

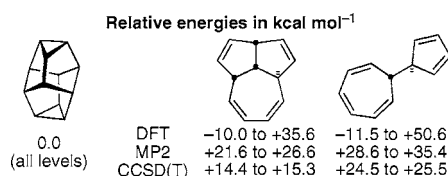
# Many Density Functional Theory Approaches Fail To Give Reliable Large Hydrocarbon Isomer Energy Differences

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## ABSTRACT



Several DFT methods were found to be unreliable for computing hydrocarbon isomer energy differences. The errors grow with system size up to 20 kcal mol<sup>-1</sup> for the relative energies of the (CH)<sub>12</sub> isomers; octahedrane is the most stable (CH)<sub>12</sub> hydrocarbon. While DFT geometries generally are good, problems arise for structures with single bonds only, especially for small rings. We recommend the use of higher level, non-DFT energy single points computed at DFT-optimized structures.

Strange as it may appear, *D*<sub>3d</sub>-octahedrane (**1**) is the most stable (CH)<sub>12</sub> hydrocarbon (Figure 1), despite considerable strain (83.7 kcal mol<sup>-1</sup>, B3LYP/6-311+G(d)).<sup>1</sup> This conclusion was reached by comparing **1** to a large number of other (CH)<sub>12</sub> isomers at different levels of theory. This is a tedious exercise, and “chemical intuition” can only go so far as to exclude some of the obvious high energy structures. The problem is that **1** would probably be one of them, and conjugated structures such as **30–38** seem far better candidates for the lowest energy structure. On the other hand,  $\sigma$ -bonds are more stable than  $\pi$ -bonds so that the  $\sigma$ -strain energy must be considerable to make up for this energy difference. This brings the polycyclic derivatives without unsaturation (**1–3** and **39**<sup>2</sup>) back into play. Hence, a safe conclusion cannot be drawn on the basis of empirical structural arguments alone.

The logical next step is to utilize theory to evaluate the isomer energy differences—an exercise that seems almost trivial. But what level of theory is appropriate? This is an

important question because the potentially huge number of isomers will usually force chemists to use DFT methods. These have proven quite accurate, for instance, for the G2 structural test set<sup>3</sup> that contains 148 different small molecules having well-established enthalpies of formation. Among the many DFT methods tested, B3LYP showed the best overall performance with the smallest average absolute deviation at 3.1 kcal mol<sup>-1</sup>.<sup>4</sup> Undoubtedly, this has led to the use of B3LYP as the “jack of all trades” when DFT is used for organic molecules. The G3 test set, which contains 75 additional heats of formation of larger molecules, however, revealed that DFT methods tend to have significantly larger errors for larger structures. Hence, the errors with B3LYP for the G3 set are double those for the G2 set, and this error can be traced back to the additional larger molecules and

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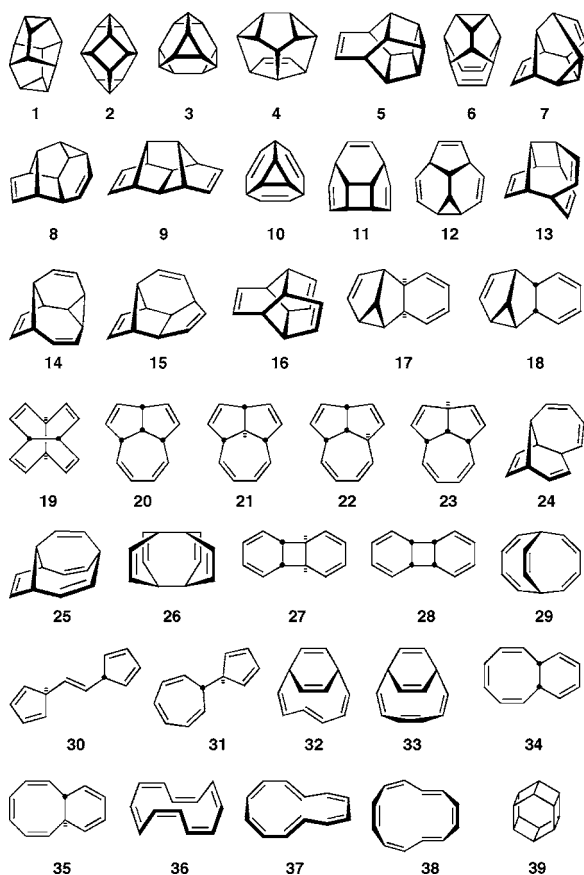
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**Figure 1.**

