

Stability of Hydrocarbons of the Polyhedrane Family Containing Bridged CH Groups: A Case of Failure of the Colle–Salvetti Correlation Density Functionals. [*Journal of Chemical Theory and Computation*, 2010, 6, 3442]. Grigory A. Shamov* Georg Schreckenbach and Peter H. M. Budzelaar

With this Erratum, we would like to correct our paper published in the November 2010 issue of the *Journal of Chemical Theory and Computation*.¹ In the paper, we have used MP2 and one of its spin-scaled variants (first invented by Grimme²), as benchmark values for determining the performance of a variety of density functionals. In our paper,¹ in the method labeled as “SOS-MP2”, we have (inadvertently) used an opposite-spin correlation energy scaling factor of 2.0 instead of the value of 1.3 recommended by Head-Gordon and co-workers.³ We apologize to the readers of the *Journal of Chemical Theory and Computation* for any inconvenience this error might have caused. The results in our paper (we label them as “2SOS-MP2” here to distinguish from the original one) thus had some overestimation of the correlation energy for all the compounds, acetylene to **1–8**. Unfortunately, the method was used as a base method to present and compare MP2 and DFT results against. To avoid the confusion resulting from the fact that our benchmarking method was not what it was called in the paper, we would like to provide the results relative to a correct spin-scaling scheme. Among several proposed^{2–6} scaling schemes for MP2, the scheme by King,⁶ with the same-spin scaling of 0.5 and the opposite-spin scaling of 1.28, correspondingly, was chosen, since it was shown to yield the best agreement with accurate CCSD(T) results for ethylene dimer potential energy surfaces. We label the scheme SCS-MP2(King) below.

We provide the corrected versions of Tables 2–4, substituting the wrong 2SOS-MP2 values with the SCSMP2(King) ones. The results incorrectly called “SOS-MP2” in our paper, now labeled 2SOS-MP2, are retained/provided for comparison. We also present the corrected Figure 2, with MAD’s for the density functionals plotted against the SCS-MP2(King) values, instead of the 2SOS-MP2. The following corrections to the discussion of results have to be made.

In all the occurrences throughout the article, SCS-MP2(King) should be read instead SOS-MP2 (Page 3447, right column, last paragraph should read “We have also computed canonical MP2 as spin-scaled MP2, SCS-MP2(King)”; page 3452, left column, paragraph 4, should be “closer to SCS-MP2(King) values”; same page, second paragraph, “the largest difference from SCS-MP2-(King) isomerization energies”; page 3453, right column, second and fourth paragraphs, etc.).

The statement on the page 3448, first paragraph, “SOS-MP2 energy differences are closer to CCSD(T) than the SCS-MP2” is incorrect and should be dropped.

On the page 3450, second last paragraph: The RHF method for the binding energies of **1a–4a** from the acetylene has now MAD of 6.44, which is not “under 5 kcal/mol”; the functionals enumerated next however still perform worse than RHF (Table 2).

On page 3451, right column, the first paragraph: “HFB and HFG, which have MADs of about 24 kcal/mol” instead of “22 kcal/mol”.

On page 2452, left column, second paragraph, MAD for the RHF methods should be 22.03, for OLYP 15.24 kcal/mol, correspondingly.

Table 2. Binding Enthalpies Per Acetylene Monomer ΔE_b ^a of Polyhedranes **1a–4a (kcal/mol)^b**

