ORGANIC LETTERS

2006
Vol. 8, No. 17
3631−3634

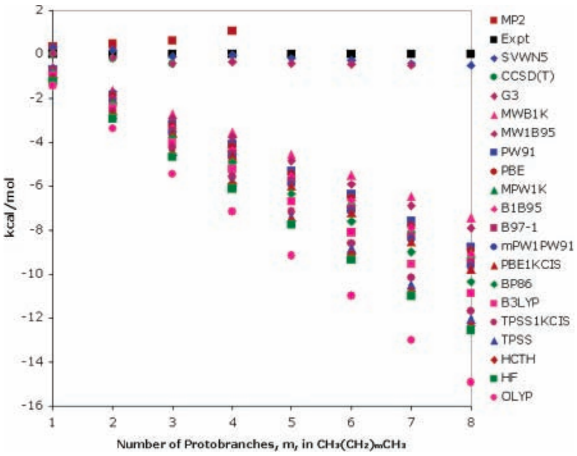
Systematic Errors in Computed Alkane Energies Using B3LYP and Other Popular DFT Functionals

Matthew D. Wodrich, Clémence Corminboeuf, and Paul von Ragué Schleyer*

Department of Chemistry and Center for Computational Chemistry,
University of Georgia, Athens, Georgia 30602
schleyer@chem.uga.edu

Received April 27, 2006

ABSTRACT



Energies computed by B3LYP and other popular DFT functionals are flawed by systematic errors, which can become considerable for larger molecules. These errors, predominately due to inadequacies in assessing longer-range nonbonded attractive effects (dispersion), are illustrated by the isodesmic stabilization energies of *n*-alkanes (based on methane and ethane, which have no stabilizing 1,3-alkyl group interactions). Newer functionals, designed to describe weak interactions, give somewhat better agreement with experiment, but are not fully satisfactory.

Kohn−Sham density functional theory has become the standard computational chemistry method. Based on its superior performance in numerous energy assessments of small molecules, B3LYP is the most widely used functional. B3LYP reproduces the geometries of smaller and larger molecules very well. Despite such successes, there is increasing awareness that B3LYP can fail badly in describing the energies of van der Waals molecules, hydrogen-bonded systems, reaction barrier heights, and larger molecules.[1] B3LYP computations of even the most basic organic molecules, the *n*-alkanes, result in systematic errors in the predicted heats of formation[2] and bond energies.[3] Redfern et al.[4] reported increasing deviations between B3LYP and G3 theory as the *n*-alkane chain is lengthened (Figure 1). Errors in B3LYP computations of experimental homolytic

---

[1] (a) Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4811. (b) Zhao, Y.; Tishchenko, O.; Truhlar, D. G. *J. Phys. Chem. B* **2005**, *109*, 19046. (c) Tsuzuki, S.; Luthi, H. P. *J. Chem. Phys.* **2001**, *114*, 3949. (d) Duncan, J. A.; Spong, M. C. *J. Phys. Org. Chem.* **2005**, *18*, 462.

[2] (a) Raghavachari, K.; Stefanov, B. B.; Curtiss, L. A. *Mol. Phys.* **1997**, *91*, 555. (b) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063. (c) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople J. A. *J. Chem. Phys.* **2000**, *112*, 7374. (d) Saeys, M.; Reyniers, M.-F.; Marin, G. B.; van Speybroeck, V.; Waroquier, J. *J. Phys. Chem. A* **2003**, *107*, 9147.

[3] (a) Feng, Y.; Liu, L.; Wang, J.-T.; Huang, H.; Guo, Q.-X. *J. Chem. Inf. Comput. Sci.* **2003**, *43*, 2005. (b) Fu, Y.; Dong, X. Y.; Wang, Y. M.; Liu, L.; Guo, Q.-X. *Chin. J. Chem.* **2005**, *23*, 474. (c) Coote, M. L.; Pross, A.; Radom, L. In *Fundamental World of Quantum Chemistry*; Brandas, E. J., Kryachko, E. S., Eds.; Kluwer Academic Publishers: The Netherlands, 2004; Vol. III, p 563. (d) Izgorodina, E. I.; Coote, M. L.; Radom, L. *J. Phys. Chem. A* **2005**, *109*, 7558.

[4] Redfern, P. C.; Zapol, P.; Curtiss, L. A.; Raghavachari, K. *J. Phys. Chem. A* **2000**, *104*, 5850.