the fact that the DFT errors seem to be cumulative.<sup>5</sup> Similar trends have been observed recently for B3LYP reaction energies.<sup>6</sup>

Computing isomer energy differences is an easier task than estimating the heats of formation. If one considers unimolecular rearrangement transition structures as isomers of ground-state molecules, then the ability of a computational method to reproduce isomer energy differences also has implications for determining activation barriers of chemical reactions. As the number of reliable experimental activation barriers for larger molecules is rather limited, we concentrate here on hydrocarbon isomer energy differences.

For the (CH)<sub>12</sub> isomers, only **1**, **22**, and **31** are close in energy at the highest levels of theory that we had employed recently;<sup>1</sup> Table 1 presents the data for these (CH)<sub>12</sub> isomers utilizing different levels of theory (relative energies of all other species depicted in Figure 1 can be found in the Supporting Information). B3LYP<sup>7,8</sup> performs very poorly and shows a strong basis set dependence. It was noted earlier in the relative energy comparison of propyne and allene (propyne is 1.4 kcal mol<sup>-1</sup> more stable but most popular DFT

**Table 1.** Energies of (CH)<sub>12</sub> Isomers **22** and **31** Relative to Octahedrane (**1**) (kcal mol<sup>-1</sup>) ( $\Delta E$ )

level of theory	<b>22</b>	<b>31</b>
HF/6-31G(d)	6.9	13.8
HF/6-311+G(d)	0.1	6.1
HF/6-311+G(d,p)	2.5	9.4
BLYP/6-31+G(d)	-9.0	-10.9
BLYP/6-311+G(d,p)	-10.0	-11.5
BLYP/aug-cc-pVDZ	-8.4	-9.2
G96LYP/6-31+G(d)	-5.3	-6.5
G96LYP/aug-cc-pVDZ	-4.8	-4.9
G96LYP/6-311+G(d,p)	-6.4	-6.8
KMLYP/6-31G(d)	35.6	50.6
KMLYP/6-311+G(d,p)	28.4	41.7
B3LYP/6-31G(d)	4.5	7.2
B3LYP/6-31G(d,p)	4.3	7.2
B3LYP/6-31+G(d)	0.6	2.5
B3LYP/6-311+G(d,p)	-0.2	1.9
B3LYP/6-311++G(2d,p)//B3LYP/6-311+G(d,p)	-2.1	-0.2
B3LYP/aug-cc-pVDZ	0.4	3.1
B3LYP/cc-pVTZ//B3LYP/6-311+G(d,p)	-1.7	-0.4
B3PW91/6-31+G(d)	17.3	23.2
B3PW91/6-311+G(d,p)	14.4	19.8
B3PW91/6-311+G(d,p)//B3LYP/6-311+G(d,p)	17.3	23.7
B3PW91/aug-cc-pVDZ	16.8	23.5
BHandH/6-31+G(d)	33.0	46.8
BHandH/6-311+G(d,p)	32.6	47.3
BHandHLYP/6-31+G(d)	8.2	14.2
BHandHLYP/6-311+G(d,p)	7.4	14.0
MP2(fc)/6-31G(d)	23.0	30.0
MP2(full)/6-31G(d)	25.1	32.5
MP2(fc)/6-31G(d,p)	26.6	35.4
MP2(fc)/6-311+G(d,p)//B3LYP/6-311+G(d,p)	23.2	31.2
MP2(fc)/cc-pVDZ	21.9	28.6
MP2(fc)/aug-cc-pVDZ	21.6	29.1
CCSD(T)/cc-pVDZ//BLYP/6-31+G(d)	14.4	24.5
CCSD(T)/cc-pVDZ//BLYP/6-311+G(d,p)	14.6	24.7
CCSD(T)/cc-pVDZ//B3LYP/6-31+G(d)	14.9	25.0
CCSD(T)/cc-pVDZ//B3LYP/6-311+G(d,p)	15.3	25.5
CCSD(T)/cc-pVDZ//KMLYP/6-31+G(d)	14.5	24.6
CCSD(T)/cc-pVDZ//MP2(fc)/aug-cc-pVDZ	14.3	25.0

