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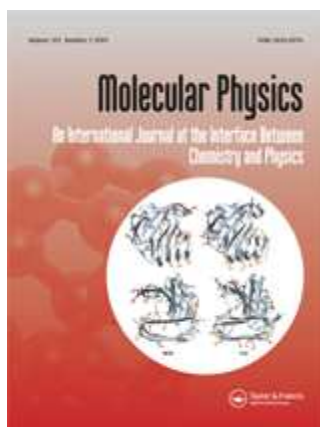
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<p>Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.</p> <p>bsr36-TMPH-2010-0229.tgz source files.zip</p>	

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RESEARCH ARTICLE

*Thermochemical benchmarking of hydrocarbon bond separation reaction energies: Jacob's ladder is not reversed!*Helge Krieg[†] and Stefan Grimme^{†,*}[†]*Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, D-48149 Münster, Germany**(9 June 2010; final version received xx xxxx 2010)*

We reinvestigate the performance of Kohn-Sham density functional (DF) methods for a thermochemical test set of bond separation reactions of alkanes (BSR36) published recently by Steinmann et al (J. Chem. Theory Comput. 2009, 5, 2950). According to our results, the tested approximations perform for this rather special benchmark as usual. We show that the choice of reference enthalpies plays a crucial role in the assessment. Due to the large stoichiometric factors involved, errors of various origin are strongly amplified. Inconsistent reference data are avoided by computing reference energies at the CCSD(T)/CBS level. These are compared to results for a variety of standard DFs. Two different versions of London dispersion corrections (DFT-D2 and DFT-D3) are applied and found to be very significant. The most accurate results are obtained with B2GPPLYP-D2 (MAD=0.4 kcal · mol⁻¹) B2PLYP-D2 (MAD=0.5 kcal · mol⁻¹) and B97-D2 (MAD=0.9 kcal · mol⁻¹) methods. Dispersion corrections not only improve the computed BSR energies but also diminish the accuracy differences between the DFs. The previous DFT-D2 version performs better due to error compensation of medium-range correlation effects between the semi-classical and the density-based description. We strongly recommend not to overinterpret results regarding DF accuracy when based on a single set of chemical reactions and to use high-level theoretical data for benchmarking purposes.

Keywords: Molecular quantum mechanics, thermochemical benchmarking, density functional theory, dispersion correction (DFT-D)

1. Introduction

Understanding non-covalent interactions and describing them accurately at reasonable computational cost represents an enormous step forward in computing properties of biomacromolecules like DNA and proteins. [1–6] London dispersion (also termed van der Waals, vdW) interactions [7, 8] are attractive forces that arise from fluctuations of the charge density due to the correlated motion of the electrons. Dispersion forces are ubiquitous even in the absence of charges or electric moments. In the non-overlapping regime, the energy of dispersion interactions decreases as R^{-6} with the distance R between the particles, whereas the counter-acting exchange repulsion decreases exponentially. Due to their non-local character and a fundamental contribution of excited states (virtual orbitals), dispersion interactions cannot be described accurately by current approximations in the framework of Kohn-Sham density functional theory (KS-DFT) [9, 10]. On the other hand, correlated wavefunction-based methods like MP2 [11], CCSD(T) [12] or fully correlated quantum-Monte-Carlo [13, 14] include these long-range interactions correctly.

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1 There exist very many and rather different approaches to correct the dispersion
2 problem in KS-DFT. [15–56] Our pragmatic ansatz for the problem was to add a
3 damped, atom pair-wise energy correction of the form $-C_6 \cdot R^{-6}$ to the standard
4 KS-DFT energy (DFT-D[41, 57]). Compared to previous approaches of similar
5 type, DFT-D is applicable with un-modified functionals in a standardized form
6 and therefore has meanwhile become a standard tool in quantum chemistry. Very
7 recently we published a basic revision of the correction termed DFT-D3[58] with
8 an emphasis on less empiricism, higher accuracy and a more clear separation of
9 long-range effects.

10
11 In recent years it has become clear that dispersion interactions significantly influ-
12 ence not only inter-molecular situations (non-covalently bound complexes) but also
13 the thermodynamic properties of isolated molecules. This has probably first been
14 demonstrated clearly for the isomerization energy of saturated hydrocarbons[59]
15 and the dimerization of aromatic molecules[60] for which standard (dispersion-
16 uncorrected) functionals like B3LYP fail miserably. Although one can of course
17 clearly distinguish between inter- and intra-molecular London dispersion inter-
18 actions, we prefer the terms long- and medium-range correlation (or dispersion)
19 effects[59] because the physical origin of the dispersion energy is basically the same.
20 This is in line with the view of Zhao and Truhlar who developed a series of density
21 functionals[61] that can account for large parts of the medium-range effects in the
22 overlapping regime.

23
24 Steinmann, Csonka and Corminboeuf (SCC)[55] have recently published a mod-
25 ification of DFT-D for generalized gradient approximation (GGA) functionals.
26 Rather unexpectedly, the authors found in special thermochemical tests (see be-
27 low) more accurate results for dispersion corrected GGA density functionals than
28 for more sophisticated ones that include higher amounts of non-locality (e.g. GGAs
29 performed better than hybrid functionals like e.g. B3LYP). Therefore the authors
30 pointed out an intriguing reversal of the performance ordering of density functionals
31 according to their theoretical sophistication (Perdew’s metaphoric view of Jacob’s
32 ladder [62]). The proposed method[55] is based on a pair-wise atomic dispersion po-
33 tential that is applied *a posteriori* in an additive manner, very similar to the DFT-D
34 schemes of Hobza and coworkers[24, 63] or to our methods. SCC try to separate
35 inter- and intra-molecular dispersion by a double-damping formula and the inclu-
36 sion of higher multipole-rank (R^{-8} , R^{-10}) terms. In addition to vdW complexes
37 it has been tested on four thermochemical benchmark sets: a modified version of
38 IDHC77[64] (the alkane folding reaction of $C_{30}H_{62}$ is excluded and the dimerization
39 of anthracene is added) and three test sets[65] consisting of isodesmic bond separa-
40 tion reactions (BSR)[66–68] of saturated hydrocarbons (corresponding to reaction
41 class two according to the nomenclature of Schleyer and coworkers[69]). The latter
42 three are subdivided into chains (H), rings (R) and cages (C) (for structures see
43 Fig. 1). SCC have chosen experimental molecular heat of formation reference values
44 taken from the NIST[70] database to derive experimental BSR enthalpies. These
45 were subsequently used to assess the performance of their double-damped disper-
46 sion correction formula in combination with several density functionals (see table
47 1 in Ref.[55]). The very good agreement of dispersion corrected and experimen-
48 tal reference values suggests that the proposed method recovers a high amount of
49 (intramolecular) dispersion energy. Remarkably (as already mentioned) SCC found
50 that a corrected GGA like their PBE-dD10 approach outperforms computationally
51 much more demanding hybrid- or double-hybrid methods.

52
53 We will show in this work that this unexpected ”reversal of Jacob’s ladder” is
54 partially rooted in an improper choice of reference values in conjunction with large
55 stoichiometric factors (up to 22) that can amplify individually small errors for the
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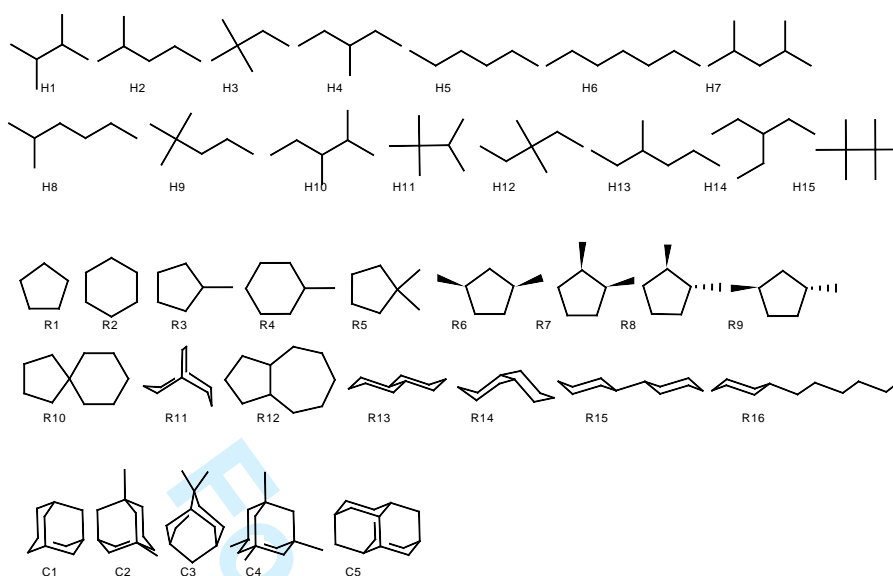


Figure 1. BSR36 test set of isodesmic bond separation reactions considered in this work. The set consists of saturated chains (H), rings (R) and cages (C)[65].

BSR significantly. In such cases, vibrational anharmonic effects, which are difficult to account for larger systems, also contribute. In one case we detected a huge deviation between theoretical and experimental data that is attributed to errors of the latter. We also provide a more consistent set of minimum energy conformer structures for all molecules in the set.

In order to avoid all the problems connected to experimental data we decided to compute *ab initio* reference values for the test sets C, H and R at the highest affordable level of theory (est. CCSD(T)/CBS). The combined set will be dubbed BSR36 from now on and is proposed as a special but important benchmark with a focus on medium-range electron correlation effects in saturated systems. It will become part of our general benchmark database GMTKN[71] with the long-term goal to provide a broad, consistent and meaningful standard meta-set of benchmarks for electronic structure methods.

We will further analyze the performance of a variety of density functionals for the computation of the 36 BSR energies and give answer to the main question if Jacob's ladder really is reversed here. Finally, the effect of standard (not specifically parameterized) dispersion corrections and the influence of medium-range correlations is discussed.

2. Computational methods

We computed the BSR energies at the CCSD(T) level in the estimated limit of a complete basis set (CBS). We employ in the calculations the approximate additivity relation between CCSD(T) and MP2 correlation energies which is based on the weak dependence of the $\Delta\text{CCSD(T)}$ term on the size of the one-particle basis set (Eq. 1). [72, 73]

$$E_{\text{large basis}}^{\text{CCSD(T)}} \approx E_{\text{large basis}}^{\text{MP2}} + \underbrace{(E_{\text{small basis}}^{\text{CCSD(T)}} - E_{\text{small basis}}^{\text{MP2}})}_{\Delta\text{CCSD(T)}} \quad (1)$$

The MP2 energies were extrapolated to the CBS (i.e., small basis=CBS in Eq. 1) by the two-point-scheme of Helgaker and coworkers[74]. Dunning's aug-ccpVXZ

(X=3,4) basis sets were used[75–79] in this step and the HF energies were taken from the X=4 calculation. The ORCA program[80–82] was applied for the coupled-cluster computations which employ the aug-cc-pVDZ basis sets. We performed the MP2 computations with the Turbomole program[83, 84] exploiting the resolution of the identity approximation (RI)[85] for the HF (RI-K[86]) as well as the MP2 part (RI-MP2[87]).

Inspection of the molecular structures used by SCC[88] reveals inconsistencies regarding the correct minimum conformation in some cases. Therefore we performed a full conformational analysis for each of the molecules. Starting geometries were generated with PCModel[89] and optimized at the force-field (MMX[90]) level. By the same software the conformational space was automatically screened by rotating every possible single bond and sorting out unfavorable conformations. The large number of resulting conformers was reduced by two subsequent steps. First, geometrically very similar structures were merged. Second, the conformational energy was estimated with the density functional based tight-binding method (SCC-DFTB+[91, 92]) and energetically high-lying conformers were rejected ($> 2 \text{ kcal} \cdot \text{mol}^{-1}$ above the lowest conformation). The first step was carried out via minimization of the root mean square deviation (RMSD) of the coordinates of every possible pair of conformers by rotating one conformer until maximum overlap between the two structures was reached. For RMSD values < 0.1 Bohr the structures were considered to be identical. In some cases quite close-lying conformational energies were verified by a B3LYP/TZVPP[76, 93–96] computation. These DFT computations did not change the energetic ordering predicted by SCC-DFTB+. The resulting most stable structure was re-optimized at the RI-MP2/cc-pVTZ level and finally used for the computation of the reference values as described above. All RI-MP2 optimizations were carried out with Turbomole. Matching auxiliary basis functions[97] were taken from the program's basis set library. The reader may refer to the supporting information or to our benchmark-related web page[98] for a complete listing of cartesian coordinates.

