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A Density Functional That Accounts for Medium-Range Correlation Energies in Organic Chemistry

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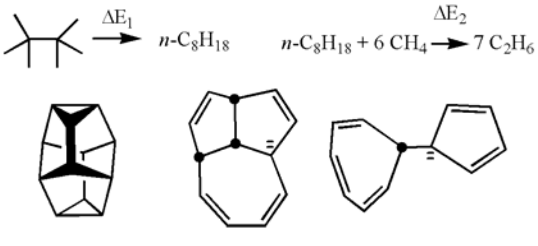
ABSTRACT



1 **2** **3**

Relative energies in kcal/mol

	ΔE_1	ΔE_2	E_2 - E_1	E_3 - E_1
Best est.	1.9	19.8	14.3	25.0
B3LYP	-8.4	11.8	-0.2	1.9
M05-2X	1.4	16.8	16.9	25.4

It has recently been pointed out that current density functionals are inaccurate for computing stereoelectronic effects and energy differences of isomerization reactions and isodesmic reactions involving alkanes; this has been interpreted as an incorrect prediction of medium-range correlation energies. This letter shows that the recently published M05-2X functional has good accuracy for all three of the recently highlighted problems, and it should be useful for a wide variety of problems in organic chemistry.

Density functional theory (DFT) is now the main tool for calculating the structure and energetics of complex molecular systems and materials.[1] Recently, Grimme claimed that all state-of-the-art density functionals provide a qualitatively incorrect picture of the stereoelectronic effects in alkane isomers,[2] and these observations are reinforced by two independent works[3,4] in this journal. Table 1 compares Grimme's results for four standard density functionals[5-9] to experimentally derived[2,10] data for the zero-point exclusive energy of *n*-octane minus that of 2,2,3,3-tetramethylbutane. All four density functionals that he studied get the sign wrong. Grimme[2] pointed out that a related problem is the increasing size of the errors per bond in heats of formation and alkyl bond dissociation energies predicted by most density functionals when molecules get larger.[3,11] We had pointed out earlier that the new M05-2X density functional has much better performance than all previous density functionals for alkyl bond dissociation energies as a function of alkyl group size.[12] Unfortunately, Grimme did not test the M05-2X density functional for this problem. In fact, we report here that the M05-2X functional, with the 6-311+G(2df,2p) basis set,[13] yields +2.1 kcal/mol (+1.4 kcal/mol with the cQZV3P[14] basis set and MP2/TZV(d,p) geometries) for the quantity in Table 1, which is quantitatively correct.

Table 1: Energy Difference (kcal/mol) between *n*-octane and 2,2,3,3-tetramethylbutane

method	△*E* (kcal/mol)
experiment	+1.9 [a]
PBE [b]	– 5.5 [c]
TPSSh [d]	– 6.3 [c]
B3LYP [e]	– 8.4 [c]
BLYP [f]	– 9.9 [c]
B3PW91 [g]	-7.0 [h]
M05-2X [i]	+2.1[h]
M05-2X [i]	+1.4[j]
MP2 [k]	+4.6 [c]

[a] Refs. 2, 10. [b] Ref. 5. [c] Calculations were performed with the cQZV3P basis set and MP2/TZV(d,p) geometries, and results were taken from Ref. 2. [d] Ref. 6. [e] Ref. 7-9. [f] Ref. 7. [g] Ref. 8. [h] present work with the 6-311+G(2df,2p) basis set; the geometry was optimized at the same level of theory and with the same basis set as was used for the calculation of the energy. [i] Ref. 12. [j]Present work with the cQZV3P basis set and MP2/TZV(d,p) geometries [k] Ref. 15

Wodrich et al.[3] showed that the systematic errors in DFT as the alkane size is increased are related to the stabilizing interaction of geminal methyl or methylene groups, an effect they call "protobranching," which is sensitive to medium-range correlation energy. A good measure of this effect is provided by the energies of reaction for reactions such as

$$n\text{-}C_6H_{14} + 4\,CH_4 \rightarrow 5\,C_2H_6 \qquad (1)$$

or

$$n\text{-}C_8H_{18} + 6\,CH_4 \rightarrow 7\,C_2H_6 \qquad (2)$$

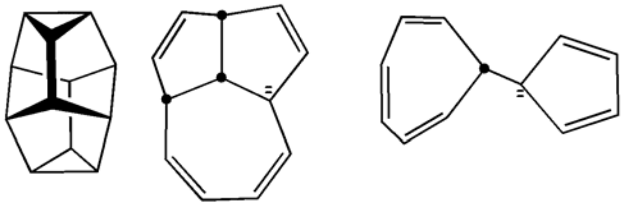
Table 2: ΔE (kcal/mol) of reaction for isodesmic reactions (1) and (2)

method	*n*-hexane	*n*-octane
Experiment	13.1 [a]	19.8 [a]
B3LYP [b]	7.8 [a]	11.8 [a]
PBE [c]	8.9 [a]	13.9 [a]
OLYP [d]	5.9 [a]	8.8 [a]
MPWB1K [e]	9.5 [a]	14.4 [a]
TPSS1KCIS [f]	7.5 [a]	11.3 [a]
B3PW91[g]	8.0 [h]	12.0 [h]
M05-2X [i]	11.5 [h]	17.2 [h]
M05-2X [i]	11.2[j]	16.8[j]
MP2 [k]	14.1 [a]	