methods place allene energetically lower) that the HF exchange and associated problems with the self-interaction are responsible for the poor performance of B3LYP.<sup>9</sup> However, as BLYP<sup>7</sup> and G96LYP<sup>10</sup> perform even more poorly, this cannot be the only reason for the inferior performance of B3LYP. B3PW91<sup>11</sup> is best relative to the highest level coupled cluster {CCSD(T)}<sup>12</sup> energy single points. The latter theoretical level also indicates that the quality of the molecular *geometries* is acceptable and rather similar at B3LYP, BLYP, and MP2, even with different basis sets.

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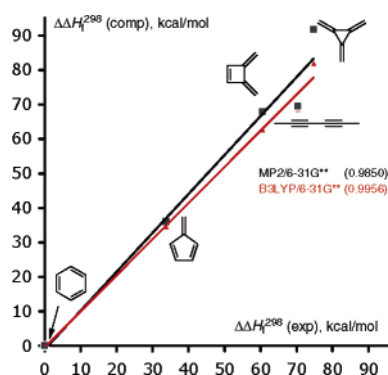
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Nevertheless, it is highly discomfiting to see that the various DFT flavors give such different isomer energy differences.

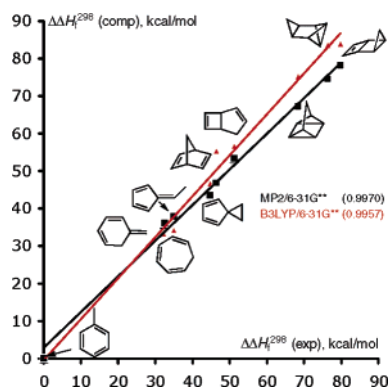
But how reliable is this assessment? As there are no experimental heats of formation available for the species under consideration, we systematically examined the isomers of  $C_6H_6$ ,  $C_7H_8$ ,  $C_8H_{10}$ ,  $C_9H_{12}$ ,  $C_{10}H_{10}$ ,  $C_{10}H_{14}$ , and  $C_{12}H_{16}$ . We compare two levels of theory (MP2 and B3LYP) with a moderate basis set {6-31G(d,p)} commonly used for larger hydrocarbons to the experimental isomer energy differences derived from the experimental heats of formation ( $\Delta_f H_{298}$ )<sup>13</sup> and compare these with the  $\Delta_f H_{298}$  data at the respective level of theory.

The  $(CH)_6$  isomer energy differences carry no surprises. B3LYP outperforms MP2 slightly, but the agreement of both with experiment is generally quite good (Figure 2, with



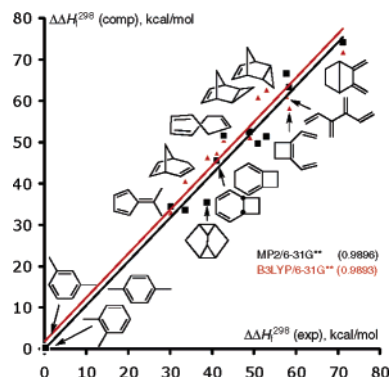
**Figure 2.** Computed  $C_6H_6$  isomer energy differences at B3LYP and MP2 versus experiment.