method	1a	2a	3a	4a	MAD
SCS-MP2(King)	−46.0	−50.1	−54.6	−53.0	
2SOS-MP2	1.7	1.5	1.6	1.5	1.6
MP2	−2.7	−2.6	−2.6	−2.6	2.6
B2PLYP(0)	3.9	4.1	4.2	4.5	4.2
B2PLYP(2)	2.8	2.9	3.0	3.1	3.0
HFB	29.5	30.8	31.9	32.4	31.1
HFO	21.6	23.6	25.3	26.0	24.1
HFG	29.6	31.0	32.3	32.9	31.4
M06-L	−2.5	−1.2	−0.5	−0.5	1.2
M06-2X	−2.1	−1.5	−1.3	−1.4	1.6
KT3	−8.6	−8.7	−8.3	−8.2	8.4
B86LYP	12.1	12.4	12.9	13.0	12.6
BLYP ^c	10.9	11.3	11.8	11.9	11.5
BLYP-D ^c	7.0	6.2	6.3	6.0	6.4
BPBE ^c	0.7	1.5	2.2	2.4	1.7
BPBE-D ^c	−2.6	−3.0	−2.6	−2.8	2.8
OLYP ^c	3.7	5.1	6.2	6.5	5.4
OLYP-D ^c	−0.2	−0.1	0.6	0.5	0.3
PBE ^c	−3.8	−3.4	−2.9	−2.9	3.2
PBE-D ^c	−6.2	−6.6	−6.4	−6.6	6.5
BW	23.2	24.2	25.1	25.5	24.5
RHF	6.1	6.4	6.5	6.9	6.4
BLYP-LC ^d	−8.1	−7.2	−8.5	−8.5	8.1
GLYP-LC ^d	−9.0	−7.8	−9.4	−9.4	8.9
BOP-LC ^d	−5.8	−5.8	−5.7	−5.5	5.7
BOP ^d	13.4	14.1	14.8	15.1	14.3
B97 ^d	−0.4	−1.5	−0.3	−0.1	0.6
B97-D ^d	4.8	0.5	4.6	4.3	3.6
O2PLYP(2)	−0.7	−0.2	0.2	0.4	0.4
O2PLYP(0)	0.2	0.8	1.2	1.6	1.0
GLYP	11.3	11.8	12.5	12.8	12.1
oBLYP	8.2	8.4	8.9	9.0	8.6
oBLYP-D	4.6	4.7	4.8	4.6	4.7
BPW92	19.1	19.9	20.7	21.0	20.2
OPBE	−8.6	−7.2	−6.0	−5.5	6.8
PBEsol	−12.8	−12.8	−12.5	−12.5	12.7
B2PLYP-D	0.4	0.5	0.4	0.3	0.4
B3LYP-Cpot ^d	−9.0	−9.3	−10.5	−10.4	9.8
B3LYP	4.9	5.1	5.4	5.5	5.2
RGE2	−3.8	−3.5	−3.0	−2.9	3.3
O3LYP	−8.0	−7.6	−7.2	−7.0	7.5
TCA	11.3	12.8	13.8	14.0	13.0

^a $\Delta E_b = (E(C_2H_2)_m - mE(C_2H_2))/m$. ^b The SCS-MP2(King) are actual values (*in italics*); for the other methods, and differences with respect to SCS-MP2(King) values are shown. ^c Priroda L22 energies on optimized geometries a DFT/L11 level. ^d GAMESS-US cc-CVTZ energies on Priroda MP2/L2 geometries.

Table 3. Relative Energies of Hydrogenated Species of 1a, 5a–c, and 7 with Respect to Tricyclododecatetraene 1b and Its Hydrogenated Derivatives 6 and 8, Correspondingly (kcal/mol)^a

