy difference and BSSE difference between *n*-butane (C₄H₁₀) conformers: *gauche* and *trans*. All values are in cal/mol.

	Basis set				
	6-31G(<i>d</i>)	6-31G(<i>d,p</i>)	6-311G(<i>d,p</i>)	6-311G(2 <i>d,p</i>)	6-311G(3 <i>df,3dp</i>)
Energy difference (ΔE)					
HF	994	996	1006	1046	1050
MP2	681	633	519	552	519
MP4	692	652	527	560	523
CCSD(<i>T</i>)	696	655	540	575	540
Corrected energy difference (ΔE_{corr})					
HF	1288	1287	1092	1135	1122
MP2	1066	999	628	681	642
MP4	1047	991	641	690	650
CCSD(<i>T</i>)	1027	970	643	697	662
BSSE difference (ΔBSSE)					
HF	294	291	86	89	72
MP2	385	367	109	129	123
MP4	354	338	114	130	127
CCSD(<i>T</i>)	331	315	103	123	123

tion energy difference that does not include basis set superposition between different parts of the molecule. Ghost orbitals of all other fragments are used for CP calculation

Figure 1 represents a division of C₄H₁₀ molecule into 4 parts (CH₃, CH₂, CH₂, and CH₃). In the case of alkanes, molecule division of the whole molecule into methyl and methylene fragments is clear and straightforward. In the case of other hydrocarbons (e.g., benzene), this procedure is not that clear (see Ref. 2 for discussion). Alternatively, a division can be made using atoms as fragments (14 parts in the case of butane). In our case, following this procedure would lead to extra calculations and problems with SCF convergence in the case of *n*-butane *gauche* conformation, so the four-part BSSE procedure was applied instead.

The same division of *n*-hexane (CH₃(CH₂)₄CH₃) molecule into six fragments containing one carbon atom each (two CH₃ and four CH₂) has been applied.

Figure 1 (and SF1 in Ref. 35) shows that the effect of basis set superposition in the case of linear and nonlinear conformation is expected to be completely different.

III. RESULTS AND DISCUSSION

A. Normal butane: Pople-type basis sets

The results of following the BSSE procedure for *n*-butane using Pople basis sets are shown in Table I. Even though the magnitude of BSSE is just ~ 100 cal/mol (~ 420 J/mol), it is obvious that in all cases, BSSE is large in comparison to energy difference of butane conformations: The average values are 46%, 47%, 20%, 19%, and 19% for 6-31G(*d*), 6-31G(*d,p*), 6-311G(*d,p*), 6-311G(2*d,p*), and 6-311G(3*df,3dp*) basis sets, respectively. Even though the use of larger basis set [e.g., 6-311G(2*d,p*)] decreases BSSE in comparison to the smaller one (e.g., 6-31G(*d*)), the rela-

tive value is still large. A great difference between the results of split-valence double- and triple-zeta basis sets should be noted.

It appears that for a large 6-311G(3*df,3dp*) basis set, a kind of saturation for all electron correlation methods is observed. The BSSE difference value is more than 120 cal/mol (502 J/mol) and it is constant for MP2, MP4, and CCSD(*T*) methods (Table I).

The relative BSSE values for HF method are approximately twice less than that for any method including electron correlation. They reach the level of 72 cal/mol or 6.4% [6-311G(3*df,3dp*)], but this seems to be the limit.

Table I shows that the use of small basis set leads to an error compensation. BSSE decreases the predicted energy difference between *n*-butane conformers and (by this fact) compensates the basis set incompleteness. For example, by using 6-31G(*d*) basis set at CCSD(*T*) level without BSSE correction, one obtains a value of 696 cal/mol (2.9 kJ/mol), which is close to complete basis set (CBS) value (see below) of 571 cal/mol (2.4 kJ/mol); CP correction leads to an increase in relative difference from 22% to 80% (corrected value is 1027 cal/mol or 4.3 kJ/mol). The same effect has already been observed for different systems by Sellers and Almlöf.³

One can conclude that even for large Pople-type basis sets, BSSE is comparable with ZPE correction (~ 100 cal/mol¹⁷) and should be included for comparison of *ab initio* and experimental data.