A variety of density functionals covering each rung was tested in comparison to the newly created BSR36 reference values, first rung (LDA): SVWN[96, 99], second rung (GGA): PBE[100], BP86[101, 102], BLYP[94, 102], B97-D[41], third-rung (meta-GGA): M06L[103], TPSS[104], fourth rung (hybrid (meta) GGA): PBE0[105], TPSSh[106, 107], B3LYP[93–96], B3LYP[94, 102, 108–110] M06-2X[48, 111], PW6B95[112], fifth rung (double-hybrid): B2PLYP[64], B2GPPLYP[113], mPW2PLYP[114]. The same cc-pVTZ/MP2 structures as for the reference energies were employed. The computations for SVWN, PBE, TPSS, BP86, BLYP, B97-D, PBE0, TPSSh, B3LYP, B3LYP, PW6B95 and B2PLYP were performed with Turbomole 6.0 and sped up via the RI-J[115] and (in case of the hybrid functionals) by RI-K. The RI approximation was exploited for the computation of the MP2 part within the B2PLYP functional as well. The computations employing M06L and M06-2X were performed with NWChem[116, 117]. ORCA was applied for the two double-hybrid functionals mPW2PLYP and B2GPPLYP.

All DFT computations were carried out with Ahlrich's quadruple- ζ basis set including (3d2f1g/3d2p1f) sets of polarization functions (QZVP[118, 119]) which gives results very close to the Kohn-Sham limit. Weigend's optimized *def2*-auxiliary basis sets[120] were applied for coulomb fitting, as well as his auxiliary basis sets for exchange fitting[121] and in case of B2PLYP Hättig's optimized auxiliary basis sets of quadruple- ζ quality[122] were used for the RI-MP2 part of the Turbomole calculations. The grids m4, ultrafine, xfine and grid5 were used for the numerical integration within the Turbomole, Gaussian, NWChem and Orca computations.

In order to compare our results with experimental data, zero-point vibrational

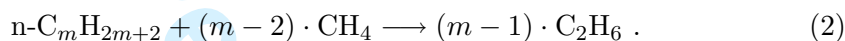
1 energy (ZPVE) as well as the thermal contributions to the BSR enthalpy within
2 the harmonic approximation were calculated using SNF[123]. This is in all cases
3 based on the single conformation with minimum energy in accordance with the
4 procedure of SCC. These corrections to standard enthalpies were computed at the
5 PBE/def2-TZVPP level.

6
7 We corrected the results for the density functionals PBE, BP86, BLYP, TPSS,
8 M06L, M06-2X, PBE0, TPSSh, B3LYP, BHLYP, PW6B95, mPW2PLYP, B2PLYP
9 and B2GP-PLYP for London dispersion contributions using the second version
10 of DFT-D[41] (see supporting information for a complete list of the applied s_6
11 scaling parameters). Results with our new scheme[58] are labeled DFT-D3 (or "-
12 D3" appended to a functional name) while the old version is dubbed DFT-D2 (or
13 similar as above appended as "-D2").
14

15 16 17 3. Results and discussion

18 19 3.1. Problems related to the choice and accuracy of reference data

20 An isodesmic reaction of class two satisfies the following generalized scheme for
21 linear and branched saturated hydrocarbons
22



24
25
26 In the reaction one transforms one larger and many small molecules to only many
27 small molecules which resembles an atomization process but without the problem
28 of an appropriate theoretical description of open-shell compared to closed-shell
29 molecules. With regard of testing intramolecular dispersion effects the reaction
30 scheme has been well chosen because the corresponding energies are absolutely
31 larger on the left side of the reaction equation simply due to the size of the
32 molecules.
33

34 The main problem in our context is the potentially many equivalents of methane
35 and ethane involved. The maximum values are 22 CH_4 and 18 C_2H_6 molecules
36 that are needed for the isodesmic transformation of diadamantane (reaction C5).
37 At least 4(5) equivalents of methane (ethane) enter the equation for the smaller
38 structures in the BSR36 test set. Due to these large stoichiometric factors any error
39 in the experimental measurement of the heats of formation of methane and ethane
40 is accumulated which in turn leads to large uncertainties for the experimental BSR
41 enthalpies. An extreme example is reaction C5. For the (latest) reported values,
42 the error limits are ± 0.07 , ± 0.10 and $\pm 0.58 \text{ kcal} \cdot \text{mol}^{-1}$ for methane, ethane and
43 diadamantane, respectively. Using these values we calculate an unacceptably large
44 total uncertainty of the BSR enthalpy of $\pm 3.92 \text{ kcal} \cdot \text{mol}^{-1}$.
45

46 Martin and coworkers recently published a thorough investigation of saturated
47 hydrocarbon thermochemistry [124, 125]. We use their data in order to estimate
48 how large theoretically non-trivial contributions to the BSR enthalpy can be. Be-
49 side the standard thermal contributions of vibrations and rotations to the enthalpy
50 (RRHO approximation), the existence of different thermally populated conforma-
51 tions must not be neglected. For n -hexane (n -octane) these authors reported a
52 conformational contribution to the enthalpy by the 12 (96) considered conformers
53 of 0.68 (1.08) $\text{kcal} \cdot \text{mol}^{-1}$ [124]. Because there is no conformational contribution in
54 ethane and methane the effect never cancels. Thus, aiming at chemical accuracy (1
55 $\text{kcal} \cdot \text{mol}^{-1}$) in comparison to experimental BSR enthalpies would require a huge
56 computational effort for the more flexible systems in the set. This problem could
57 be avoided by just eliminating all flexible systems but there are further factors also
58
59
60

1 for the rigid structures to consider.

2 The ZPVE and thermal RRHO corrections to the BSR enthalpy are also prob-
3 lematic again due to the large factors involved. The values are e.g. 1.78, 2.22 and
4 20.57 kcal · mol⁻¹ for the ZPVE plus RRHO correction to the BSR enthalpy of
5 *n*-hexane, *n*-heptane and diadamantane corresponding to 17%, 17% and 30% of
6 the total values which again is substantial.

7 Martin and coworkers also estimated the contribution of anharmonicity to the
8 ZPVE of organic systems containing many hydrogens to be in the order of 1 kcal ·
9 mol⁻¹ [125]. Anharmonic effects give additional contributions of 0.17, 0.41 and
10 0.51 kcal · mol⁻¹ compared to the ZPVE plus RRHO values of methane, ethane
11 and propane. Thus, even for the BSR enthalpy of propane (which is the smallest
12 possible reactant that can undergo the investigated BSR scheme) the account of
13 anharmonic vibrational corrections yields 0.14 kcal · mol⁻¹ for the BSR enthalpy
14 [125, 126]. From this value one can easily estimate corresponding contributions for
15 the larger systems in BSR36 of > 1 kcal · mol⁻¹.

16 Higher-order contributions to the energy stemming from inner shell and core-
17 valence correlation, relativistic effects, spin-orbit coupling and the diagonal Born-
18 Oppenheimer correction cancel effectively in the BSR (estimated for *n*-heptane to
19 be all < 0.1 kcal · mol⁻¹).

20 But even if an accurate calculation of all of the above mentioned terms is com-
21 putationally feasible, would this yield a meaningful comparison of theoretical and
22 experimental data? As demonstrated below the answer is no. We collected all
23 currently available experimental standard formation enthalpies ($\Delta H_{f,298}$) for the
24 structures in the BSR36 test set from the NIST database and identified the up-
25 per ($\Delta H_{298,NIST}^{upper}$) and lower ($\Delta H_{298,NIST}^{lower}$) values. These were derived from the low-
26 est/highest entries including experimental error bars. We also calculated their mean
27 ($\Delta H_{298,NIST}^{mean}$) and separately considered only the latest experiments ($\Delta H_{298,NIST}^{latest}$).

28 The table 1 presents these data together with the values used by SCC (ΔH_{298}^{SCC}),
29 our best theoretical (CCSD(T)/CBS) energies ($\Delta E^{theo.}$) and the same values in-
30 cluding harmonic vibrational corrections to enthalpies ($\Delta H_{298}^{theo.,harm.}$)

31 From comparison of the experimental values in the first four columns one can
32 conclude that the use of experimental reference values makes no sense here. The
33 difference between the upper and lower values is often on the order of 2-3 kcal ·
34 mol⁻¹ and in about 20% of the cases it is > 5 kcal · mol⁻¹. Even if one compares only
35 mean and latest values, the uncertainties are 1 kcal · mol⁻¹ on average. This is far
36 too large to benchmark theoretical methods that inherently have a similar accuracy
37 for the considered property. Inspection of table 1 also indicates that SCC seemed
38 to choose the latest published experimental values. However, we find differences
39 on the order of 0.1-0.2 kcal · mol⁻¹ (0.7 kcal · mol⁻¹ on average) between the
40 numbers we took from the NIST database strictly selecting the latest published
41 one and those used by SCC. A comparison of the differences between latest and
42 mean experimental with harmonically corrected CCSD(T)/CBS enthalpy values is
43 shown in Fig. 2. The MADs are 1.2 and 1.6 kcal · mol⁻¹ (1.0 and 1.4 kcal · mol⁻¹
44 without entry C2, see below) for mean and latest references, respectively, which
45 is considered as being large keeping in mind that the CCSD(T)/CBS level for
46 electronically relatively simple alkanes should yield electronic BSR energies with
47 errors smaller than about 0.5 kcal · mol⁻¹. Based on the above arguments we
48 attribute the deviation between theory and experiment to a) the limitation of
49 the harmonic approximation for the computation of the vibrational contributions
50 and b) to the neglect of thermal population of other conformers. The first point
51 seems to be of particular importance here because the product of the BSR (ethane)
52 contains a hindered rotational degree of freedom which might be problematic in a

Table 1. Comparison of different approaches to compute experimental reference values for the BSR based on the NIST database entries. $\Delta H_{298,NIST}^{lower}$ is the BSR enthalpy computed from the lowest published experimental values and $\Delta H_{298,NIST}^{upper}$ gives the upper bound, respectively. $\Delta H_{298,NIST}^{mean}$ is the arithmetic mean of all available NIST values. $\Delta H_{298,NIST}^{latest}$ corresponds to the latest experimental entry. Reported experimental errors are not included. ΔH_{298}^{SCC} refers to the experimental reference values used by SCC[55]. $\Delta E^{theo.}$ is the reference BSR energy computed in this work at the CCSD(T)/CBS level which has been corrected theoretically (RRHO) yielding $\Delta H_{298}^{theo.,harm.}$. All values are given in $\text{kcal} \cdot \text{mol}^{-1}$.

reaction	$\Delta H_{298,NIST}^{lower}$	$\Delta H_{298,NIST}^{upper}$	$\Delta H_{298,NIST}^{mean}$	$\Delta H_{298,NIST}^{latest}$	ΔH_{298}^{SCC}	$\Delta H_{298}^{theo.,harm.}$	$\Delta E^{theo.}$
H1	12.8	11.9	13.2	13.7	13.9	12.1	9.8
H2	18.9	11.0	15.9	12.9	13.0	11.7	9.7
H3	14.6	13.7	15.0	15.6	15.7	13.9	11.4
H4	11.3	10.4	11.7	12.2	12.4	11.1	9.0
H5	10.2	9.4	10.6	11.2	11.3	10.5	8.7
H6	12.9	11.7	13.4	13.9	14.1	13.1	10.9
H7	16.7	15.1	17.0	17.3	17.5	15.9	13.1
H8	14.6	13.3	15.1	15.6	15.8	14.4	11.9
H9	17.7	16.0	18.0	18.3	18.5	16.5	13.5
H10	15.6	14.3	15.9	16.6	16.8	14.1	11.4
H11	16.9	15.7	17.4	18.0	18.2	16.1	13.0
H12	16.9	15.0	17.0	17.2	17.4	15.7	12.8
H13	13.9	12.7	14.4	15.0	15.2	13.7	11.2
H14	13.4	12.1	13.9	14.3	14.6	12.6	10.2
H15	19.7	17.9	20.1	20.9	21.1	19.0	15.1
R1	6.7	5.0	6.8	7.3	7.5	6.4	2.4
R2	15.4	13.5	15.7	16.6	16.5	15.0	10.7
R3	11.5	9.6	11.7	12.1	12.6	11.2	6.3
R4	21.4	18.4	21.4	21.6	21.9	20.0	14.9
R5	16.6	14.4	16.9	17.7	18.0	16.4	10.6
R6	15.5	13.2	15.8	16.5	16.9	15.7	10.1
R7	14.5	12.3	14.8	15.6	15.9	14.6	9.1
R8	16.2	14.0	16.5	17.3	17.6	16.1	10.5
R9	16.0	13.8	16.3	17.1	17.4	15.4	9.8
R10	26.8	22.6	27.1	28.3	28.9	28.9	19.3
R11	18.7	12.0	17.7	18.9	19.5	18.5	9.7
R12	23.6	18.7	23.5	24.7	25.3	24.5	15.2
R13	35.7	31.5	35.7	37.1	37.8	35.4	26.0
R14	32.6	28.4	32.9	34.1	34.7	32.6	23.4
R15	39.7	34.7	39.6	41.4	42.1	38.0	28.0
R16	32.5	28.9	33.1	34.4	35.0	32.7	25.4
C1	40.3	33.0	40.0	41.3	42.1	40.0	27.6
C2	44.7	38.1	44.3	45.8	58.0	54.0	39.6
C3	46.8	40.9	46.9	48.5	49.4	46.3	32.4
C4	69.0	58.3	66.9	70.9	69.4	68.0	51.4
C5	64.2	56.3	64.4	66.5	67.7	67.6	47.1

harmonic ZPVE calculation. As mentioned above this already for propane yields a contribution of $0.14 \text{ kcal} \cdot \text{mol}^{-1}$. The reaction C2 deserves a special comment. The observed huge deviation of about $10 \text{ kcal} \cdot \text{mol}^{-1}$ can not be explained by the arguments given above. Note that the structurally very similar systems C1,C3-C5 are very well described at the CCSD(T)/CBS level. We attribute the discrepancy to an experimental problem and note in passing that the experimental value given by SCC of $58 \text{ kcal} \cdot \text{mol}^{-1}$ can not be verified by us.