10.1021/ol061016i CCC: $33.50

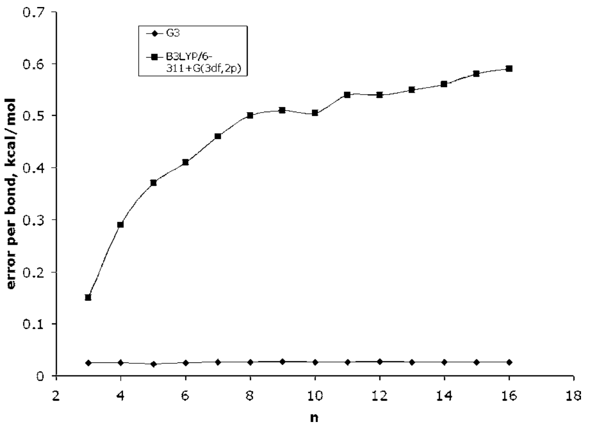


Figure 1. Error per bond in calculated enthalpies of formation for *n*-alkanes. Reproduced from ref 4. Copyright 1998 American Institute of Physics.

C−C bond-breaking energies of methyl-substituted ethanes and the relative stabilities of isomers become more serious as the molecules become larger.[5] The “cumulative effect of the errors in large molecules”[2c] “discourage the use of the B3LYP model for reaction energy calculations of organic compounds containing more than four carbon atoms.”[5a] Possible origins of these shortcomings (e.g., dispersion) have been considered,[5a,c] but the problems have not been overcome.

We computed the isodesmic stabilization energies (eq 1) of the linear conformations of the *n*-alkanes in order to assess and to help understand the errors given by numerous early and more recent DFT functionals. Figure 2 compares the results against the experimental data and emphasizes the poor performance of most of the functionals with these basic organic molecules.

$$n\text{-CH}_3(\text{CH}_2)_m\text{CH}_3 + m\text{CH}_4 \rightarrow (m+1)\text{C}_2\text{H}_6 \tag{1}$$

Our computations with the Gaussian 98, Gaussian 03, and Molpro programs[6] employed one LDA functional (SVWN5),[7] the widely used hybrid GGA, B3LYP,[8] and several pure GGA functionals (BP86,[9] OLYP,[8b,10] PBE,[11] PW91,[12] and HCTH).[13] In addition, we ascertained the performance of the more recently proposed hybrid GGA’s (B97-1[13] and mPW1PW91),[14] the kinetic energy dependent meta-GGA (TPSS),[15] and the hybrid meta-GGA functionals (TPSS1KCIS,[15−17] PBE1KCIS,[11,16,18] MPW1B95,[14,19] MPWB1K,[14,19] MPW1K,[14,20] and B1B95).[9,19a] The 6-311+G(d,p) basis set was used with all these functionals for uniformity. In addition, comparison with HF, MP2, G3,[21] and CCSD(T) data were obtained (also included in Figure 2). The computed energies refer to the linear zigzag *n*-alkane conformations and include zero-point vibrational corrections for comparison with the experimental heats of formation at 0 K.[22]

We attribute the increasingly large discrepancies between the computed and experimental energies apparent in Figures 1 and 2 to “protobranching”.[23] Protobranching, defined as the stabilizing interactions between two 1,3-disposed methyl (or methylene) groups in propane, higher linear, and branched alkanes, offers new insight into hydrocarbon stabilization. Each homologation of linear alkanes results in a further stabilization of ca. 2.8 kcal/mol, relative to methane and ethane (evaluated using Pople’s isodesmic bond energy (BSE) separation reaction, eq 1,[24] where *m* also gives the number of protobranches). Topologically branched alkanes such as isobutane and neopentane have more protobranches and are stabilized to an even larger extent than linear alkanes.[23] These 1,3 stabilizations between geminal groups can be attributed predominantly to attractive intramolecular van der Waals interactions arising from London dispersion forces[25] (i.e., long-range R^{-6} electron correlation effects). However, Grimme’s very recent analysis[5c] points instead to the greater importance of medium-range electron correlation

---

(5) (a) Check, C. E.; Gilbert, T. M. *J. Org. Chem.* **2005**, *70*, 9828. (b) Schreiner, P. R.; Fokin, A. A.; Pascal, R. A.; deMeijere, A. *Org. Lett.* **2006**, *8*, 3635. (c) Grimme, S. *Angew. Chem. Int. Ed.* **2006**, *45*, 625−629 and references cited.