B. Normal butane: Correlation consistent basis sets

Table II lists the results of single-point energy calculations of *n*-butane conformers using Dunning's correlation

TABLE II. Corrected energy difference and BSSE difference between *n*-butane (C_4H_{10}) conformers at the basis set limit: *gauche* and *trans*. Extrapolation procedure of Helgaker *et al.* (Ref. 26) is used to evaluate complete basis set (CBS) energy values. See also Ref. 24 to compare the results of two- and three-point extrapolation schemes. Basis sets: aCCD = aug-cc-pVDZ, aCCT = aug-cc-pVTZ, aCCQ = aug-cc-pVQZ. All values are in cal/mol.

	aCCD	Basis set aCCT	aCCQ	CBS
Energy difference (ΔE)				
HF	1030	1091	1095	1117
MP2	557	555	...	554
MP4	572	557	...	551
CCSD(<i>T</i>)	583	575	...	571
Corrected energy difference (ΔE_{corr})				
HF	1106	1097	1098	1094
MP2	637	591	...	572
MP4	647	592	...	568
CCSD(<i>T</i>)	658	609	...	589
BSSE difference (ΔBSSE)				
HF	76	6	3	...
MP2	81	37
MP4	75	35
CCSD(<i>T</i>)	75	35

consistent basis sets (up to aug-cc-pVQZ). These values can be used for extrapolation at the basis set limit (CBS) using the procedure of Helgaker *et al.*²⁶

Standard calculation without CP correction leads to a quick energy difference saturation for electron correlation methods: The average change in predicted values with aug-cc-pVDZ and aug-cc-pVTZ basis sets is just -8 ± 6 cal/mol. A different result is observed for the HF method only: The change is $+61$ cal/mol. Note that the error bars reported have no statistical meaning.^{27–29}

BSSE-corrected values converge in a different way since the difference between aug-cc-pVDZ and aug-cc-pVTZ values is -50 ± 5 cal/mol. The decrease in energy difference is observed even for the HF method.

The CBS energy difference does not depend on the type of data (CP corrected or not) used for extrapolation. The difference between standard and CP-corrected CBS values is just 18 cal/mol (not including HF). The HF value is 23 cal/mol and has an opposite sign (corrected energy difference is smaller). This means that BSSE correction is not necessary if extrapolation to CBS is applied (as it should be since BSSE is zero at CBS). Thus, standard energy difference values can be used for extrapolation.

From Table II one can see that convergence of uncorrected values (to its basis set limit) is much quicker than corrected ones. It seems to be that more basis functions are needed to come to *n*-butane CBS than it is believed now. It also makes correction of intermolecular BSSE not a good

TABLE III. Corrected energy difference and BSSE difference between *n*-hexane (C_6H_{14}) conformers: *gauche*(+)-*gauche*(+)-*gauche*(+) and *trans-trans-trans*. All values are in cal/mol.

	Basis set		
	6-31G(<i>d</i>)	6-31G(<i>d,p</i>)	6-311G(<i>d,p</i>)
Energy difference (ΔE)			
HF	3099	3091	3112
MP2	1422	1218	719
MP4	1556	1391	871
CCSD(<i>T</i>)	1590	1428	958
Corrected energy difference (ΔE_{corr})			
HF	4305	4294	3455
MP2	3153	2893	1400
MP4	3192	2975	1584
CCSD(<i>T</i>)	3127	2907	1620
BSSE difference (ΔBSSE)			
HF	1207	1204	343
MP2	1731	1675	681
MP4	1636	1585	714
CCSD(<i>T</i>)	1537	1479	662

idea if extrapolation to basis set limit is applied. Extra research is needed to clarify the generality of this conclusion.