The error due to effect a) as mentioned above should multiply with an increasing number of equivalents of methane and ethane entering the equation. However, neither inspection of Fig. 2 (in which the molecules are approximately ordered according to size) nor analysis of the subsets (H set: $\text{MAD}(\Delta H_{298}^{theo.,harm.} - \Delta H_{298,NIST}^{latest}) = 1.5 \text{ kcal} \cdot \text{mol}^{-1}$ R set: $\text{MAD}(\Delta H_{298}^{theo.,harm.} - \Delta H_{298,NIST}^{latest}) = 1.3 \text{ kcal} \cdot \text{mol}^{-1}$ C set: $\text{MAD}(\Delta H_{298}^{theo.,harm.} - \Delta H_{298,NIST}^{latest}) = 1.9 \text{ kcal} \cdot \text{mol}^{-1}$, excluding C2) really supports this assumption. For the H and R sets the deviations between best ex-

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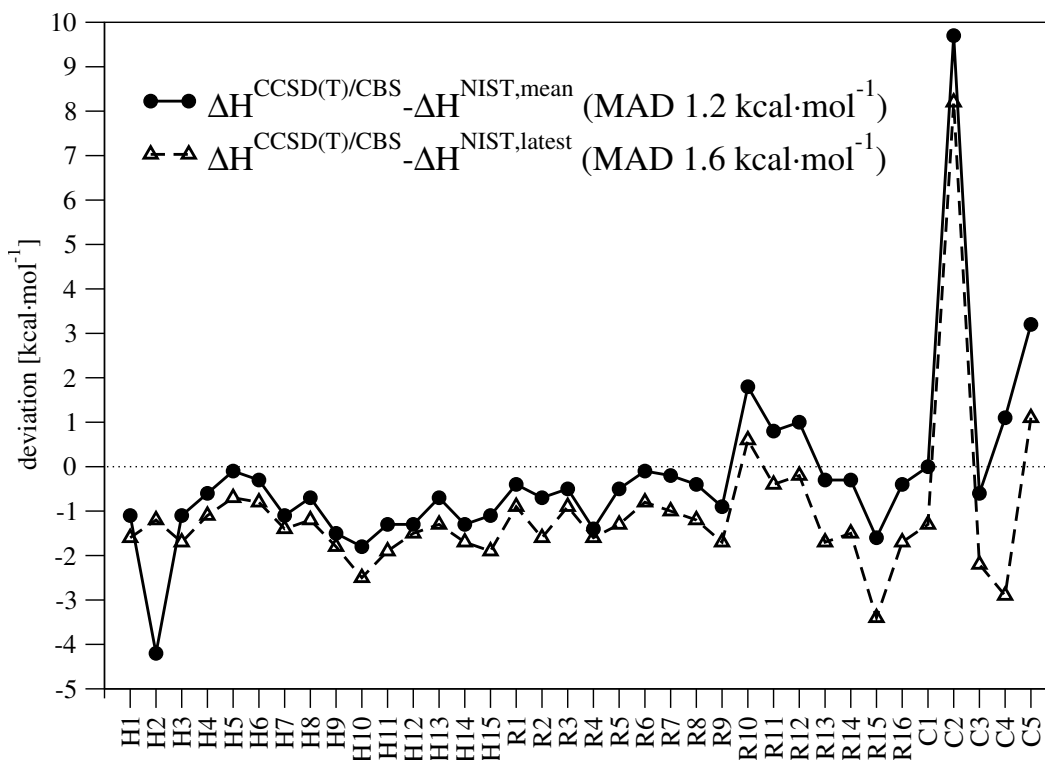


Figure 2. Deviation between experimental and theoretical BSR enthalpies. The lines are just drawn to guide the eye.

perimental and theoretical values seems to be rather systematic (the theoretical BSR enthalpy is mostly too small, cf. MAD=1.4 vs. signed mean deviation of 1.3 kcal·mol⁻¹). The only remaining explanation are condensed phase effects because many of the molecules have been measured as liquids (due to low vapor pressure) and the values have then subsequently been corrected by phase change data.

In any case we are very sure that our CCSD(T)/CBS BSR *energy* values are accurate to about 0.5 kcal·mol⁻¹ which is sufficient to meaningfully benchmark contemporary density functionals. Considering all the above mentioned problems we strongly recommend the use of such values in favor of experimental enthalpies. The experimental reference values used by SCC are definitely not accurate enough for the desired purpose and the mentioned theoretical issues put serious doubt if the previous assessment had a solid numerical basis.

3.2. Is Jacob's ladder reversed for BSR36?

The table 2 presents the MADs with respect to the new theoretical reference values ($\text{MAD}(\Delta E^{\text{DFT}} - \Delta E^{\text{theo.}})$) for all tested functionals. The corresponding values including RRHO corrections to enthalpy and with respect to the experimental data used by SCC are included as well ($\text{MAD}(\Delta H_{298}^{\text{DFT}} - \Delta H_{298}^{\text{SCC}})$). The reader may refer to the supporting information for detailed results of the different density functionals. The figure 3 presents a graphical plot of the same data with the functionals sorted by increasing accuracy. The MAD values based on CCSD(T) reference energies for the tested methods span a rather large range from about 0.5 to 12 kcal·mol⁻¹. The average BSR energy is 16.7 kcal·mol⁻¹. Dispersion uncorrected functionals are in all cases significantly less accurate. The averaged MAD over all methods is 4.7 kcal·mol⁻¹ and 7.5 kcal·mol⁻¹, respectively, with and without D3-dispersion correction. The older DFT-D2 version performs better than the new one (averaged MAD of 1.7 kcal·mol⁻¹) which is discussed further below. Overall,

Table 2. Comparison of mean absolute deviations (MAD in $\text{kcal} \cdot \text{mol}^{-1}$) of DFT methods from reference energies computed in this work ($\text{MAD}(\Delta E^{\text{DFT}} - \Delta E^{\text{theo.}})$) and from experimental reference values used by SCC ($\text{MAD}(\Delta H_{298}^{\text{DFT}} - \Delta H_{298}^{\text{SCC}})$).

rung	DF	$\text{MAD}(\Delta E^{\text{DFT}} - \Delta E^{\text{theo.}})$	$\text{MAD}(\Delta H_{298}^{\text{DFT}} - \Delta H_{298}^{\text{SCC}})$
1	SVWN	1.76	2.06
2	PBE	8.17	9.90
	PBE-D2	1.24	2.64
	PBE-D3	4.78	6.50
	BP86	8.95	10.67
	BP86-D2	1.26	0.95
	BP86-D3	3.01	4.73
	BLYP	12.09	13.81
	BLYP-D2	1.21	2.26
	BLYP-D3	5.85	7.57
	B97-D2	0.94	2.48
	B97-D3	6.15	7.87
3	M06-L	6.19	7.91
	M06-L-D2	4.26	5.98
	M06-L-D3	5.63	7.36
	TPSS	10.70	12.42
	TPSS-D2	1.23	2.74
	TPSS-D3	6.18	7.90
4	PBE0	8.13	9.86
	PBE0-D2	2.33	4.05
	PBE0-D3	4.58	6.30
	TPSSH	10.48	12.20
	TPSSH-D2	1.77	3.49
	TPSSH-D3	6.03	7.75
	B3LYP	11.25	12.97
	B3LYP-D2	1.52	2.81
	B3LYP-D3	5.93	7.65
	BH-LYP	10.84	12.56
	BH-LYP-D2	3.10	4.82
	BH-LYP-D3	6.53	8.25
	M06-2X	3.56	5.28
	M06-2X-D2	2.98	4.70
	M06-2X-D3	3.09	4.81
	PW6B95	6.63	8.36
	PW6B95-D2	1.79	3.52
	PW6B95-D3	4.08	5.80
5	mPW2PLYP	5.40	7.13
	mPW2PLYP-D2	1.53	3.25
	B2PLYP	5.28	7.00
	B2PLYP-D2	0.52	1.68
	B2PLYP-D3	2.45	4.17
	B2GP-PLYP	3.69	5.42
	B2GP-PLYP-D2	0.43	1.54
	B2GP-PLYP-D3	1.66	3.38
1	AVG ^a	1.8	2.1
2	AVG ^a	9.7	11.5
3	AVG ^a	8.4	10.2
4	AVG ^a	8.5	10.2
5	AVG ^a	4.8	6.5
2	AVG-D2 ^b	1.2	2.1
3	AVG-D2 ^b	2.7	4.4
4	AVG-D2 ^b	2.2	3.9
5	AVG-D2 ^b	0.8	2.2
2	AVG-D3 ^c	4.9	6.7
3	AVG-D3 ^c	5.9	7.6
4	AVG-D3 ^c	5.0	6.8
5	AVG-D3 ^c	2.1	3.8

^a AVG is the arithmetic mean calculated from the MAD values of the DFs belonging to the corresponding rung. ^b AVG-D2 is calculated from the MAD values of DFT-D2 corrected DFs only. ^c same as ^b but using DFT-D3.

the most accurate method is B2GP-PLYP-D2 ($\text{MAD}=0.43 \text{ kcal} \cdot \text{mol}^{-1}$) followed by B2PLYP-D2 ($\text{MAD}=0.52 \text{ kcal} \cdot \text{mol}^{-1}$) and B97-D2 ($\text{MAD}=0.94 \text{ kcal} \cdot \text{mol}^{-1}$). Other good performers are PBE-D2, TPSS-D2 and BP86-D2. Uncorrected BLYP and B3LYP provide the worst results with MAD values of 11-12 $\text{kcal} \cdot \text{mol}^{-1}$. In general we observe that the pronounced differences in performance of the functionals diminish very strongly in the corresponding "-D2/3" version. The error seems not to be related to the amount of Fock-exchange in the functional. Uncorrected DF that are more "medium-range" attractive like the M06 family, PBE, or B2PLYP perform better than other more "repulsive" approximations.

As can be seen from table 2, our data do not support the conclusion of SCC that lower-rung functionals perform better than theoretically more sophisticated ones. We investigate this by averaging the MAD values over all functionals in one rung of the ladder (AVG values). When the AVG is derived from $\text{MAD}(\Delta E^{\text{DFT}} - \Delta E^{\text{theo.}})$ data one finds, $9.7 > 8.4 \approx 8.5 > 4.8 \text{ kcal}$ for dispersion uncorrected rungs 2-5. When BSR energies are compared with the corresponding enthalpies

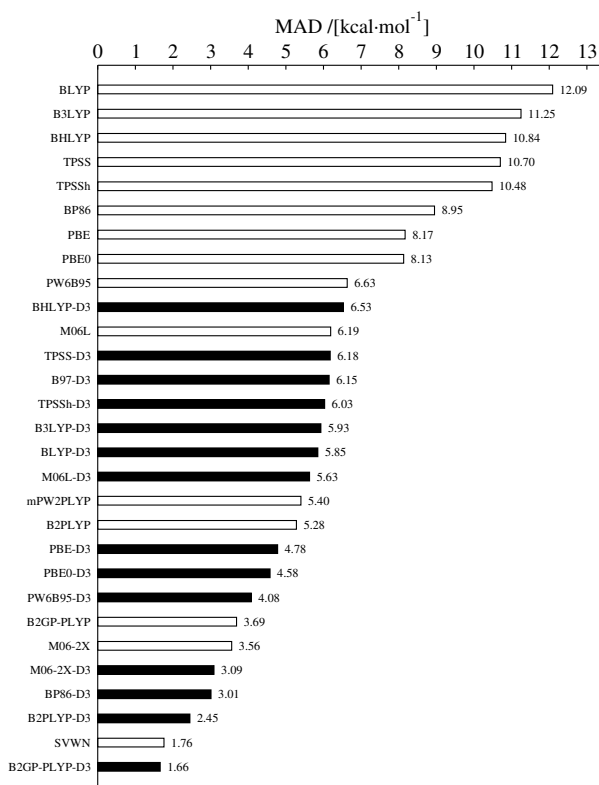


Figure 3. Mean absolute deviations (MAD) of DFT methods from CCSD(T)/CBS reference energies computed in this work.