(6) (a) *Gaussian 98*, Revision A.11: Frisch, M. J.; et al. Gaussian, Inc.: Pittsburgh, 1998. (b) *Gaussian 03*, Revision C.02: Frisch, M. J.; et al. Gaussian, Inc., Wallingford CT, 2004. (c) MOLPRO, a package of ab initio programs designed by Werner, J.-J.; Knowles, P. J. version 2002.1, contributed by Amos, R. D.; Bernhardsson, A.; Berning, A.; et al. Full references for 6 are in the Supporting Information.

(7) (a) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200. (b) Slater, J. C. *Quantum Theory of Molecular Solids: The Self-Consistent Field for Molecular and Solids*; McGraw-Hill: New York, 1974; Vol. 4.

(8) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(9) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(10) (a) Handy, N. C.; Cohen, A. J. *Mol. Phys.* **2001**, *99*, 403. (b) Hoe, W. M.; Cohen, A. J.; Handy, N. C. *Chem. Phys. Lett.***2001**, *341*, 319.

(11) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(12) Perdew, J. P. In *Electronic Structure in Solids ‘91*; Ziesche, P., Eschig, H., Eds.; Akademie Verlag: Berlin, 1991; p 11.

(13) Hamprecht, F. A.; Cohen, A. J.; Tozer, D. J.; Handy, N. C. *J. Chem. Phys.* **1998**, *109*, 6264.

(14) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.

(15) (a) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2003**, *119*, 12129. (b) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(16) (a) Rey, J.; Savin, A. *Int. J. Quantum Chem.* **1998**, *69*, 581. (b) Krieger, J. B.; Chen, J.; Iafrate, G. J.; Savin, A. In *Electron Correlations and Materials Properties*; Gonis, A., Kioussis, N., Eds.; Plenum: New York, 1999; p 463. (c) Toulouse, J.; Savin, A.; Adamo, C. *J. Chem. Phys.* **2002**, *117*, 10465.

(17) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2005**, *7*, 43.

(18) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2005**, *1*, 415.

(19) (a) Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040. (b) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 6908.

(20) Becke, A. D. *J. Chem. Phys.* **1997**, *107*, 8554.

(21) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rasslov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.

(22) NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101 Release 12, Aug 2005, Editor: Russell D. Johnson III http://srdata.nist.gov/cccbdb.

(23) (a) Wodrich, M. D.; Wannere, C. S.; Mo, Y.; Jarowski, P. D.; Houk, K. N.; Schleyer, P. v. R. To be submitted. (b) Schleyer, Paul v. R. Abstracts of Papers (COMP-301), 229th ACS National Meeting, San Diego, CA, March 13−17, 2005.

(24) (a) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. (b) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 289. (c) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986; p 300.

(25) (a) Pitzer, K. S.; Catalano, E. *J. Am. Chem. Soc.* **1956**, *78*, 4844. (b) Pitzer, K. S. *Adv. Chem. Phys.* **1959**, *2*, 59.