method	5a → 6	5b → 6	5c → 6	7 → 8	MAD
SCS-MP2(King)	35.8	11.2	−5.33	47.23	
2SOS-MP2	3.54	3.23	3.31	2.57	3.36
MP2	−0.78	−1.29	−0.11	−0.55	0.82
B2PLYP(0)	−14.66	−9.94	−13.59	−11.55	13
B2PLYP(2)	−11.57	−7.95	−9.87	−9.08	10.22
HFB	−47.47	−36.24	−39.18	−38.17	42.87
HFO	−28.48	−19.02	−21.34	−25.53	24.52
HFG	−43.99	−33.56	−36.3	−35.41	39.68
M06-L	−6.14	2.29	0.65	−10.2	4.24
M06-2X	−5.3	1.47	−0.94	−8.19	3.52
KT3	0.59	3.58	2.4	−0.34	2.04
B86LYP	−31.27	−22.5	−25.22	−25.19	27.74
BLYP ^c	−28.19	−39.17	−3.72	−23.09	25.12
BLYP-D ^c	−26.24	−36.98	−1.88	−21.28	23.24
BPBE ^c	−9.44	−21.48	12.98	−9.95	12.25
BPBE-D ^c	−7.9	−19.73	14.55	−8.56	11.39
OLYP ^c	−10.18	−21.96	12.68	−11.24	12.71
OLYP-D ^c	−8.38	−19.92	14.34	−9.58	11.66
PBE ^c	−7.06	−19.57	14.79	−7.84	10.84
PBE-D ^c	−6.04	−18.41	15.91	−6.94	10.29
BW	−40.61	−30.23	−33.27	−32.65	36.4
RHF	−13.29	−10.12	−14.66	−9.76	12.37
BLYP-LC ^b	0.94	3.8	1.82	−1.24	2.5
GLYP-LC ^b	2.14	4.68	2.72	−0.25	3.17
BOP-LC ^b	1.31	4.53	2.52	−1.44	3.12
BOP ^b	−28.21	−19.83	−22.16	−23.06	24.73
B97 ^b	−10.42	−6.85	−8.87	−8.34	8.92
B97-D ^b	−21.97	−12.68	−15.31	−19.32	18.45
O2PLYP(2)	−2.57	0.31	−1.28	−3.18	1.59
O2PLYP(0)	−5.27	−1.24	−4.5	−5.43	3.84
GLYP	−24.67	−17.48	−19.79	−19.85	21.74
oBLYP	−25.12	−17.64	−20.02	−20.24	22.11
oBLYP-D	−28.08	−17.35	−19.07	−23.56	21.8
BPW92	−36.2	−26.35	−29.53	−29.1	32.25
OPBE	12.04	15.09	14.47	5.4	13.43
PBEsol	4.97	7.95	7.21	1.72	6.21
B2PLYP-D	−13.14	−7.41	−9.14	−10.8	9.7
B3LYP-Cpot ^b	0.12	0.27	−1.48	0.6	0.72
B3LYP	−18.59	−12.4	−15.29	−15.11	16.21
RGE2	−6.69	−1.41	−2.85	−7.31	4.53
O3LYP	1.66	5.39	3.59	−0.79	3.44
TCA	−24.15	−13.86	−16.27	−22.48	20.02

^a The SCS-MP2(King) are actual values (*in italics*), while for other methods differences with respect to it are shown. ^b Priroda L22 energies on optimized geometries a DFT/L11 level. ^c GAMESS-US cc-CVTZ energies on Priroda MP2/L2 geometries.

On page 3452, left column, fourth paragraph, we stated “The OPTX-based double hybrid, in contrast to B2PLYP, performs very well also. Among the pure, uncorrected GGAs, the KT3 functional is the best”. This should be modified as follows. The KT3 functional yields a reasonably good performance for