(data not shown) the AVG values are about twice as large but the "normal" order of functionals does not change. The only exception to this general finding is at the lowest LDA level. Uncorrected SVWN yields a very small MAD of $1.8 \text{ kcal} \cdot \text{mol}^{-1}$ which is attributed to a fortuitous error cancellation between its well-known overbinding tendency and the missing "true" dispersion effects. Comparably small errors of SVWN for BSR have been observed before. [127] By correction of the DFT energies for intramolecular dispersion contributions the MAD values drop significantly. Note that these corrections make no sense at the LDA level and hence only rungs 2-5 are considered further. At both DFT-D levels, we observe a partial reversal of the ladder. The meta- and (meta)hybrid-GGAs perform worse than GGAs (AVG-D2 values are $1.2 < 2.7 > 2.2 \text{ kcal} \cdot \text{mol}^{-1}$ for the rungs 2-4) although the effect is not very pronounced and occurs at a rather low (accurate) level. As expected the additional account for non-locality and the inclusion of virtual orbitals leads to the most accurate results at the double-hybrid level (AVG values of 0.8 and $2.1 \text{ kcal} \cdot \text{mol}^{-1}$ for DFT-D2 and DFT-D3, respectively) which disagrees with the conclusion of SCC. Most importantly, rungs 3, 4, and 5 do not change their (decreasing) ordering at the DFT-D levels. We also tested the hypothesis if a many electron self interaction error (also termed delocalization error [128]) is important here. The admixture of 10%, 25% and 50% non-local Fock-exchange in TPSSh, PBE0 and BHLYP lowers the MAD values compared to their corresponding semi-local GGAs by only 2%, 0.5% and 10% which is negligible compared to the lowerings of several hundred percent due to DFT-D.

We obtain a different picture when the ranking of the AVG values is based on the experimental reference data used by SCC ($\text{MAD}(\Delta H_{298}^{\text{DFT}} - \Delta H_{298}^{\text{SCC}})$). In this way the GGA functionals become clearly most accurate and also the conclusion regarding the higher rungs changes to $2 > 5 > 4 > 3$ at the D2 level. With DFT-D3 no contradiction to the CCSD(T) energy based conclusion is observed. This shows

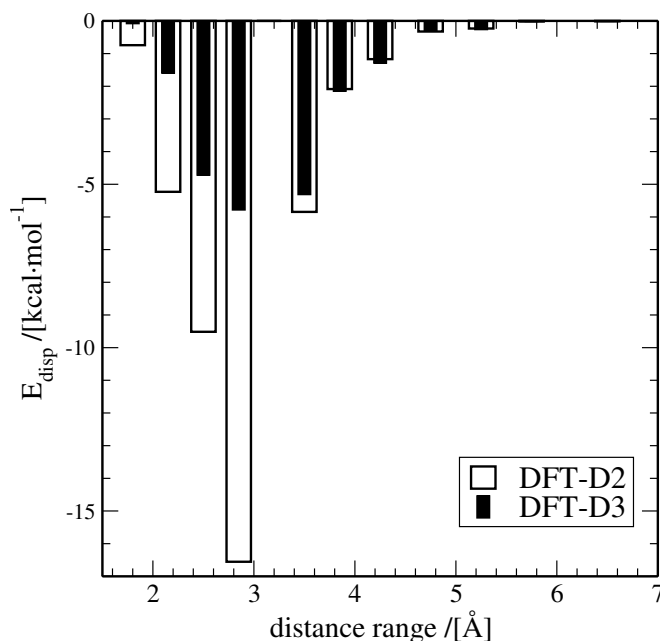


Figure 4. Range separated TPSS-D dispersion energies for diadamantane (reaction C5) as an example ($s_6 = 1$ in DFT-D2) with bin widths of 0.3-1.0Å. The bar is always placed in the middle of the considered interval and the left most one includes all contributions $<2\text{\AA}$.

how sensitive the final conclusions are with respect to the choice of reference data and the details of the dispersion correction. This is further supported by the results of an analysis when e.g. mean, latest, upper or lower NIST experimental values are used as reference for which we obtain $5 > 2 > 4 > 3$, $2 > 5 > 4 > 3$, $4 > 3 > 5 > 2$ and $5 > 2 > 4 > 3$, respectively. Essentially one can produce any "rung-ordering" by a choice of particular set of experimental reference data.

Finally we want to comment on the at first sight unpleasant finding that our new D3-correction performs worse than DFT-D2. According to the very many benchmarks given in Ref.[58], DFT-D3 is clearly superior for almost all typical non-covalent interaction energies either being of inter- or intra-molecular origin. Regarding the thermochemistry that is considered here we already observed similar (but much smaller effects) in preliminary "organic" benchmarks presented in Ref.[58]. The effect seems to be most pronounced to carbon-rich molecules and is related to a somewhat different description of the medium-distance range effects in the two versions. DFT-D3 more strictly separates long- and short-range correlation effects and yields usually smaller corrections for short inter-atomic distances. This is shown for the example of diadamantane (reaction C5) in Fig. 4. The range separated dispersion energies given for TPSS as an example in Fig. 4 show that the long-range description is very similar in both approaches. For inter-atomic distances smaller than about 3Å (which is the typical range for medium-range correlation of carbon; organic chemists call this region "1,3-interactions") DFT-D2 provides more than twice of intra-molecular dispersion energy. This quantity is missing in many approximate density functionals especially those based on B88 exchange which is known to be too repulsive at short distances (see e.g. recent work of Becke on this topic[129]). This part is effectively simulated by the DFT-D2 scheme but taken out of DFT-D3. We meanwhile think that such a sharper separation is physically more sound and propose as a solution to the problem the specific adaption of functionals to DFT-D3. Of course, for a single benchmark set as BSR36 a freely parameterized dispersion correction can be used to empirically cut down the error of any density functional close to zero. This, however, does not yield in our opinion any reasonable progress or understanding.

4. Summary

We have shown in this work that for a test set of 36 bond separation reactions of saturated hydrocarbons, a variety of standard as well as dispersion-corrected functionals perform more or less as expected. Hybrid or double-hybrid functionals perform mostly better than GGAs or meta-GGAs. The problematic part of the property tested in this benchmark set is basically the change of the medium-range correlation energy in localized, non-polar covalent bonds by spatial reorganization. This type of electron correlation problem is ubiquitous in chemistry.

We find no indications that a delocalization-type error as proposed recently in similar cases[130] plays a role here. This view is supported by the observation that a) dispersion uncorrected DF which are more "medium-range" attractive like the M06 family, PBE or B2PLYP perform better than other more "repulsive" approximations and b) there is no correlation of the performance of hybrid functionals with the amount of Fock-exchange. Instead the results are sensitive on how truly long-range and more short-range effects are handled by the density functional and an appropriate dispersion correction.

Although the older DFT-D2 version performs better than its recently revised version for this property, we can not recommend the use of the older version in general. The seemingly better results are not obtained for the right answer and many other non-covalent problems are better with DFT-D3 than with DFT-D2. In our opinion one should restrict the range of the atom-pair wise non-electronic terms more to the long-range regime as in DFT-D3 and handle the medium-range correlation by the density functional. This requires an adjustment in particular of the gradient enhancement factors.

Another outcome of the present study is the importance of a proper choice of reference energies (enthalpies). The experimental values are strongly contaminated by inconsistent data, thermal as well as anharmonic effects and can not be recommended when the focus is on methods with about 1-2 kcal · mol⁻¹ accuracy on average. Therefore we computed *ab initio* reference values based on the CCSD(T) method in the estimated limit of an infinite basis set (CCSD(T)/CBS) and propose these for future use in this thermochemical benchmark set.

Our work represents a clear example that contemporary quantum chemical methods can validate experimental data opposed to the reverse process in the early days of theory. This was perfectly foreseen by Prof. H. F. Schaefer III[131] to whom this work is dedicated.

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Supporting information available

The electronic supporting information contains:

- BSR energies of all tested density functionals.
- parameters for the dispersion correction of the density functionals.
- Thermal corrections to BSR enthalpies.
- Cartesian coordinates of the molecules included in the BSR36 test set.

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Supporting information

Thermochemical benchmarking of hydrocarbon bond separation reaction energies: Jacob's ladder is not reversed!

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The supporting information contains:

- BSR energies of all tested density functionals (tables SI1 and SI2).
- Values of the thermal correction of vibrations to the enthalpy (table SI2).
- Parameters for the dispersion correction of the density functionals (table SI3).
- Coordinates of the molecules included in the BSR36 test set (listing 1).

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Table S11 - DFT results^a for the BSR36 test set of bond separation reactions in kcal · mol⁻¹. All DFT computations with the (def2-)QZVPP basis set.

Name	SVWN		PBE		BP86			BLYP			B97-D		M06-L			TPSS			PBE0		
	KS	KS	D2	D3	KS	D2	D3	KS	D2	D3	D2	D3	KS	D2	D3	KS	D2	D3	KS	D2	D3
H1	11.71	4.42	10.29	7.26	3.16	11.37	8.38	1.26	10.65	6.81	10.04	6.77	6.48	8.05	6.81	2.15	9.97	6.03	4.45	9.15	7.44
H2	11.11	5.54	9.85	7.71	4.50	10.54	8.48	3.17	10.07	7.40	9.62	7.25	6.29	7.44	6.60	3.52	9.27	6.48	5.50	8.95	7.79
H3	13.20	5.36	11.55	8.34	4.02	12.67	9.57	1.96	11.85	7.87	11.24	7.86	7.41	9.06	7.73	2.94	11.19	7.05	5.46	10.41	8.61
H4	10.79	4.65	9.47	6.99	3.56	10.31	7.84	2.01	9.73	6.56	9.21	6.46	5.96	7.25	6.28	2.60	9.03	5.79	4.62	8.48	7.09
H5	9.69	5.65	8.71	7.27	4.84	9.12	7.80	3.94	8.83	7.09	8.55	6.88	5.75	6.56	6.02	3.97	8.05	6.17	5.59	8.04	7.31
H6	12.06	7.01	10.88	9.08	6.01	11.42	9.76	4.87	11.06	8.87	10.72	8.60	7.16	8.20	7.53	4.92	10.08	7.73	6.96	10.05	9.15
H7	15.13	6.81	13.44	10.13	5.31	14.59	11.40	3.22	13.83	9.70	13.18	9.57	8.55	10.31	9.02	4.03	12.87	8.56	6.81	12.12	10.32
H8	13.51	6.91	12.06	9.55	5.67	12.88	10.47	4.10	12.34	9.20	11.83	9.00	7.73	9.10	8.15	4.48	11.34	8.06	6.87	10.98	9.66
H9	15.45	6.57	13.71	10.10	5.02	15.01	11.51	2.72	14.13	9.60	13.45	9.55	8.66	10.56	9.13	3.76	13.28	8.58	6.66	12.37	10.38
H10	13.67	4.81	12.12	8.36	3.29	13.52	9.75	0.95	12.64	7.81	11.90	7.78	7.46	9.41	7.93	2.11	11.86	6.94	4.83	10.68	8.57
H11	15.57	4.57	13.52	8.76	2.78	15.31	10.52	-0.26	14.06	7.96	13.12	8.05	8.11	10.50	8.60	1.56	13.50	7.31	4.72	11.88	9.13
H12	15.21	4.97	13.41	9.02	3.26	15.08	10.77	0.43	13.94	8.43	13.13	8.59	8.51	10.76	9.00	2.09	13.35	7.66	5.14	11.90	9.44
H13	13.11	5.96	11.65	8.79	4.67	12.64	9.80	2.90	12.00	8.34	11.42	8.19	7.28	8.80	7.72	3.51	11.10	7.35	5.91	10.46	8.89
H14	12.27	4.70	10.90	7.74	3.38	12.07	8.79	1.43	11.36	7.16	10.68	6.99	6.30	7.96	6.80	2.28	10.56	6.36	4.56	9.52	7.78
H15	18.27	2.98	15.51	8.74	0.64	18.18	11.43	-3.90	16.14	7.63	14.81	8.08	8.97	12.31	9.64	-0.52	16.19	7.43	3.37	13.39	9.54
R1	0.82	0.40	1.35	0.75	0.69	2.02	1.15	-0.36	1.16	0.08	1.38	-0.42	-0.08	0.17	0.01	0.18	1.45	0.60	-0.02	0.74	0.28
R2	10.47	6.90	9.88	8.20	6.90	11.06	9.13	5.23	9.99	7.55	9.99	7.33	7.51	8.30	7.71	5.60	9.56	7.31	6.97	9.35	8.32
R3	5.15	2.98	5.27	4.07	2.95	6.15	4.76	1.47	5.12	3.34	5.27	2.69	2.78	3.39	2.98	2.04	5.09	3.47	2.58	4.41	3.66
R4	15.06	9.45	14.02	11.58	9.08	15.49	12.84	6.90	14.22	10.85	14.11	10.57	10.33	11.56	10.67	7.38	13.48	10.23	9.52	13.19	11.77
R5	9.79	4.30	9.53	6.75	3.73	11.04	8.08	1.26	9.62	5.85	9.53	5.34	5.57	6.96	5.91	2.60	9.56	5.90	4.07	8.25	6.60
R6	9.21	5.32	8.97	7.18	4.95	10.06	8.13	3.07	8.90	6.40	8.96	5.57	5.32	6.30	5.66	3.69	8.55	6.15	4.94	7.85	6.82
R7	8.32	3.27	8.21	5.61	2.78	9.69	6.92	0.39	8.29	4.76	8.25	4.26	4.79	6.11	5.14	1.72	8.31	4.88	3.02	6.97	5.43
R8	9.77	5.36	9.48	7.44	4.92	10.68	8.51	2.86	9.44	6.64	9.48	5.92	5.84	6.94	6.19	3.63	9.11	6.39	5.01	8.30	7.13
R9	8.84	5.00	8.67	6.88	4.62	9.76	7.82	2.76	8.63	6.11	8.67	5.27	4.95	5.92	5.28	3.40	8.30	5.88	4.60	7.54	6.51
R10	17.49	8.69	17.58	12.85	8.27	20.71	15.40	3.97	18.19	11.45	18.19	10.87	11.64	14.01	12.38	6.15	17.99	11.63	8.61	15.72	12.90
R11	9.51	-0.87	10.02	3.77	-1.23	14.02	6.52	-5.56	11.87	2.48	11.30	2.03	2.50	5.40	3.29	-4.16	10.37	1.84	-1.30	7.42	3.55
R12	13.63	6.12	13.98	9.88	5.82	16.83	12.10	2.28	14.86	8.83	14.79	7.94	7.62	9.71	8.35	3.29	13.78	8.17	5.65	11.94	9.55
R13	25.30	16.13	24.17	19.93	15.83	27.08	22.34	11.85	24.70	18.66	24.72	18.22	18.09	20.23	18.82	12.88	23.60	17.87	16.37	22.80	20.33
R14	22.53	12.83	22.06	17.08	12.49	25.42	19.80	8.22	23.00	15.86	22.89	15.55	16.12	18.59	16.87	9.85	22.17	15.44	13.11	20.50	17.55
R15	27.76	15.26	26.62	20.74	14.44	30.33	23.79	9.46	27.63	19.26	27.33	18.92	18.85	21.88	19.93	11.31	26.45	18.49	15.49	24.57	21.21
R16	26.45	15.27	24.61	20.00	13.86	26.94	22.15	10.30	25.24	19.05	24.78	18.58	16.93	19.42	17.87	11.13	23.58	17.43	15.32	22.79	20.30
C1	23.54	15.79	23.81	18.96	16.33	27.57	21.39	11.26	24.11	16.40	24.67	16.18	18.03	20.17	18.60	13.90	24.60	17.90	16.31	22.73	19.60
C2	36.31	22.56	35.54	28.35	22.12	40.30	31.92	15.45	36.22	25.64	36.51	25.30	26.08	29.54	27.12	18.63	35.95	26.18	23.20	33.59	29.26
C3	29.48	14.67	29.32	20.77	14.28	34.79	24.57	6.94	30.38	17.61	30.26	17.57	20.19	24.09	21.23	11.59	31.12	19.52	15.31	27.03	21.69
C4	49.18	29.47	47.51	38.00	28.03	53.29	42.72	19.66	48.53	35.04	48.58	34.59	33.85	38.67	35.44	23.65	47.71	34.87	30.21	44.64	39.15
C5	39.13	27.00	40.49	32.43	28.09	46.98	36.54	19.62	41.21	28.19	42.44	27.76	30.69	34.29	31.86	24.16	42.15	30.91	27.87	38.66	33.47