correlation coefficients in parentheses). However, this test set only contains structures with conjugated multiple bonds. The  $C_7H_8$  structures also offer more structural diversity, and  $\Delta_f H_{298}$ 's are also available for compounds with single bonds only (Figure 3). Here, MP2 begins to perform slightly better than B3LYP, and this can mainly be traced back to structures with single bonds only, for which the B3LYP errors are



**Figure 3.** Computed  $C_7H_8$  isomer energy differences at B3LYP and MP2 versus experiment.

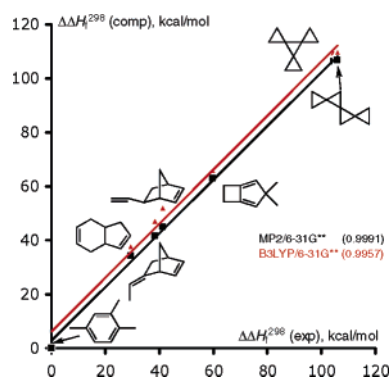
noticeably larger than for other species. This pattern and the finding that bicyclic structures are not described as well applies to the  $C_8H_{10}$  structures (Figure 4) as well. Here, the



**Figure 4.** Computed  $C_8H_{10}$  isomer energy differences at B3LYP and MP2 versus experiment.

maximum deviations at B3LYP ( $10.0 \text{ kcal mol}^{-1}$ ) and MP2 ( $8.6 \text{ kcal mol}^{-1}$ ) begin to be significantly different.

These findings recur for the isomers of  $C_9H_{12}$ ,  $C_{10}H_{10}$ ,  $C_{10}H_{14}$ , and  $C_{12}H_{16}$  (Figures 5–8), for which the B3LYP

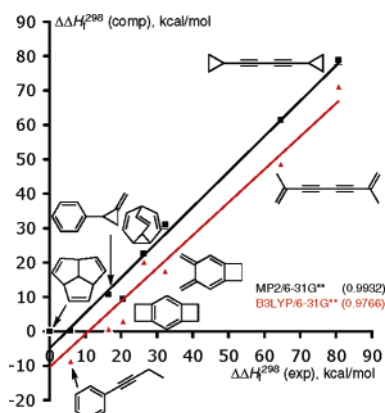


**Figure 5.** Computed  $C_8H_{12}$  isomer energy differences at B3LYP v and MP2 versus experiment.

errors *accumulate* as the molecules become larger. While this is also true for MP2, the effect is much smaller. B3LYP clearly has difficulties in describing structures with single bonds only and with bicyclic hydrocarbons. This is not the case for B3PW91; it outperforms B3LYP for the  $(CH)_{12}$  structures (Table 1). The B3PW91 errors for  $C_{10}H_{14}$  and  $C_{12}H_{16}$  are considerably smaller and more evenly spread than for B3LYP with the same basis set (Figures 7 and 8).

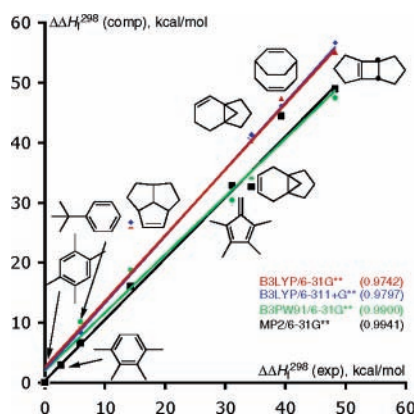
We now return to the question of *why* octahedrane (**1**) is the most stable  $(CH)_{12}$  hydrocarbon, despite its considerable strain. A straightforward explanation is that the strain originates mostly from the three-membered rings because

(13) Data taken from <http://webbook.nist.gov>.