Table 4. Calculated Relative Energies of Isomers of Compounds 1–4 (kcal/mol)^a

method	1a → 1e	1a → 1d	1b → 1a	1b → 1c	2b → 2a	2b → 2c	3b → 3a	3b → 3c	4b → 4a	4b → 4c
SCS-MP2(King)	−41.5	26.0	−37.1	5.1	−55.4	−48.4	−84.0	−40.8	−69.9	−33.0
MP2	6.7	−1.4	1.9	0.3	−0.6	4.0	−1.4	−0.5	−0.3	−2.7
2SOS-MP2	−0.6	4.2	−4.5	−0.1	−4.3	−6.9	−5.1	−9.0	−5.3	−12.0
B2PLYP(0)	−25.4	−15.3	15.1	−1.9	21.8	8.1	27.6	27.7	21.5	39.5
B2PLYP(2)	−20.6	−12.6	12.3	−2.2	16.6	1.1	21.0	11.8	15.4	14.9
HFB	−70.8	−53.3	51.3	−15.0	68.0	−1.7	87.1	30.4	73.0	42.4
HFO	−43.2	−28.2	28.0	−11.4	40.6	5.0	56.6	35.5	42.0	50.6
HFG	−66.7	−49.2	47.6	−14.1	63.1	0.2	81.5	31.9	67.0	42.8
M06-L	−10.8	−1.9	1.4	−2.8	11.3	−3.7	22.8	5.5	16.3	2.5
M06-2X	−4.0	−1.7	1.4	−1.4	10.0	3.7	14.2	11.1	11.9	16.9
KT3	−2.7	3.3	−1.4	2.6	−6.0	5.8	−5.5	13.3	−14.9	13.3
B86LYP	−47.7	−34.5	33.4	−8.1	43.3	−1.2	55.0	19.8	43.4	25.9
BLYP ^b	−42.7	−31.4	30.0	−8.8	39.3	−0.1	49.7	18.3	38.7	24.0
BLYP-D ^b	−35.0	−29.8	27.2	−5.0	28.1	−6.0	35.8	−0.1	30.1	0.9
BPBE ^b	−14.9	−7.4	8.3	−4.3	13.0	5.1	19.7	17.3	9.5	20.1
BPBE-D ^b	−8.2	−6.2	6.0	−0.7	3.1	−0.3	7.3	1.0	1.8	−0.1
OLYP ^b	−17.0	−7.5	8.3	−7.0	15.3	6.3	24.1	24.1	13.2	34.1
OLYP-D ^b	−9.4	−6.1	5.8	−2.3	3.7	0.5	9.6	5.5	4.0	11.0
PBE ^b	−11.2	−4.9	6.0	−2.2	9.3	4.4	14.2	13.4	5.3	14.4
PBE-D ^b	−6.4	−4.2	4.4	−0.2	2.1	0.3	5.3	1.5	−0.2	0.1
BW	−61.8	−45.2	43.4	−12.5	57.5	−1.1	73.4	27.6	59.3	36.9
RHF	−21.1	−14.0	13.8	−0.6	21.6	17.3	27.8	42.7	24.9	64.2
BLYP-LC ^c	5.2	4.7	−3.4	2.7	8.1	12.7	−2.3	18.1	−5.0	22.7
GLYP-LC ^c	6.8	6.1	−4.7	3.1	8.4	13.0	−4.6	18.0	−7.2	22.5
BOP-LC ^c	5.7	5.8	−4.5	1.8	−2.5	13.8	−2.1	21.5	−6.2	27.0
BOP ^c	−43.4	−30.4	29.6	−8.3	39.3	1.4	50.8	23.4	37.8	28.9
B97 ^c	−17.5	−10.1	10.6	−1.8	2.9	6.0	14.5	19.9	5.0	24.9
B97-D ^c	−28.4	−23.0	21.1	−5.4	−9.1	−6.5	29.5	0.5	23.8	3.8
O2PLYP(2)	−7.5	−0.6	1.3	−0.4	3.6	4.8	6.7	14.8	0.7	19.3
O2PLYP(0)	−11.5	−2.8	3.5	−0.1	8.0	11.2	12.2	29.5	5.5	42.3
GLYP	−39.9	−26.9	26.7	−6.0	34.4	2.1	44.7	21.3	32.8	24.4
oBLYP	−39.4	−27.5	27.1	−5.7	34.8	0.4	44.3	17.7	33.5	20.8
oBLYP-D	−28.1	−20.9	19.6	−5.7	26.0	−5.8	31.6	3.5	25.3	7.7
BPW92	−56.4	−40.1	38.3	−10.9	51.0	−0.9	65.0	25.8	50.9	33.7
OPBE	14.7	20.1	−16.8	2.7	−18.0	12.9	−15.2	22.6	−25.6	26.1
PBEsol	5.8	9.2	−6.6	3.9	−8.1	7.0	−6.9	8.8	−13.6	4.7
B2PLYP-D	−12.9	−8.0	7.0	−1.5	11.3	−2.4	14.3	2.6	11.4	4.6
B3LYP	−0.1	1.1	−5.1	1.4	−3.5	0.0	−15.6	−1.6	−16.9	−5.5
Cpot ^c										
B3LYP	−31.0	−19.7	19.5	−3.6	26.3	3.2	33.5	20.5	24.6	26.3
RGE2	−11.2	−4.4	5.6	−0.7	8.1	4.4	13.0	13.8	3.9	13.8
O3LYP	−1.5	5.7	−3.9	2.1	−2.6	8.0	0.1	17.2	−7.8	19.9
TCA	−35.7	−23.3	22.9	−8.0	36.0	1.5	49.0	23.4	37.2	31.4