^aKS denotes the result for the uncorrected Kohn-Sham energy. D2 and D3 indicate the second and third version of the applied dispersion correction formula.

Table S12 - DFT results^a for the BSR36 test set of bond separation reaction energies. The last column contains the thermal correction of vibrations including unscaled zero-point energy. All values in kcal · mol⁻¹.

Name	TPSSh			B3LYP			M06-2X			PW6B95			mPW2PLYP		B2PLYP			B2GP-PLYP			$\Delta H_{\text{vib.}}^{298K}$
	KS	D2	D3	KS	D2	D3	KS	D2	D3	KS	D2	D3	KS	D2	KS	D2	D3	KS	D2	D3	PBE/def2-TZVPP
H1	2.35	9.39	6.17	2.20	10.41	6.84	8.58	9.05	8.86	5.01	8.92	7.17	6.50	9.63	6.10	10.41	8.59	7.20	10.33	8.99	2.28
H2	3.69	8.86	6.60	3.84	9.88	7.38	8.43	8.78	8.70	5.66	8.54	7.36	7.16	9.46	6.85	10.01	8.75	7.68	9.98	9.06	2.07
H3	3.18	10.60	7.22	3.01	11.67	7.94	9.99	10.48	10.25	5.94	10.07	8.24	7.78	11.08	7.35	11.89	10.00	8.58	11.88	10.50	2.54
H4	2.77	8.56	5.91	2.77	9.52	6.57	7.88	8.27	8.15	4.94	8.15	6.75	6.31	8.88	5.98	9.51	8.01	6.87	9.44	8.34	2.04
H5	4.10	7.77	6.27	4.42	8.70	7.06	7.60	7.85	7.84	5.56	7.60	6.87	6.85	8.49	6.62	8.87	8.05	7.23	8.87	8.27	1.78
H6	5.09	9.73	7.85	5.48	10.90	8.83	9.48	9.79	9.81	6.93	9.50	8.59	8.54	10.60	8.26	11.09	10.06	9.03	11.09	10.34	2.22
H7	4.27	12.23	8.73	4.28	13.56	9.68	11.40	11.93	11.81	7.26	11.68	9.86	9.27	12.81	8.81	13.67	11.71	10.08	13.62	12.18	2.81
H8	4.68	10.86	8.21	4.91	12.11	9.18	10.33	10.74	10.69	7.03	10.46	9.11	8.86	11.61	8.50	12.27	10.80	9.49	12.24	11.17	2.52
H9	4.03	12.59	8.78	3.89	13.88	9.66	11.72	12.29	12.12	7.17	11.93	9.92	9.35	13.16	8.87	14.11	11.97	10.28	14.08	12.52	2.97
H10	2.35	11.12	7.10	2.08	12.32	7.83	9.84	10.43	10.25	5.56	10.44	8.28	7.30	11.20	6.83	12.19	9.90	8.16	12.05	10.37	2.68
H11	1.86	12.60	7.51	1.20	13.74	8.07	11.12	11.84	11.53	5.72	11.69	8.94	7.80	12.57	7.22	13.79	10.91	8.92	13.69	11.58	3.15
H12	2.40	12.53	7.88	1.85	13.67	8.53	11.25	11.92	11.66	6.28	11.91	9.43	8.00	12.50	7.45	13.64	11.04	9.04	13.54	11.64	2.89
H13	3.71	10.53	7.48	3.76	11.73	8.32	9.67	10.12	10.05	6.22	10.01	8.43	7.95	10.98	7.56	11.73	10.01	8.61	11.65	10.39	2.48
H14	2.43	9.88	6.46	2.27	10.96	7.13	8.42	8.91	8.85	5.01	9.15	7.36	6.66	9.97	6.27	10.83	8.88	7.37	10.68	9.25	2.44
H15	-0.11	14.92	7.74	-1.76	15.78	7.88	12.81	13.81	13.37	5.55	13.90	10.12	7.56	14.24	6.80	15.99	12.03	9.22	15.90	13.01	3.96
R1	0.00	1.14	0.37	-0.81	0.52	-0.45	0.25	0.33	0.33	1.10	1.73	1.26	0.34	0.85	0.85	1.55	1.01	1.16	1.67	1.27	4.06
R2	5.74	9.31	7.43	5.54	9.70	7.55	8.89	9.13	9.05	7.73	9.71	8.67	8.14	9.73	8.39	10.58	9.46	9.15	10.73	9.90	4.36
R3	1.94	4.69	3.30	1.26	4.46	2.81	3.72	3.91	3.90	3.70	5.23	4.43	3.50	4.72	3.92	5.60	4.72	4.52	5.74	5.09	4.83
R4	7.58	13.08	10.40	7.47	13.88	10.84	12.54	12.90	12.83	10.25	13.30	11.87	11.37	13.81	11.51	14.87	13.31	12.60	15.04	13.90	5.14
R5	2.62	8.89	5.83	1.60	8.91	5.42	7.46	7.88	7.75	5.72	9.20	7.51	6.09	8.88	6.35	10.18	8.37	7.54	10.33	8.99	5.73
R6	3.67	8.04	6.03	3.10	8.20	5.85	6.91	7.20	7.20	6.05	8.48	7.36	6.45	8.40	6.79	9.47	8.23	7.67	9.62	8.70	5.59
R7	1.73	7.66	4.79	0.67	7.59	4.29	6.22	6.61	6.51	4.77	8.06	6.47	4.79	7.43	5.07	8.69	6.98	6.17	8.80	7.54	5.44
R8	3.62	8.56	6.29	2.98	8.74	6.12	7.36	7.69	7.66	6.22	8.96	7.71	6.60	8.80	6.91	9.93	8.56	7.86	10.06	9.04	5.57
R9	3.38	7.78	5.77	2.78	7.92	5.56	6.56	6.86	6.85	5.71	8.16	7.03	6.16	8.12	6.49	9.19	7.95	7.38	9.34	8.42	5.59
R10	6.29	16.96	11.66	4.66	17.10	11.00	14.09	14.80	14.72	11.35	17.27	14.40	11.84	16.58	12.40	18.92	15.76	14.39	19.13	16.79	9.57
R11	-4.08	8.99	1.89	-5.01	10.24	2.07	5.50	6.37	6.17	1.01	8.27	4.37	2.24	8.05	2.68	10.67	6.43	4.60	10.41	7.26	8.80
R12	3.34	12.78	8.14	2.53	13.54	8.18	10.23	10.86	10.86	7.49	12.73	10.23	8.60	12.80	9.19	14.96	12.17	10.81	15.00	12.93	9.35
R13	13.26	22.90	18.18	12.80	24.05	18.66	21.44	22.08	22.07	17.84	23.19	20.72	19.57	23.85	19.99	25.88	23.11	21.92	26.21	24.17	9.35
R14	10.20	21.29	15.73	9.28	22.21	15.87	18.89	19.63	19.54	15.23	21.39	18.42	16.49	21.41	16.91	23.68	20.41	18.96	23.88	21.47	9.14
R15	11.73	25.35	18.82	10.83	26.72	19.26	22.61	23.52	23.56	17.52	25.09	21.68	19.61	25.67	19.88	28.20	24.36	22.31	28.37	25.54	10.06
R16	11.52	22.72	17.73	11.58	24.66	19.02	21.27	22.02	22.10	16.17	22.40	19.89	18.95	23.93	18.81	25.66	22.79	20.77	25.75	23.66	7.29
C1	14.24	23.87	18.24	12.05	23.28	16.74	20.54	21.18	21.02	19.90	25.25	22.10	19.60	23.88	20.72	26.60	23.17	22.99	27.27	24.71	12.40
C2	19.18	34.76	26.68	17.05	35.23	25.97	30.87	31.91	31.76	26.63	35.29	30.93	28.63	35.55	29.46	38.99	34.19	32.80	39.73	36.19	14.48
C3	12.04	29.62	19.93	8.64	29.15	18.02	23.73	24.90	24.61	20.00	29.77	24.47	20.61	28.42	21.46	32.20	26.42	24.88	32.69	28.42	13.90
C4	24.39	46.05	35.52	22.08	47.34	35.37	40.98	42.42	42.36	34.26	46.29	40.76	37.65	47.27	38.25	51.48	45.32	42.59	52.21	47.69	16.59
C5	24.69	40.88	31.45	20.83	39.72	28.68	34.26	35.34	35.26	33.78	42.78	37.56	33.43	40.63	35.51	45.41	39.60	39.31	46.51	42.19	20.57

^aKS denotes the result for the uncorrected Kohn-Sham energy. D2 and D3 indicate the second and third version of the applied dispersion correction formula. All computations with the (def2-)QZVPP basis set.

Table S13 - parameters for the dispersion correction of the density functionals.

DF	D2		D3	
	s_6	s_6	$s_{r,6}$	s_8
BLYP	1.2 ^a	1.0	1.094	1.682 ^e
B3LYP	1.05 ^a	1.0	1.261	1.703 ^e
BHLYP	0.8 ^b	1.0	1.370	1.442 ^e
TPSS	1.0 ^a	1.0	1.166	1.105 ^e
TPSSH	0.9 ^b	1.0	1.223	1.219 ^e
BP86	1.05 ^a	1.0	1.139	1.683 ^e
B97	1.25 ^a	1.0	0.892	0.909 ^e
PBE	0.75 ^a	1.0	1.217	0.722 ^e
PBE0	0.6 ^b	1.0	1.287	0.982 ^e
PW6B95	0.5 ^b	1.0	1.532	0.862 ^e
M06L	0.2 ^c	1.0	1.581	0.000 ^f
M062X	0.06 ^c	1.0	1.619	0.000 ^f
mPW2PLYP	0.4 ^d			
B2PYP	0.55 ^d	0.5	1.332	1.000 ^e
B2GP-PLYP	0.4 ^c	0.4	1.438	0.761 ^g

^ataken from Grimme, S. *J. Comp. Chem.* **2006**, *27*, 1787–1799.