C. Normal hexane: A hydrocarbon size effect

Normal butane is the simplest (smallest) normal alkane in which conformation equilibrium is possible. It is interesting to investigate how large is a BSSE for larger normal alkanes. Normal hexane (C_6H_{14}) is a suitable candidate for such analysis since it has three torsion angles (so a “really stranded” conformation is possible; see Ref. 35 for a figure); however, it is still small enough to be treated at a relatively high *ab initio* level.

Energy differences between *gauche*(+)-*gauche*(+)-*gauche*(+) and *trans-trans-trans* conformers with three Pople-type basis sets are listed in Table III. The relative BSSE difference for electron-correlation method values with a 6-311G(*d,p*) basis set is $40 \pm 6\%$ (compared with $20 \pm 1\%$ for *n*-butane). Absolute values are more than six times larger than that for C_4H_{10} .

The difference between split-valence double- and triple-zeta basis sets is the same as for C_4H_{10} with the only difference that triple-zeta basis set usage leads to two times (2.3 ± 0.1) lower ΔBSSE values (compared with 3.1 ± 0.2 in case of *n*-butane).

It is also clear that all electron correlation methods have approximately the same BSSE difference. This fact can be used for CP correction if BSSE values at the highest level are unavailable or cost too much of CPU time. Such scheme will be close to a well-known extrapolation scheme presented in Refs. 16–18.

It can be concluded that for a stranded conformation, BSSE correction becomes more important. The BSSE cor-

rection is needed for accuracy better than 1 kcal/mol. Only quantitative results can be obtained by standard single-point energy calculation methods.

IV. CONCLUSIONS

The following conclusions are drawn:

- (1) The influence of intramolecular BSSE on energy difference of *n*-alkane conformers can be estimated by standard CP method.
- (2) BSSE correction for *n*-butane has a value of ~ 100 cal/mol (~ 418 J/mol) for any electron correlation method [up to 6-311G(3*df*,3*dp*) basis set], which is comparable with ZPE correction.
- (3) BSSE correction for stranded conformation of *n*-hexane has a value of more than 700 cal/mol [or 40%; 6-311G(*d,p*) basis set] and ignoring it in the calculation of energy difference between conformations is completely unacceptable. The same effect is expected for all larger alkanes.
- (4) The reason for an error compensation leading to unexpectedly precise results in *ab initio* conformation research with small basis sets is clarified.

Of course, one should note that BSSE (including intermolecular one) is expected to have a zero value with CBS.

One can conclude that BSSE can be regarded as an extra error source for high-quality <1 kcal/mol *ab initio* calculations and its influence should be discussed in the same way as zero-point energy (ZPE) and enthalpy thermal correction (ΔH_T) values. Presented analysis shows that the results of structure optimization can also depend on intramolecular BSSE magnitude and sign. Extra research (e.g., CP optimization) is needed to clarify this issue. The presented results can be helpful for larger systems research.³⁰⁻³⁵

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¹D. Moran, A. C. Simmonett, F. E. Leach, W. D. Allen, P. V. Schleyer, and H. F. Schaefer, *J. Am. Chem. Soc.* **128**, 9342 (2006).

²D. Asturiol, M. Duran, and P. Salvador, *J. Chem. Phys.* **128**, 144108

(2008).

³H. Sellers and J. Almlof, *J. Phys. Chem.* **93**, 5136 (1989).

⁴N. Kobko and J. J. Dannenberg, *J. Phys. Chem. A* **105**, 1944 (2001).

⁵F. Jensen, *Chem. Phys. Lett.* **261**, 633 (1996).

⁶N. Y. Palermo, J. Csontos, M. C. Owen, R. F. Murphy, and S. Lovas, *J. Comput. Chem.* **28**, 1208 (2007).

⁷T. van Mourik, *J. Comput. Chem.* **29**, 1 (2008).

⁸J. Csontos, N. Y. Palermo, R. F. Murphy, and S. Lovas, *J. Comput. Chem.* **29**, 4 (2008).