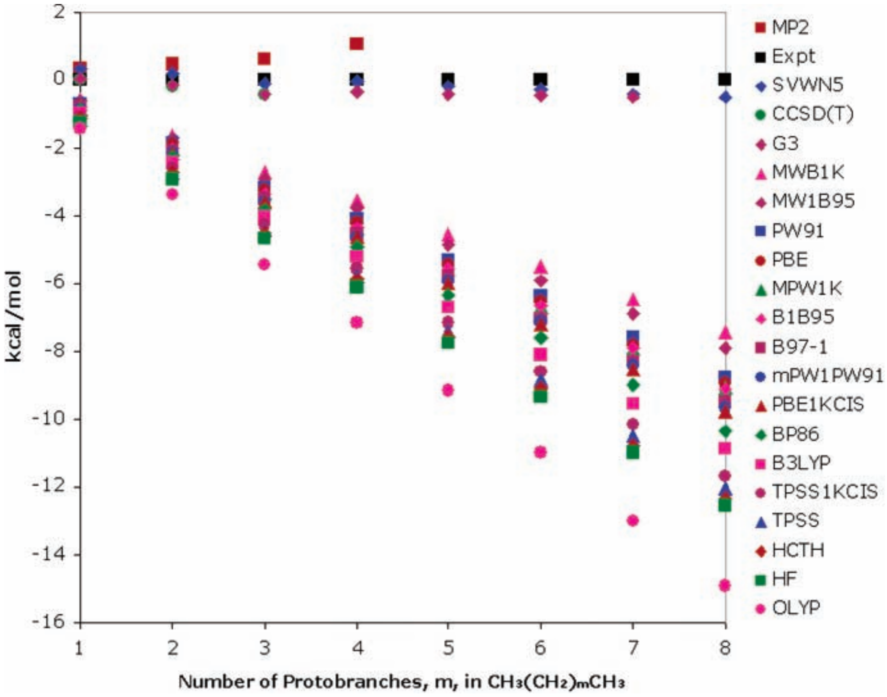


Figure 2. Deviations of various DFT functionals from experimental (0 K) protobranching stabilization energies. Negative values denote underestimation. Stabilization energies are based on eq 1. CCSD(T) and MP2 refer to CCSD(T)/aug-cc-pVTZ//MP2/6-311+G(d,p) and MP2/aug-cc-pVTZ//MP2/6-311+G(d,p), respectively, and include MP2/6-311+G(d,p) zero-point corrections. All other computations employed the 6-311+G(d,p) basis set.

differences. Hartree−Fock (HF), B3LYP, and many other functionals give unsatisfactory results (Figures 1 and 2) since they strongly underestimate the 1,3 group-group stabilization effects.

The Hartree−Fock approximation completely neglects dynamic electron correlation. B3LYP as well as most well-established density functionals only use local electron densities to describe correlation and do not account for medium[5c] and longer range dispersion interactions.[26] However, the design of DFT functionals that perform well for such interactions is the goal of much current research.[5c,18,27] DFT energies are affected by additional sources of error. For instance, correlation functionals that eliminate the "self-exchange" problem are being sought.[28] This error (not shared by Hartree−Fock) arises from the spurious interaction of an electron with itself.

Nearly all of the DFT functionals systematically underestimate the energies of *n*-alkane chains (Figure 2). Shockingly, the widely used B3LYP is among the worst functionals and underestimates each protobranching stabilization by 1.33 kcal/mol on average. Note that this 40% underestimation is comparable to the 47% of HF. OLYP, the poorest performer in our set, underestimates the stabilizazion energy by 1.8 kcal/mol on average. Indeed, the exchange functional for OLYP was fit with a restricted set of data which lacked weakly bonded systems.[10b] Other functionals, including the nonempirical TPSS meta-GGA and the semiempirical HCTH GGA, underestimate branching; their mean absolute deviations (MAD) range from 1.10 to 1.50 kcal/mol. Although the LDA approximation generally strongly overestimates weak interaction energies,[2a,29] SWVN5 performs best here (Figure 2). Similarly small errors have been reported before for propane, butane, and isobutane, *provided that error-canceling isodesmic evaluations (cf., eq 1) were employed.*[2c] Of course, caution must be excercised because of the well documented deficiencies of LDA.[2a,c,26]

The PW91 and the closely related "parameter-free" PBE exchange correlation GGA functionals describe the binding in attractive van der Waals regions more accurately;[30] their MADs are 1.05 and 1.08 kcal/mol, respectively, per protobranch. Somewhat better results are given by the recently developed hybrid meta-GGAs, MPW1B95 and MPW1B1K of Zhao and Truhlar, designed partially for the description of weakly interacting systems.[27a] Not surprsingly, these new functionals outperform B3LYP and other early functionals.

---

[26] Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley-VCH: Weinheim, 2001; p 236.

[27] (a) Wu, X.; Vargas, M. C.; Nayak, S.; Lotrich, V.; Scoles, G. *J. Chem. Phys.* **2001**, *115*, 8748. (b) Zimmerli, U.; Parrinello, M.; Koumoutsakos, P. *J. Chem. Phys.* **2004**, *120*, 2693. (c) von Lilienfeld, O. A.; Tavernelli, I.; Rothlisberger, U.; Sebastiani, D. *Phys. Rev. Lett.* **2004**, *93*, 153004. (d) Sato, T.; Tsuneda, T.; Hirao, K. *Mol. Phys.* **2005**, *103*, 1151.

[28] Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040.

[29] (a) Zhechkov, L.; Heine, T.; Patchkovskii, S.; Seifert, G.; Duarte, H. A. *J. Chem. Theory Comput.* **2005**, *1*, 841. (b) Lein, M.; Dobson, J. F.; Gross, E. K. U. *J. Comput. Chem.* **1999**, *20*, 12. (c) Valdes, H.; Sordo, J. A. *J. Comput. Chem.* **2002**, *23*, 444.

[30] Zhang, Y. K.; Pan, W.; Yang, W. T. *J. Chem. Phys.* **1997**, *107*. 7921.