^bunpublished. ^ctaken from Karton, A.; Tarnopolsky, A.;

Martin, J. M. L. *J. Phys. Chem. A* **2008**, *112*, 12868–12886.

^dtaken from Schwabe, T.; Grimme, S. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3397–3406.

^etaken from Grimme, S. *et al. J. Chem. Phys.* **2010**, *132*, 154104.

^ftaken from Goerigk, L.; Grimme, S. manuscript in preparation.

^gtaken from Goerigk, L.; Grimme, S. *J. Chem. Theo. Comp.* **2010** submitted.

Listing 1 BSR36 XYZ coordinates in [a.u.]

1				1.1186185	2.0788156	-1.6542014	h
2				3.6784204	-1.8796859	1.6525974	h
3	#h1			3.6784204	-1.8796859	-1.6525974	h
4				5.9620373	2.2799527	1.6623693	h
5				7.6977335	-0.0226069	0.0000000	h
6				5.9620373	2.2799527	-1.6623693	h
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	-2.1917217	-4.2823303	1.6685426	h	4.5652868	-1.5332952	-0.5833066	c
	-4.8621470	-3.1745281	0.0000000	h	2.0550008	-1.8280036	0.7980965	c
					0.0000000	0.0000000	-0.0988708	c
#h10					0.5555972	2.6936847	0.7980965	c
	-3.8846865	-3.6075160	0.3377565	c	-0.9547708	4.7203019	-0.5833066	c
	-1.2345244	-2.7035031	-0.3399688	c	-2.6105980	-0.8656810	0.7980965	c
	-0.9004555	0.1622590	-0.1450883	c	-3.6105160	-3.1870068	-0.5833066	c
	1.5596742	1.0323856	-1.4292773	c	5.3521663	0.3540144	-0.3572901	h
	3.9401796	0.0874712	-0.1024916	c	5.9614554	-2.8729368	0.1176950	h
	1.6655256	3.8990457	-1.7195473	c	4.3225210	-1.8743077	-2.6003417	h
	-1.1175066	1.0471939	2.5925332	c	2.3270655	-1.5504753	2.8290773	h
	-5.2966721	-2.6609321	-0.8269906	h	1.4022851	-3.7692621	0.5624768	h
	-4.0765929	-5.6341974	0.0359189	h	0.0000000	0.0000000	-2.1728445	h
	-4.3377327	-3.2311211	2.3083782	h	2.5631342	3.0990456	0.5624768	h
	-0.7962281	-3.2896115	-2.2715312	h	0.1792183	2.7905355	2.8290773	h
	0.1392630	-3.6393727	0.8846285	h	-0.5380625	4.6805669	-2.6003417	h
	-2.4491767	1.0273090	-1.2160657	h	-0.4926915	6.5992402	0.1176950	h
	1.5323980	0.2171413	-3.3305453	h	-2.9826686	4.4581048	-0.3572901	h
	4.1131991	0.9122925	1.7774288	h	-2.5062838	-1.2400601	2.8290773	h
	5.6145067	0.6328908	-1.1710651	h	-3.9654193	0.6702165	0.5624768	h
	3.9616037	-1.9609129	0.0913835	h	-2.3694977	-4.8121191	-0.3572901	h
	1.8426429	4.8287147	0.1097694	h	-5.4687639	-3.7263035	0.1176950	h
	-0.0303983	4.6204952	-2.6408564	h	-3.7844586	-2.8062592	-2.6003417	h
	3.2934165	4.4562731	-2.8520689	h				
	0.2786966	0.1069961	3.7814305	h	#h15			
	-2.9768318	0.6181796	3.3606935	h	2.1644462	-1.6109834	-2.5268359	c
	-0.8403000	3.0785191	2.7655756	h	0.0000000	0.0000000	-1.4786590	c
					0.0000000	0.0000000	1.4786590	c
#h11					2.1644462	1.6109834	2.5268359	c
	-2.3144485	-2.2018880	0.0000000	c	0.3129294	2.6799571	-2.5268359	c
	-1.1312175	0.4328557	0.0000000	c	-2.4773756	-1.0689737	-2.5268359	c
	1.7936382	0.3345697	0.0000000	c	0.3129294	-2.6799571	2.5268359	c
	2.9066946	-0.9292655	2.3454563	c	-2.4773756	1.0689737	2.5268359	c
	2.9066946	-0.9292655	-2.3454563	c	3.9875511	-1.0608934	-1.7422185	h
	-2.0566012	1.8666127	2.3340002	c	1.8762435	-3.6137828	-2.1504067	h
	-2.0566012	1.8666127	-2.3340002	c	2.2697430	-1.3699474	-4.5718668	h
	-1.7766362	-3.2796702	1.6701231	h	3.9875511	1.0608934	1.7422185	h
	-4.3700051	-2.0400047	0.0000000	h	1.8762435	3.6137828	2.1504067	h
	-1.7766362	-3.2796702	-1.6701231	h	2.2697430	1.3699474	4.5718668	h
	2.4162796	2.3105066	0.0000000	h	2.1915060	3.4317659	-2.1504067	h
	2.3883465	-2.9220283	2.4275259	h	0.0515377	2.6506288	-4.5718668	h
	2.2975345	-0.0328461	4.0919756	h	-1.0750149	3.9837673	-1.7422185	h
	4.9630473	-0.8339179	2.2815967	h	-2.9125362	-2.9228738	-1.7422185	h
	2.3883465	-2.9220283	-2.4275259	h	-4.0677494	0.1820169	-2.1504067	h
	4.9630473	-0.8339179	-2.2815967	h	-2.3212808	-1.2806814	-4.5718668	h
	2.2975345	-0.0328461	-4.0919756	h	2.1915060	-3.4317659	2.1504067	h
	-1.6699828	0.8374700	4.0730431	h	0.0515377	-2.6506288	4.5718668	h
	-4.0939615	2.1589374	2.2239147	h	-1.0750149	-3.9837673	1.7422185	h
	-1.1554278	0.8374700	2.4652781	h	-2.9125362	2.9228738	1.7422185	h
	-1.6699828	0.8374700	-4.0730431	h	-4.0677494	-0.1820169	2.1504067	h
	-1.1554278	3.7176176	-2.4652781	h	-2.3212808	1.2806814	4.5718668	h
	-4.0939615	2.1589374	-2.2239147	h				
#h12					#r1			
	-3.0093218	-1.5351170	-2.4829533	c	-1.1118542	-0.9187874	-1.9339087	c
	-2.3484563	0.5144235	-0.5696836	c	-2.2768217	-0.4989879	0.6808078	c
	0.0000000	0.0000000	1.0563225	c	1.1118542	0.9187874	-1.9339087	c
	2.3484563	-0.5144235	-0.5696836	c	2.2768217	0.4989879	0.6808078	c
	3.0093218	1.5351170	-2.4829533	c	0.0000000	0.0000000	2.4446448	c
	0.4420132	2.2973372	2.7500122	c	-2.4446979	-0.6049894	-3.4699441	h
	-0.4420132	-2.2973372	2.7500122	c	-0.4027883	-2.8508027	-2.0941483	h
	-3.3389635	-3.3498759	-1.5708232	h	-3.4935980	1.1629270	0.6165776	h
	-4.7229733	-1.0391873	-3.5094828	h	-3.4334944	-2.0795066	1.3085702	h
	-1.5089596	-1.7887041	-3.8689562	h	0.4027883	2.8508027	-2.0941483	h
	-3.9473218	0.7956868	0.7095553	h	2.4446979	0.6049894	-3.4699441	h
	-2.0908666	2.3081863	-1.5585643	h	3.4935980	-1.1629270	0.6165776	h
	3.9473218	-0.7956868	0.7095553	h	3.4334944	-2.0795066	1.3085702	h
	2.0908666	-2.3081863	-1.5585643	h	0.3627779	-1.6118943	3.6698304	h
	3.3389635	3.3498759	-1.5708232	h	-0.3627779	1.6118943	3.6698304	h
	4.7229733	1.0391873	-3.5094828	h				
	1.5089596	1.7887041	-3.8689562	h	#r2			
	0.6581194	4.0243105	1.6494119	h	2.3765004	1.3720732	0.4440203	c
	-1.1562456	2.5653730	4.0251552	h	-2.3765004	1.3720732	0.4440203	c
	2.1371181	2.0479466	3.8982070	h	0.0000000	-2.7441463	0.4440203	c
	-0.6581194	-4.0243105	1.6494119	h	2.3765004	-1.3720732	-0.4440203	c
	1.1562456	-2.5653730	4.0251552	h	-2.3765004	-1.3720732	-0.4440203	c
	-2.1371181	-2.0479466	3.8982070	h	0.0000000	2.7441463	-0.4440203	c
#h13					4.0631927	2.3458854	-0.2321647	h
	-5.9886410	1.8524048	-0.5301728	c	2.4474043	1.4130095	2.5098989	h
	-3.7893277	0.0127484	-0.7897441	c	-4.0631927	2.3458854	-0.2321647	h
	-1.3093639	1.1525453	0.1290053	c	-2.4474043	1.4130095	2.5098989	h
	1.0260232	-0.4917949	-0.3017444	c	0.0000000	-2.8260190	-2.5098989	h
	3.4099476	0.9947833	0.3753413	c	0.0000000	-4.6917707	-0.2321647	h
	5.8726924	-0.3400829	-0.2928103	c	2.4474043	-1.4130095	-2.5098989	h
	0.8666881	-2.9578685	1.1822047	c	-4.0631927	-2.3458854	0.2321647	h
	-5.6511820	3.5588916	-1.6328785	h	0.0000000	4.6917707	0.2321647	h
	-7.7563477	1.0206325	-1.1765406	h	0.0000000	2.8260190	-2.5098989	h
	-6.2385591	2.4179765	1.4346643	h				
	-3.5803860	-0.5478316	-2.7667900	h	#r3			
	-4.2129829	-1.7058365	0.2652856	h	0.2681763	-2.9525745	1.4664220	c
	-1.0251740	2.9626495	-0.8291355	h	0.2681763	-2.9525745	-1.4664220	c
	-1.4590144	1.5815938	2.1492126	h	0.3221935	-0.1540596	2.2358369	c
	1.1177501	-0.9455831	-2.3216105	h	-0.8772397	1.2243748	0.0000000	c
	3.3423654	2.8129985	-0.6000104	h	0.3221935	-0.1540596	-2.2358369	c
	3.3690462	1.4182860	2.3992847	h	-0.4649600	4.0628717	0.0000000	c
	5.9065976	-0.8437973	-2.2907548	h	1.8593676	-3.9968910	2.2455236	h
	7.4947513	0.8713212	0.0773728	h	-1.4437469	-3.8482020	2.1767637	h
	6.1291069	-2.0654757	0.7959578	h	1.8593676	-3.9968910	-2.2455236	h
	0.7633409	-2.5583333	3.2048715	h	-1.4437469	-3.8482020	-2.1767637	h
	-0.7974450	-4.0500385	0.6650671	h	2.2730574	0.4996168	2.4279569	h
	2.5101139	-4.1501892	0.8539240	h	-0.6341319	0.2098380	4.0228705	h
#h14					-2.9076596	0.8206793	0.0000000	h
					-0.6341319	0.2098380	-4.0228705	h