[a] Ref. 3. All DFT and MP2 calculation in Ref. 3 employed the aug-cc-pVTZ basis set. [b] Ref. 7-9. [c] Ref .5. [d] Ref. 16. [e] Ref. 17. [f] Ref. 18. [g] Ref. 8. [h] Present work with the 6-311+G(2df,2p) basis set; for all calculations in this table the geometry was optimized at the same level of theory and with the same basis set as was used for the calculation of the energy. [i]Ref. 12. [j]Present work with the aug-cc-pVTZ basis set. [k] Ref. 15.

Table 2 compares these energies of reaction to experiment for several common density functionals and also M05-2X. Clearly, M05-2X is more accurate than previous functionals.

A related example, in particular a case of DFT failing to account for stereoelectronic effects, was provided by Schreiner et al.,[4] who compared the energies of three isomers of $(CH)_{12}$; see Figure 1. Table 3 compares their most accurate calculation and their DFT calculations to our M05-2X calculations. Again, the M05-2X functional does quite well.



1 **2** **3**

Figure 1 Structures of $(CH)_{12}$ isomers, where **1**, **2**, and **3** correpond to the stuctures of **1**, **22**, and **31** in Ref. 4.

Table 3. Energies (kcal/mol) of $(CH)_{12}$ isomers relative to structure **1**

method	**2**	**3**
CCSD(T) [a]	14.3 [b]	25.0 [b]
BLYP [c]	–10.0 [b]	–11.5 [b]
G96LYP [d]	– 6.4 [b]	– 6.8 [b]
KMLYP [e]	28.4 [b]	41.7 [b]
B3LYP [f]	– 0.2 [b]	1.9 [b]
BHandHLYP [g]	7.4 [b]	14.0 [b]
B3PW91 [h]	14.4 [b]	19.8 [b]
B3PW91 [h]	15.9 [i]	22.1 [i]
M05-2X [j]	14.0 [i]	21.4 [i]
M05-2X [j]	16.9 [k]	25.4 [k]
MP2 [l]	23.2 [b]	31.2 [b]

[a] Ref. 13, 19, and 20. [b] from Ref. 4. For each functional and MP2, we give the result with the 6-311+G(d,p) basis set. [c] Ref. 7. [d] Ref. 21. [e]Ref. 22. [f] Ref. 7-9. [g] Ref. 23. [h] Ref. 8. [i] Present work with the 6-311+G(2df,2p) basis set; the geometry was optimized at the same level of theory and with the same basis set as was used for the calculation of the energy. [j] Ref. 12. [k] Present work with the 6-311+G(d,p) basis set; the geometry was optimized at the same level of theory and with the same basis set as was used for the calculation of the energy. [l] Ref. 15.

We believe that the success of the M05-2X functional derives from the design of its functional form,[12] building primarily on work of Becke,[23,24] and from consistent, simultaneous parametrization[12] of the M05-2X exchange and correlation functionals against a broad range of accurate data including noncovalent interactions for main group chemistry. This allowed us to better represent medium-range correlation energy. We note that the M05-2X functional involves kinetic energy density in both the exchange and correlation functionals, but unlike fifth-rung functionals,[25] it does not involve terms[26] dependent on virtual orbitals.

The calculations were carried out with a modified version of *Gaussian03*.[27] M05-2X is now available in release 5.0 of *NWChem*.[28] In addition it is scheduled to be in the next minor revision of *Gaussian03* and in the next release (version 7.0) of *Jaguar*.

The reader is referred to the original paper[12] and references therein for further details of the M05-2X functional. In one of our previous papers,[29] we analyzed the noncovalent interaction of methane with benzene and concluded that the success of M05-2X for this noncovalent interaction is due to its improved correlation functional for the description of medium-range correlation. We noted in ref. 29 that although M05-2X does not give the asymptotic $-C_6/R^6$ tail of the long-range interaction, it agrees with CCSD(T)/complete-basis results for CH_4-benzene within 0.17 kcal/mol from 3.4 to 5.4 Å (the minimum is 1.5 kcal/mol at 3.8 Å and is 4.6 times deeper than the value at 5.4 Å).

We also note that the M05-2X functional has been shown to outperform many other functionals for noncovalent interactions,[12,29,30] for torsional potentials of conjugated polyenes,[31] and for proton affinities of conjugated polyenes (a test of its ability to predict polarizabilities of conjugated double bonds).[31] It is less satisfactory for energy differences[32] between cumulenes and poly-ynes, but still better than all other functionals in Tables 1-3.[31] M05-2X also has very high quantitative accuracy for main-group thermochemistry and barrier heights.[12]

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Supporting Information Available: Cartesian coordinates and electronic total energies of all molecules involved in this letter are provided in Tables S1-S4.

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