However, significant errors (which are cumulative, Figure 2) still remain.

Unlike DFT, both MP2 and CCSD(T) results depend on basis set size.[31] The expected overestimation[32] of the branching stabilization is found at MP2/aug-cc-pVTZ, but not at the lower MP2/6-311+G(d,p) level. This suggests the possible existence of an intramolecular basis set superposition error. Similarly, CCSD(T)/6-311+G(d,p) results diverge somewhat from experiment but aug-cc-pVTZ values parallel those of experiment. Obviously, computational expense precludes application to longer *n*-alkane chains.

Figure 2 emphasizes the regularity of the increasingly large deviations from the experimental BSE stabilizations as the *n*-alkane chain is lengthened. Check and Gilbert[5a] also noted regularities in the computed bond dissociation energies of the central C−C bond of ethane as the number of methyl substituents increases. The B3LYP error increases to 21.1 kcal/mol for 2,2,3,3-tetramethylbutane; its high degree of branching enhances the long-range attractions. B3LYP fails as a consequence. Indeed, most of the functionals in Figure 2 systematically underestimate weak long-range interactions. Their poor performance appears to arise principally from their inadequacies in accounting for long and medium range electron correlation effects.[5c,33]

The accompanying paper by Schreiner et al.[5b] illustrates the problems in reproducing the experimental relative energies of hydrocarbons, especially when isomers having a different blend of single and multiple CC bonds are compared, at various DFT and ab initio levels. The preferred geometries of [*n*]annulenes were found earlier to depend strongly on the level of theory employed.[34]

Curtiss et al.[2c] have noted that homodesmotic energy evaluations improve the accuracy of B3LYP for large molecules. However, for alkanes this only arises through cancellation of the protobranching errors (eq 2, where *m* also is the number of protobranches).

$$CH_3(CH_2)_mCH_3 + (m - 1)C_2H_6 \rightarrow mC_3H_8 \qquad (2)$$

Linear and branched alkanes larger than ethane are stabilized by intramolecular 1,3 “protobranching” interactions between alkyl groups. The most commonly used DFT functionals, notably B3LYP, underestimate the protobranching stabilization mainly due to their inadequate descriptions of long-range nonbonded interactions. We join with others[5b] to discourage the use of B3LYP energy data for larger molecules. Unfortunately, the DFT alternatives are only somewhat better but are not yet fully satisfactory.

The recent hybrid meta-GGA functionals of Zhao and Truhlar, as well as other recently proposed van der Waals-corrected DFT functionals[27] with the correct R^{-6} asymptotic behavior, may provide more accurate assessments of weakly bound systems and better descriptions of intramolecular nonbonded interactions at considerably less computational cost than post-HF wave function methods. However, even the best-performing MPW1B95 and MPWB1K hybrid meta-GGA fuctionals[14,19] do not evaluate the energies of *n*-alkane chains accurately and only offer some improvement over B3LYP for larger molecules. We hope that Check and Gilbert’s pessimistic admonition that “a computational chemist cannot trust a one-type DFT calculation”[5a] can be overcome eventually.

Acknowledgment. We thank Y. Bernard (University of Geneva) and N. L. Allinger (University of Georgia) for helpful comments, J. M. Turney and H. F. Schaefer III (University of Georgia) for computational resources, as well as the authors of ref 5b for sharing their results prior to publication. The Petroleum Research Fund and NSF Grant No. CHE-0209857 supported our work.

Supporting Information Available: Calculated energies for bond separation reactions at all levels of theory are provided in addtion to data used to derive Figure 2. Full references for 6a and 6b are given. This material is available free of charge via the Internet at http://pubs.acs.org.

OL061016I

---

(31) The BSE for propane changes by only 0.07 kcal/mol in going from B3LYP/6-311+G(d,p) to B3LYP/cc-pVTZ.

(32) (a) Grimme, S. *J. Comput. Chem.* **2004**, *25*, 1463. (b) Tsuzuki, S.; Uchimaru, T.; Matsumara, K.; Mikami, M.; Tanabe, K. *Chem. Phys. Lett.* **2000**, *319*, 547. (c) Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Phys. Chem.* **1996**, *100*, 18790.

(33) Special attention is called to the important, just published paper of Grimme,[5c] which provides further examples and an illuminating analysis of “disasterous” DFT failures.

(34) Wannere, C. S.; Sattelmeyer, K. W.; Schaefer, H. F.; Schleyer, P. v. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 4296.