**Figure 6.** Computed  $C_{10}C_{10}$  isomer energy differences at B3LYP and MP2 versus experiment.

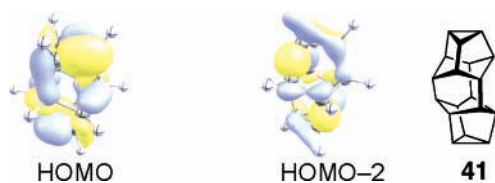
the five-membered rings are fixed in their preferred conformation, as is the central cyclohexane moiety. An MO analy-



**Figure 7.** Computed  $C_{10}H_{14}$  isomer energy differences at B3LYP, B3PW91, and MP2 versus experiment.

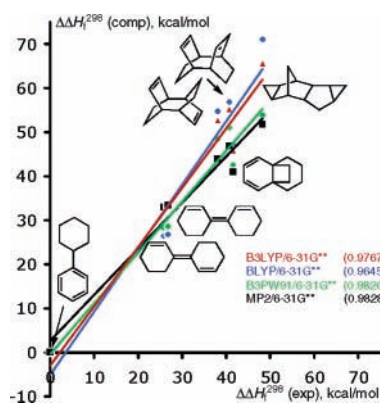
sis (Scheme 1) shows that the cyclopropane  $\sigma_{CC}$ -orbitals that comprise the HOMO of **1** significantly overlap with the

**Scheme 1.** Stabilizing MO Interactions in the High-Lying Orbitals (Only One of Each Degenerate MO is Shown) in **1**



$\sigma_{CC}$ -MOs of both the five- and the six-membered rings. The cyclopropyl  $p$ -type orbitals overlap with the MOs of corresponding size and symmetry in HOMO-2.

Our analysis allows the prediction of isomer energy differences for larger hydrocarbons. An intriguing example



**Figure 8.**  $C_{12}H_{16}$  isomer energy differences at B3LYP, BLYP, B3PW91, and MP2 with a 6-31G(d,p) basis set relative to experiment.

is the  $(CH)_{18}$  family of which [18]annulene (**40**) is the most popular; the symmetry of its ground-state equilibrium geometry is still under discussion.<sup>14</sup> Based on the stabilizing effect of three-membered rings as in **1**, we predict that the experimentally unknown analogue **41** ( $D_{3h}$ ) (Scheme 1) is considerably more stable ( $62.8 \text{ kcal mol}^{-1}$  at B3PW91/cc-pVDZ) than  $C_2$ -**40** and most if not all other  $(CH)_{18}$  isomers. Regarding the structure of **40**, CCSD(T)/cc-pVDZ energy single points for the MP2/cc-pVDZ  $C_2$ ,  $D_2$ , and  $D_{6h}$  geometries are the same within  $10^{-5}$  au ( $-694.63277$  au). The CCSD(T)/cc-pVDZ single point energies for the  $C_2$  and  $D_{6h}$  geometries optimized at KMLYP/cc-pVDZ are  $-694.61467$  au. Hence, the MP2 geometries are likely to be of higher quality.

DFT methods have to be applied with caution. B3LYP and several other popular functionals show *increasing* energy errors with *increasing* system size. We find that these errors are connected to the inferior DFT description of structures with single bonds only and those containing small rings. *Some* of these errors can systematically be traced back to the neglect of dispersion interactions in DFT, which are key for the energy evaluations of, e.g., alkanes. This is the topic of the accompanying paper by Schleyer et al.<sup>15</sup> The reasonably good performance of B3PW91, however, indicates that neglect of dispersion cannot be the only source of error.<sup>16</sup> Our recommendation is to use higher level, non-DFT energy single points on DFT- or MP2-optimized structures.

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**Supporting Information Available:** Tables of electronic total energies of all computed species. This material is available free of charge via the Internet at <http://pubs.acs.org>. OL0610486

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