Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Concave or convex π-dimers: the role of the pancake bond in substituted phenalenyl radical dimers

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Electronic Supplementary Information

I. Computational and crystal modeling of the monomers.

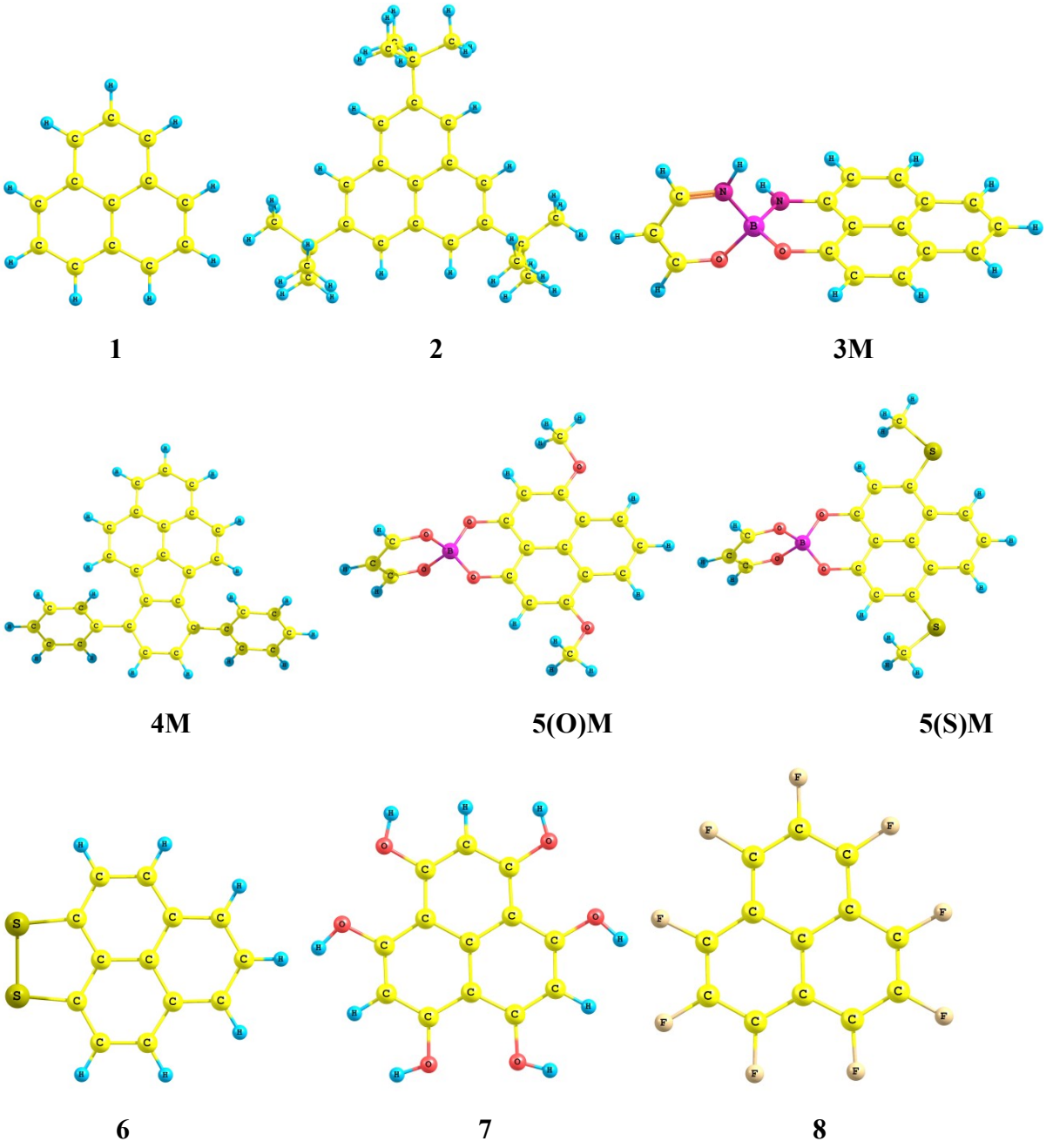


Chart S1. Computational modeling of the monomers for PLY-bearing dimers. Compounds designated with an M are models used in the geometry optimizations and energy calculations.

II. Tables of the refcodes of the crystal structures.

Table S1. The CSD[1] refcodes of crystal structures used in the analysis. Green: small |Δ|, blue: Δ>0, *red*: Δ<0.

Type ($\mathbf{2_2}$)	Type ($\mathbf{3_2}$)	Type ($\mathbf{4_2}$)	Type ($\mathbf{5_2}$)	Type ($\mathbf{6_2}$)
CORFIY	UBUREO[a]	UGEFOC	QAMVUX	DIBTEO
	UBUQIR[a]	OPOPOZ	QAMVUX01	
	LIHFOY	RAYBEA	QAMWEI(I)	
	ECUBAG(II)	UGEFUI	QAMWEI(II)	
	BIJWEX	UGEFUI01	QAMWEI01	
	NAFPIU	UGEFUI02	ECUBEK	
	FUTHEI(I)	TAXHUW	QIXWEA	
	FUTHEI01		LIHFIS	
			ECAFIY	
			DIBSUD	

[a]There are 13 and 14 additional crystal structures for UBUREO and UBUQIR with different temperatures, respectively.