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	2.2730574	0.4996168	-2.4279569	h	2.0394900	2.2362874	-2.7115926	c	
	1.5533951	4.4856701	0.0000000	h	-2.5859120	1.2106720	-0.6383929	h	
	-1.2963291	4.9449118	1.6652075	h	-3.5721123	-1.8342696	2.6786851	h	
	-1.2963291	4.9449118	-1.6652075	h	-0.8379295	-3.5781081	1.9756185	h	
					2.5859120	-1.2106720	-0.6383929	h	
#r4					3.5721123	1.8342696	2.6786851	h	
	-1.0851723	1.6003068	0.0000000	c	0.8379295	3.5781081	1.9756185	h	
	0.1745295	0.5247330	2.3626796	c	1.1801862	-1.1562961	5.0573100	h	
	0.1507576	-2.3584366	2.3733676	c	-1.1801862	1.1562961	5.0573100	h	
	1.4079337	-3.4066057	0.0000000	c	-0.7922317	-3.8791117	-2.6920650	h	
	0.1507576	-2.3584366	-2.3733676	c	-1.8527697	-1.3153905	-4.5438898	h	
	0.1745295	0.5247330	-2.3626796	c	-3.9775205	-2.9142784	-2.5458601	h	
	-1.0161688	4.4752701	0.0000000	c	0.7922317	3.8791117	-2.6920650	h	
	-3.0628900	0.9836121	0.0000000	h	1.8527697	1.3153905	-4.5438898	h	
	2.1336078	1.1921899	2.4220121	h	3.9775205	2.9142784	-2.5458601	h	
	-0.7576844	1.2616129	4.0505697	h					
	-1.8067191	-3.0189200	2.4499270	h					
	1.0902931	-3.0763607	4.0624323	h	#r9	0.0000000	0.0000000	-1.8897970	c
	3.4047856	-2.8707681	0.0000000	h	1.7909865	-1.5168499	-0.1482137	c	
	1.3400196	-5.4671685	0.0000000	h	-1.7909865	1.5168499	-0.1482137	c	
	-1.8067191	-3.0189200	-2.4499270	h	-1.4018547	0.3288850	2.4633097	c	
	1.0902931	-3.0763607	-4.0624323	h	1.4018547	-0.3288850	2.4633097	c	
	-0.7576844	1.2616129	-4.0505697	h	4.5226975	-1.5397108	-1.0323845	c	
	2.1336078	1.1921899	-2.4220121	h	-4.5226975	1.5397108	-1.0323845	c	
	0.9357258	5.1415233	0.0000000	h	-1.0746389	-1.2598254	-3.1188013	h	
	-1.9466523	5.2470909	-1.6681065	h	1.0746389	1.2598254	-3.1188013	h	
	-1.9466523	5.2470909	1.6681065	h	1.1092941	-3.4643891	-0.0489794	h	
					-1.1092941	3.4643891	-0.0489794	h	
#r5					-1.9721625	1.5770935	3.9992697	h	
	2.5150675	1.9823560	-1.4654897	c	-2.5217542	-1.4032761	2.6066174	h	
	2.5150675	1.9823560	1.4654897	c	2.5217542	1.4032761	2.6066174	h	
	-0.0998024	0.9772937	-2.2346453	c	1.9721625	-1.5770935	3.9992697	h	
	-0.9635938	-0.6524360	0.0000000	c	5.2449209	0.3878859	-1.1528570	h	
	-0.0998024	0.9772937	2.2346453	c	4.7027903	-2.3988815	-2.8958517	h	
	-3.8006032	-1.1081206	0.0000000	c	5.7263067	-2.5899744	0.2688353	h	
	0.4336582	-3.1780919	0.0000000	c	-5.2449209	-0.3878859	-1.1528570	h	
	4.0027869	0.7567180	-2.1861128	h	-4.7027903	2.3988815	-2.8958517	h	
	2.8635189	3.8560719	-2.2384092	h	-5.7263067	2.5899744	0.2688353	h	
	4.0027869	0.7567180	2.1861128	h					
	2.8635189	3.8560719	2.2384092	h	#r10	0.6184013	0.3778605	0.5354446	c
	-0.0740574	-0.0686536	-4.0111469	h	3.1823785	1.6749093	0.8947552	c	
	-1.4236916	2.5469328	2.4547853	h	-1.0058578	2.6254920	-0.3230699	c	
	-0.0740574	-0.0686536	4.0111469	h	-0.3265528	-0.8379754	2.9739967	c	
	-1.4236916	2.5469328	2.4547853	h	0.7983113	-1.6429205	-1.5365684	c	
	-4.8276155	0.6792305	0.0000000	h	-1.6742700	-3.0827293	-1.9108050	c	
	-4.3770278	-2.1781175	-1.6658113	h	-2.5714533	-4.2516206	0.5668221	c	
	-4.3770278	-2.1781175	1.6658113	h	-2.8215884	-2.2408514	2.6178053	c	
	2.4775263	-2.9236183	0.0000000	h	3.4387500	3.4903935	-1.3569233	c	
	-0.0662265	-4.2817651	1.6681980	h	0.6909708	4.1217655	-2.1479166	c	
	-0.0662265	-4.2817651	-1.6681980	h	4.7318399	0.3207150	1.0269536	h	
#r6					3.1341992	2.7421137	2.6636606	h	
	-1.4924817	1.0634103	0.0000000	c	-2.7948773	2.0778167	-1.1809802	h	
	-0.6274367	-0.5033591	2.2623626	c	-1.4481247	3.7743085	1.3367736	h	
	-0.6274367	-0.5033591	-2.2623626	c	-0.5124161	0.6200117	4.4266793	h	
	2.0287564	-1.3810773	-1.4615891	c	1.1020942	-2.1772816	3.6465700	h	
	2.0287564	-1.3810773	1.4615891	c	1.4027619	-0.7898748	-3.3164896	h	
	-0.6755647	0.8805070	4.7757849	c	2.2747932	-2.9882155	-0.9929193	h	
	-0.6755647	0.8805070	-4.7757849	c	-1.4204945	-4.5447217	-3.3430997	h	
	-0.4951546	2.8791098	0.0000000	h	-3.1296387	-1.8051182	-2.6280292	h	
	-3.5172341	1.4509108	0.0000000	h	-4.3641837	-5.2326097	0.2930804	h	
	-1.8591330	-2.1599896	2.3810751	h	-1.1965822	-5.6694792	1.1801735	h	
	-1.8591330	-2.1599896	-2.3810751	h	-4.3005012	-0.8996475	2.0871058	h	
	2.4978243	-3.2198263	-2.2588102	h	-3.4099300	-3.1012457	4.3971649	h	
	3.4245607	-0.0422291	-2.1783926	h	4.5071570	5.1751920	-0.8566206	h	
	2.4978243	-3.2198263	2.2588102	h	4.4460867	2.5839040	-2.9056636	h	
	3.4245607	-0.0422291	2.1783926	h	0.3014973	6.1394608	-2.0553833	h	
	0.5196828	2.5582902	4.6852563	h	0.3472295	3.5403477	-4.0923969	h	
	0.0261190	-0.3121045	6.3020918	h					
	-2.5823464	1.4831941	5.2694306	h	#r11	-1.0206013	2.9105113	-1.4633874	c
	0.5196828	2.5582902	-4.6852563	h	-1.0206013	2.9105113	1.4633874	c	
	-2.5823464	1.4831941	-5.2694306	h	-0.3078123	0.4769773	-2.8577502	c	
	0.0261190	-0.3121045	-6.3020918	h	-0.3078123	0.4769773	2.8577502	c	
#r7					2.4745599	-0.2954726	2.4647966	c	
	-1.5854815	-1.0483404	0.2347468	c	-2.1740136	-1.6982878	2.4214204	c	
	0.2011076	-3.2276682	-0.4174267	c	-2.1740136	-1.6982878	-2.4214204	c	
	-0.5206369	1.0798307	-1.4307451	c	2.4745599	-0.2954726	-2.4647966	c	
	2.3568784	0.8206249	-1.1097468	c	3.6860118	0.5941688	0.0000000	c	
	2.8408141	-1.9988470	-0.5066974	c	-1.8325294	-3.2070207	0.0000000	c	
	-1.5065345	-0.4289124	3.0476828	c	0.2448955	4.4017522	-2.1252969	h	
	-1.5129967	3.7193440	-0.8923730	c	-2.8999146	3.4497796	-2.1238926	h	
	-3.5301254	-1.4874015	-0.2999802	h	0.2448955	4.4017522	2.1252969	h	
	0.0897348	-4.7868689	0.9242971	h	-2.8999146	3.4497796	2.1238926	h	
	-0.2872092	-3.9712550	-2.2781202	h	-0.5080256	0.9503383	-4.8601032	h	
	-0.9912670	0.5877032	-3.3837658	h	-0.5080256	0.9503383	4.8601032	h	
	3.3610787	1.4514296	-2.7920222	h	2.6588196	-2.3454618	2.6372413	h	
	2.9902964	2.0180680	0.4446893	h	3.5959857	0.4997892	4.0042376	h	
	4.0440497	-2.9003121	-1.9098967	h	-2.0063970	-3.0027225	4.0150815	h	
	3.7921042	-2.1961611	1.3074764	h	-4.0984067	-0.9412635	2.4901310	h	
	0.3934299	0.0945063	3.6512879	h	-2.0063970	-3.0027225	-4.0150815	h	
	-2.0845208	-2.0655058	4.1566666	h	-4.0984067	-0.9412635	-2.4901310	h	
	-2.7674490	1.1272105	3.5210398	h	2.6588196	-2.3454618	-2.6372413	h	
	-0.9961665	4.3283842	1.0058192	h	3.5959857	0.4997892	-4.0042376	h	
	-3.5658860	3.8014783	-1.0546451	h	5.6633505	-0.0003301	0.0000000	h	
	-0.7212205	5.0826927	-2.2182868	h	3.7253975	2.6582244	0.0000000	h	
					0.0298375	-4.0946073	0.0000000	h	
#r8					-3.1899126	-4.7622671	0.0000000	h	
	-1.3689041	-0.4653550	-0.5569254	c	#r12	0.3055462	1.3060592	-1.4766646	c
	-1.6151064	-1.6672634	2.0616887	c	0.3055462	1.3060592	1.4766646	c	
	1.3689041	0.4653550	-0.5569254	c	-0.2795800	-1.1833350	2.8019868	c	
	1.6151064	1.6672634	2.0616887	c	-2.9736942	-2.1618179	2.4350746	c	
	0.0000000	0.0000000	3.8318945	c					
	-2.0394900	-2.2362874	-2.7115926	c					