⁹L. F. Holroyd and T. van Mourik, *Chem. Phys. Lett.* **442**, 42 (2007).

¹⁰M. Sodupe, R. Rios, V. Branchadell, T. Nicholas, A. Oliva, and J. J. Dannenberg, *J. Am. Chem. Soc.* **119**, 4232 (1997).

¹¹A. Reyes, L. Fomina, L. Rumsh, and S. Fomine, *Int. J. Quantum Chem.* **104**, 335 (2005).

¹²P. Kolandaivel, M. Knapp-Mohammady, and S. Suhai, *Int. J. Quantum Chem.* **99**, 28 (2004).

¹³K. Brameld, S. Dasgupta, and W. A. Goddard III, *J. Phys. Chem. B* **101**, 4851 (1997).

¹⁴I. Mayer, *Int. J. Quantum Chem.* **70**, 41 (1998).

¹⁵I. Mayer and P. Valiron, *J. Chem. Phys.* **109**, 3360 (1998).

¹⁶N. L. Allinger, J. T. Fermann, W. D. Allen, and H. F. Schaefer, *J. Chem. Phys.* **106**, 5143 (1997).

¹⁷A. Salam and M. S. Deleuze, *J. Chem. Phys.* **116**, 1296 (2002).

¹⁸S. Knippenberg, Y. R. Huang, B. Hajgató, J.-P. François, J. K. Deng, and M. S. Deleuze, *J. Chem. Phys.* **127**, 174306 (2007).

¹⁹M. S. Gordon and M. W. Schmidt, in *Theory and Applications of Computational Chemistry: The First Forty Years*, edited by C. E. Dykstra, G. Frenking, K. S. Kim, and G. E. Scuseria (Elsevier, Amsterdam, 2005).

²⁰A. A. Granovsky, PC GAMESS version 7.1, <http://classic.chem.msu.su/gran/gamess/index.html>

²¹C. Møller and M. S. Plesset, *Phys. Rev.* **46**, 618 (1934).

²²M. Head-Gordon, J. A. Pople, and J. M. Frisch, *Chem. Phys. Lett.* **153**, 503 (1988).

²³J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5968 (1987).

²⁴R. M. Balabin, *Chem. Phys.* **352**, 267 (2008).

²⁵R. M. Balabin, "Enthalpy difference between conformations of normal alkanes: Raman spectroscopy study of *n*-pentane," *J. Phys. Chem. A* (submitted).

²⁶T. Helgaker, W. Klopper, H. Koch, and J. Noga, *J. Chem. Phys.* **106**, 9639 (1997).

²⁷R. M. Balabin, R. Z. Safieva, and E. I. Lomakina, *Chemom. Intell. Lab. Syst.* **88**, 183 (2007).

²⁸R. M. Balabin, R. Z. Safieva, and E. I. Lomakina, *Chemom. Intell. Lab. Syst.* **93**, 58 (2008).

²⁹R. M. Balabin and R. Z. Safieva, *Fuel* **87**, 1096 (2008).

³⁰G. Alagona and C. Ghio, *Int. J. Quantum Chem.* **90**, 641 (2002).

³¹Y.-K. Han, K. H. Kim, S.-K. Son, and Y. S. Lee, *Bull. Korean Chem. Soc.* **23**, 1267 (2002).

³²F. Shi, *Organometallics* **25**, 4034 (2006).

³³A. E. Shields and T. van Mourik, *J. Phys. Chem. A* **111**, 13272 (2007).

³⁴H. Valdés, V. Klusák, M. Pitoňák, O. Exner, I. Starý, P. Hobza, and L. Rulíšek, *J. Comput. Chem.* **29**, 861 (2008).

³⁵See EPAPS Document No. E-JCPSA6-129-004840 for conformer geometries (tables and figures) and tables with standard energies, BSSE-corrected energies, and BSSE corrections for *n*-butane and *n*-hexane conformers. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.