^a See Scheme 2 in the original paper for a description of the isomers. The SCS-MP2(King) values are the actual isomerization energies (*in italics*); for the other methods, differences from the SCS-MP2(King) values are shown. ^b GAMESS-US cc-CVTZ energies on Priroda MP2/L2 geometries. ^c Priroda L22 energies on optimized geometries a DFT/L11 level.

both sets, but RGE2 and PBEsol have very close MADs to it. The former functional, KT3, is slightly more accurate for the polyhedrane set while the two latter are slightly more accurate for the cyclophanes; overall performance is thus similar. As to comparison of the O2PLYP with B2PLYP and especially B2PLYP-D, the former double hybrid has shown better agreement with SCS-MP2(King) for the polyhedranes, the latter two, especially B2PLYP-D, have now much smaller MADs for the cyclophanes (under 3 kcal/mol for the B2PLYP-D, about 10 kcal/mol for O2PLYP).

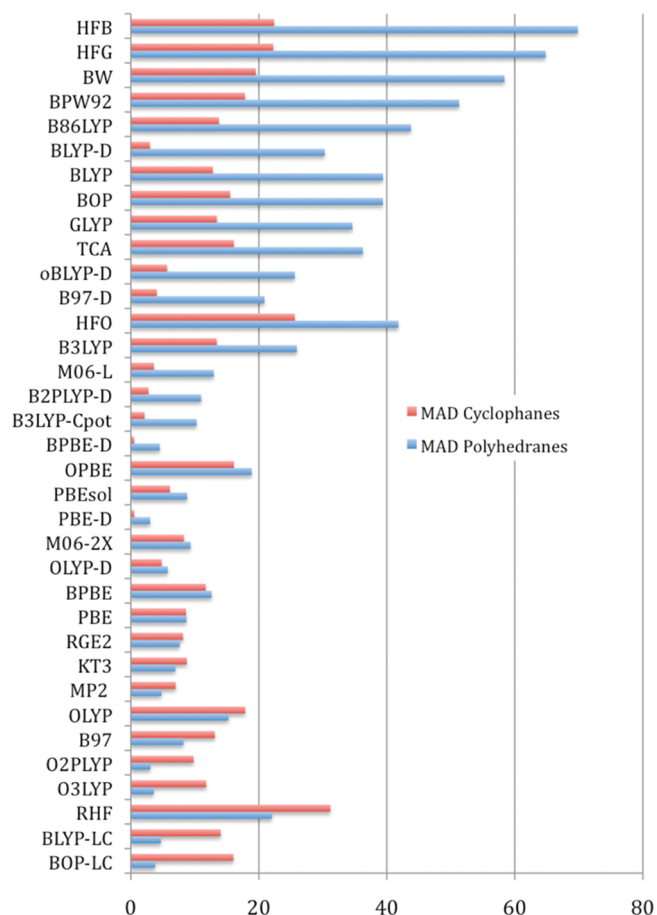


Figure 2. Mean absolute differences (MAD) for cyclophane and polyhedrane isomerization, relative to SCS-MP2(King) computed values, kcal/mol.

On page 3454, first paragraph, should read “among the pure GGA functionals, KT3 and RGE2 functionals have shown good performance on both sets of molecules.”

ACKNOWLEDGMENT

We thank Professor Dr. Stefan Grimme, University of Muenster, for notifying us of the existence of a problem with our “SOS-MP2” values.

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DOI: 10.1021/ct200004s

Published on Web 02/02/2011