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-3.3839329	-3.6457363	0.0000000	c	-1.0548530	3.7828229	2.9320319	h
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-0.2795800	-1.1833350	-2.8019868	c	5.6900018	6.6326934	-0.5979962	h
2.9184527	2.3367646	-2.2306914	c	3.4829952	-1.1064162	-1.6922031	h
3.7195817	3.9746675	0.0000000	c	1.6921522	1.3130606	-3.0936749	h
2.9184527	2.3367646	2.2306914	c	-2.2672251	-0.5110030	2.5643558	h
-1.1176978	2.6670056	-2.1050301	h	1.0060224	-4.2136965	-0.3604455	h
-1.1176978	2.6670056	2.1050301	h	1.0548530	-3.7828229	2.9320319	h
0.0525982	-0.8840237	4.8192351	h	-3.4402465	-5.0740756	3.1954534	h
1.0748157	-2.6311881	2.2135749	h	-1.6543279	-7.4476385	1.7188089	h
-3.4633338	-3.3884874	4.0203845	h	-3.0481328	-5.9491687	-2.4846721	h
-4.2879254	-0.5665527	2.5086460	h	-5.6900018	-6.6326934	-0.5979962	h
-5.3014349	-4.4099202	0.0000000	h	-6.1850840	-2.0900752	0.4227184	h
-2.1084589	-5.2735188	0.0000000	h	-6.2074209	-2.5254285	-2.8657034	h
-3.4633338	-3.3884874	-4.0203845	h	-3.4829952	1.1064162	-1.6922031	h
-4.2879254	-0.5665527	-2.5086460	h	-1.6921522	-1.3130606	-3.0936749	h
1.0748157	-2.6311881	-2.2135749	h				
0.0525982	-0.8840237	-4.8192351	h	#r16			
4.2419916	0.7596984	-2.4196966	h	5.3374804	-2.5789787	-0.0375951	c
2.8763910	3.3312004	-4.0336470	h	7.9318766	-1.7217475	0.8811472	c
2.6537491	5.7426859	0.0000000	h	8.6335524	0.8277710	-0.2649837	c
5.7245089	4.4412617	0.0000000	h	6.6090114	2.7939589	0.3173125	c
2.8763910	3.3312004	4.0336470	h	4.0145994	1.9216225	-0.5942892	c
4.2419916	0.7596984	2.4196966	h	3.2815943	-0.6334169	0.5337172	c
				0.7179638	-1.5591094	-0.4109890	c
#r13				-1.5161950	0.1056597	0.3183725	c
2.7452404	-0.3355212	2.3876184	c	-4.0451098	-1.0265904	-0.4646184	c
2.7452404	-0.3355212	-2.3876184	c	-6.2916657	0.6316095	0.2308801	c
-2.7452404	0.3355212	2.3876184	c	-8.8221075	-0.5019966	-0.5407294	c
-2.7452404	0.3355212	-2.3876184	c	-11.0469974	1.1808024	0.1676632	c
1.3592274	0.4938307	0.0000000	c	4.8333268	-4.3901888	0.8132718	h
-1.3592274	0.4938307	0.0000000	c	5.4053454	-2.8788937	-2.0851505	h
1.3541915	0.4940847	-4.7718859	c	7.8992333	-1.5516109	2.9412379	h
1.3541915	0.4940847	4.7718859	c	9.3580183	-3.1377930	0.4201686	h
-1.3541915	-0.4940847	-4.7718859	c	8.8091030	0.6228511	-2.3148208	h
-1.3541915	-0.4940847	4.7718859	c	10.4689092	1.4539077	0.4351542	h
1.3210198	2.5595684	-4.8520659	h	6.5361833	3.1035705	2.3601208	h
1.3210198	2.5595684	4.8520659	h	7.0931944	4.6040331	-0.5434719	h
-1.3210198	-2.5595684	-4.8520659	h	4.0383821	1.7413378	-2.6577522	h
-1.3210198	-2.5595684	4.8520659	h	2.5970765	3.3454239	-0.1340087	h
-2.9068313	2.3992609	-2.3725423	h	3.1688581	-0.4126761	2.5933964	h
-2.9068313	2.3992609	2.3725423	h	0.3920840	-3.4637011	0.3266357	h
2.9068313	-2.3992609	-2.3725423	h	0.7949093	-1.7401849	-2.4715373	h
2.9068313	-2.3992609	2.3725423	h	-1.5056690	0.4011078	2.3651235	h
-1.2582065	-2.5689467	0.0000000	h	-1.3262898	1.9705044	-0.5443732	h
1.2582065	2.5689467	0.0000000	h	-4.2657766	-2.8819873	0.4191262	h
2.3577115	-0.1541955	-6.4525221	h	-4.0425445	-1.3515745	-2.5060825	h
2.3577115	-0.1541955	6.4525221	h	-6.2888140	0.9652586	2.2710532	h
-2.3577115	0.1541955	-6.4525221	h	-6.0757178	2.4842278	-0.6604724	h
-2.3577115	0.1541955	6.4525221	h	-9.0345993	-2.3513319	0.3513529	h
-4.6693634	-0.4134619	-2.3726881	h	-8.8203800	-0.8350929	-2.5779187	h
-4.6693634	-0.4134619	2.3726881	h	-11.1057976	1.4960085	2.2021556	h
4.6693634	0.4134619	-2.3726881	h	-12.8422749	0.3472908	-0.3946525	h
4.6693634	0.4134619	2.3726881	h	-10.8907629	3.0207587	-0.7445370	h
#r14				#c1			
0.4318293	1.3859284	-1.3614732	c	1.6729611	1.6729611	-1.6729611	c
-0.4318293	-1.3859284	-1.3614732	c	-1.6729611	-1.6729611	-1.6729611	c
-3.3179691	-1.5541626	-1.3559001	c	-1.6729611	1.6729611	1.6729611	c
0.7682824	-2.8661703	0.8117196	c	1.6729611	-1.6729611	1.6729611	c
3.3179691	1.5541626	-1.3559001	c	3.3382000	0.0000000	0.0000000	c
-0.7682824	2.8661703	0.8117196	c	0.0000000	-3.3382000	0.0000000	c
-4.5087409	-0.0556840	0.8033853	c	0.0000000	0.0000000	3.3382000	c
3.6458278	-2.6940180	0.7287072	c	0.0000000	0.0000000	-3.3382000	c
4.5087409	0.0556840	0.8033853	c	-3.3382000	0.0000000	0.0000000	c
-3.6458278	2.6940180	0.7287072	c	0.0000000	3.3382000	0.0000000	c
-0.2567717	2.2451854	-3.1169037	h	4.5626650	1.1772004	1.1772004	h
0.2567717	-2.2451854	-3.1169037	h	1.1772004	-4.5626650	-1.1772004	h
-3.8987673	-3.5337509	-1.2663984	h	-1.1772004	-1.1772004	4.5626650	h
-4.0309123	-0.8014732	-3.1451932	h	-1.1772004	1.1772004	-4.5626650	h
0.1026893	-2.1472881	2.6287469	h	-4.5626650	1.1772004	-1.1772004	h
0.1612628	-4.8369643	0.7019315	h	-1.1772004	4.5626650	-1.1772004	h
3.8987673	3.5337509	-1.2663984	h	-1.1772004	-4.5626650	1.1772004	h
4.0309123	0.8014732	-3.1451932	h	1.1772004	1.1772004	4.5626650	h
-0.1026893	2.1472881	2.6287469	h	4.5626650	-1.1772004	-1.1772004	h
-0.1612628	4.8369643	0.7019315	h	-4.5626650	-1.1772004	1.1772004	h
-3.9827018	-0.8880866	2.6180844	h	1.1772004	4.5626650	1.1772004	h
-6.5641001	-0.1659046	0.6801826	h	1.1772004	-1.1772004	-4.5626650	h
4.4752784	-3.7538038	2.2910244	h	2.8648798	2.8648798	-2.8648798	h
4.3247711	-3.5675402	-1.0182943	h	-2.8648798	-2.8648798	2.8648798	h
3.9827018	0.8880866	2.6180844	h	-2.8648798	2.8648798	-2.8648798	h
6.5641001	0.1659046	0.6801826	h	2.8648798	-2.8648798	2.8648798	h
-4.4752784	3.7538038	2.2910244	h				
-4.3247711	3.5675402	-1.0182943	h	#c2			
				0.0000000	2.3608077	-2.4132986	c
#r15				0.0000000	-2.3608077	-2.4132986	c
1.0877892	0.9593877	0.9155793	c	2.3942614	0.0000000	0.9487680	c
5.0137101	2.6439314	-1.1883010	c	-2.3942614	0.0000000	0.9487680	c
2.3567480	5.5219940	1.4926784	c	0.0000000	0.0000000	-4.0822754	c
0.1551925	3.6723584	1.2620844	c	2.3570193	2.3508308	-0.7407544	c
4.0907500	5.3474738	-0.8035693	c	-2.3570193	2.3508308	-0.7407544	c
2.7912585	0.8166295	-1.4146280	c	-2.3570193	-2.3508308	-0.7407544	c
-1.0877892	-0.9593877	0.9155793	c	2.3570193	-2.3508308	-0.7407544	c
-0.1551925	-3.6723584	1.2620844	c	0.0000000	0.0000000	2.5743511	c
-2.3567480	-5.5219940	1.4926784	c	1.6652774	0.0000000	-5.3058647	h
-4.0907500	-5.3474738	-0.8035693	c	-1.6652774	0.0000000	-5.3058647	h
-5.0137101	-2.6439314	-1.1883010	c	2.3962560	4.0473218	0.4432988	h
-2.7912585	-0.8166295	-1.4146280	c	-2.3962560	4.0473218	0.4432988	h
2.2672251	0.5110030	2.5643558	h	-2.3962560	-4.0473218	0.4432988	h
6.2074209	2.5254285	-2.8657034	h	2.3962560	-4.0473218	0.4432988	h
6.1850840	2.0900752	0.4227184	h	4.0615940	2.3807424	-1.9130957	h
3.4402465	5.0740756	3.1954534	h	-4.0615940	2.3807424	-1.9130957	h
1.6543279	7.4476385	1.7188089	h	-4.0615940	-2.3807424	-1.9130957	h
-1.0060224	4.2136965	-0.3604455	h	4.0615940	-2.3807424	-1.9130957	h

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0.0000000	-1.6668833	3.8047651	h	-1.1789638	-4.5484504	1.1789638	h
0.0000000	1.6668833	3.8047651	h	4.5484504	-1.1789638	-1.1789638	h
0.0000000	4.0507353	-3.5996673	h	1.1789638	1.1789638	4.5484504	h
0.0000000	-4.0507353	-3.5996673	h	-1.1789638	-1.1789638	4.5484504	h
4.7337349	0.0000000	2.6160650	c	1.1789638	-4.5484504	-1.1789638	h
-4.7337349	0.0000000	2.6160650	c	4.5484504	1.1789638	1.1789638	h
4.7705613	1.6700812	3.8264587	h	-4.5484504	1.1789638	-1.1789638	h
-4.7705613	1.6700812	3.8264587	h	-1.1789638	1.1789638	-4.5484504	h
-4.7705613	-1.6700812	3.8264587	h	-1.1789638	4.5484504	-1.1789638	h
4.7705613	-1.6700812	3.8264587	h	-3.3484998	-3.3484998	-3.3484998	c
6.4498880	0.0000000	1.4713798	h	3.3484998	3.3484998	-3.3484998	c
-6.4498880	0.0000000	1.4713798	h	-3.3484998	3.3484998	3.3484998	c
				3.3484998	-3.3484998	3.3484998	c
#c3				2.1968775	4.5587125	-4.5587125	h
0.0000000	-2.3591616	-2.7624812	c	-4.5587125	4.5587125	2.1968775	h
0.0000000	2.3591616	-2.7624812	c	-4.5587125	-2.1968775	-4.5587125	h
-2.3516463	0.0000000	0.6096601	c	4.5587125	2.1968775	-4.5587125	h
2.3516463	0.0000000	0.6096601	c	-2.1968775	4.5587125	4.5587125	h
0.0000000	0.0000000	-4.4338647	c	-4.5587125	-4.5587125	-2.1968775	h
-2.3697338	-2.3413755	-1.1000406	c	4.5587125	4.5587125	-2.1968775	h
-2.3697338	2.3413755	-1.1000406	c	-4.5587125	2.1968775	4.5587125	h
2.3697338	2.3413755	-1.1000406	c	-2.1968775	-4.5587125	-4.5587125	h
2.3697338	-2.3413755	-1.1000406	c	2.1968775	-4.5587125	4.5587125	h
0.0000000	0.0000000	2.3391276	c	4.5587125	-4.5587125	2.1968775	h
-1.6662780	0.0000000	-5.6565240	h	4.5587125	-2.1968775	4.5587125	h
1.6662780	0.0000000	-5.6565240	h				
-2.4837222	-4.0736142	0.0111610	h	#c5			
-2.4837222	4.0736142	0.0111610	h	4.3654019	-0.0000095	0.0000000	c
2.4837222	4.0736142	0.0111610	h	3.3912631	-1.3607013	-2.3568101	c
2.4837222	-4.0736142	0.0111610	h	4.0942474	-0.4196153	-4.0578868	h
-4.0532260	-2.2918558	-2.2986171	h	0.5033902	-1.3607535	-2.3568956	c
-4.0532260	2.2918558	-2.2986171	h	4.0942368	-3.3044256	-2.3923605	h
4.0532260	2.2918558	-2.2986171	h	3.3912598	2.7213997	0.0000000	c
4.0532260	-2.2918558	-2.2986171	h	6.4298640	-0.0000069	0.0000000	h
0.0000000	2.3057954	4.0862041	c	3.3912631	-1.3607013	2.3568101	c
0.0000000	-2.3057954	4.0862041	c	-0.5033902	1.3607535	-2.3568956	h
0.0000000	-4.0497140	-3.9480540	h	-0.5033769	-2.7215019	0.0000000	c
0.0000000	4.0497140	-3.9480540	h	-0.1964414	-2.3350566	-4.0444253	h
-4.0428501	0.0000000	1.8033490	h	0.1964414	2.3350566	-4.0444253	h
4.0428501	0.0000000	1.8033490	h	-4.3654019	0.0000095	0.0000000	c
1.6667758	2.2654362	5.3018284	h	-3.3912631	1.3607013	-2.3568101	c
1.6667758	-2.2654362	5.3018284	h	-3.3912598	-2.7213997	0.0000000	c
-1.6667758	2.2654362	5.3018284	h	-4.0942261	-3.7240365	-1.6655457	h
-1.6667758	-2.2654362	5.3018284	h	0.1964489	-4.6701025	0.0000000	h
0.0000000	4.0982342	3.0865511	h	4.0942261	3.7240365	-1.6655457	h
0.0000000	-4.0982342	3.0865511	h	4.0942261	3.7240365	1.6655457	h
				0.5033769	2.7215019	0.0000000	c
#c4				4.0942474	-0.4196153	4.0578868	h
-1.6893365	-1.6893365	-1.6893365	c	4.0942368	-3.3044256	2.3923605	h
1.6893365	1.6893365	-1.6893365	c	0.5033902	-1.3607535	2.3568956	c
-1.6893365	1.6893365	1.6893365	c	-4.0942368	3.3044256	-2.3923605	h
1.6893365	-1.6893365	1.6893365	c	-4.0942474	0.4196153	4.0578868	h
-3.3188898	0.0000000	0.0000000	c	-0.1964489	4.6701025	0.0000000	h
0.0000000	0.0000000	-3.3188898	c	-0.1964414	-2.3350566	4.0444253	h
0.0000000	3.3188898	0.0000000	c	-0.5033902	1.3607535	2.3568956	c
0.0000000	-3.3188898	0.0000000	c	-4.0942474	0.4196153	-4.0578868	h
3.3188898	0.0000000	0.0000000	c	-3.3912631	1.3607013	2.3568101	c
0.0000000	0.0000000	3.3188898	c	-4.0942261	-3.7240365	1.6655457	h
-4.5484504	-1.1789638	1.1789638	h	-6.4298640	0.0000069	0.0000000	h
1.1789638	-1.1789638	-4.5484504	h	0.1964414	2.3350566	4.0444253	h
1.1789638	4.5484504	1.1789638	h	-4.0942368	3.3044256	2.3923605	h