Table S1 lists 54 crystal structure refcodes from CSD that were included in the analysis of the paper. Symbols (I) and (II) refer to different fragments in a given crystal structure. The symbols $\mathbf{2_2}$, $\mathbf{3_2}$, $\mathbf{4_2}$, $\mathbf{5_2}$, and $\mathbf{6_2}$ refer to models that are closest to the dimers in each column. These dimers were subject to computational the study discussed in the paper.

Type $\mathbf{2_2}$: Tert-butyl substituents at the β-carbons create vdW repulsions due to steric crowding. The effect of this is discussed in the main text.

Type $\mathbf{3_2}$: One of two PLY units retains approximately one electron, the other donates approximately one electron to the spiro-boron center. The pancake dimer is formed on the side where the radical electron resides as indicated by the crystal structure.

Type $\mathbf{4_2}$: Each phenalenyl participates in one pancake bond forming chains from diradicals containing two phenalenyl units each.

Type $\mathbf{5_2}$: Each phenalenyl participates in one pancake bond forming chains. Every other phenalenyl loses one π-electron to the central boron for all in this group except for QIXWEA (TCNQ acceptor molecules). In the case of DIBSUD (CF_3SO_3 solvents in the crystal) partial charge transfer is suspected. These are partial pancake bonded PLY units.

Type $\mathbf{6_2}$: Nonbonded S…S intermolecular interaction affect packing.

Table S2. The CSD refcodes of crystal structures not used in the analysis[a]

Type I	Type II	Type III	Type IV	Type V
BIJWIB	DAVYOQ	DIBTIS	LELFAL	KAMFOV
FUTHIM	DAVYUW	PIJCOB	LELFIT	
LIHFUE	INIREC	QAMVOR	LELFUF	
	RECZAC		MAZTEO	
	UROJIV		TASSEN	
	VALREG		TASSOX	
	VINLUZ			
	VUSPEF			

[a]There are 130 structures for fullerenes and 157 structures for polycyclic arenes. These were eliminated one-by-one from the analysis as they did not contain PLY-derivative radicals.

Type I: Charge transfer from the PLY to tetrahedral spiro-conjugated boron. BIJWIB and LIHFUE contain sigma bonded dimers. In FUTHIM the remaining electron per unit is transferred to an anion.

Type II: Localized PLY derivatives with approximate local D_{3h} symmetry broken; not a PLY radical motif.

Type III: Charges on PLY; not a PLY radical motif.

Type IV: Charge transfer between PLY and Al or Zn; not a PLY radical motif. An example in this group is discussed below this table.

Type V: Charge transfer to solvent, PLY^{+}, no pancake bonding.

The crystal structure with the refcode TASSEN (Type IV in Table S2) was investigated at the UM05-2X/6-31+G(d,p) level. We found a small Δ value of 0.004 Å. Both computed D_{cc} and $D_{\alpha\alpha}$ values (at 3.431 and 3.427 Å at the equilibrium structure, respectively) are slightly longer than the vdW distance. Due to the tetrahedral Al attached to the PLY unit a significant charge transfer occurs from the PLY fragment to Al, which leads to a loss of the SOMO electron on each molecule. Thus, the radical nature of the PLY fragment is lost. As a result of this charge

transfer, stacking is dominated by the vdW interaction rather than the SOMO-SOMO interaction. Another sign of the loss of pancake bonding in this case is a significant parallel shift seen in the X-ray structure that indicates more typical vdW packing and not maximum SOMO-SOMO overlap together with intermolecular distances also close to typical vdW values.

III. Correlations between experimental and theoretical Δ values.

Table S3 and Figure S1 show inter-radical distances and Δ values using two density functionals.[2] The performance of UM05-2X/6-31+G(d,p) is superior and these data were used in the analysis presented in the main text.

Table S3. Experimental and theoretical inter-radical distances and Δ values of phenalenyl based π dimers. ($\Delta = D_{cc} - D_{\alpha\alpha}$)

Species	Experimental[a]			UM05-2X/6-31+G(d,p)[b]			UM06-2X/6-31+G(d,p)[b]		
	D_{cc} (Å)	$D_{\alpha\alpha}$ (Å)	Δ (Å)	D_{cc} (Å)	$D_{\alpha\alpha}$ (Å)	Δ (Å)	D_{cc} (Å)	$D_{\alpha\alpha}$ (Å)	Δ (Å)
2_2	3.201	3.306	-0.105	3.239	3.334	-0.095	3.098	3.154	-0.056
3_2	3.212	3.164	0.048	3.205	3.160	0.045	3.169	3.101	0.068
4_2	3.206	3.108	0.098	3.250	3.126	0.124	3.192	3.066	0.126
$5(O)_2$	3.247	3.227	0.020	3.179	3.155	0.024	3.144	3.094	0.050
$5(S)_2$	3.265	3.257	0.008	3.205	3.187	0.018	3.151	3.116	0.035
6_2	3.218	3.177	0.041	3.246	3.238	0.008	3.178	3.154	0.024

[a]Average values.
[b]Fully geometry optimized structures. For **3_2**, **4_2**, **$5(O)_2$**, and **$5(S)_2$** models designated as M in Chart S1 were used.

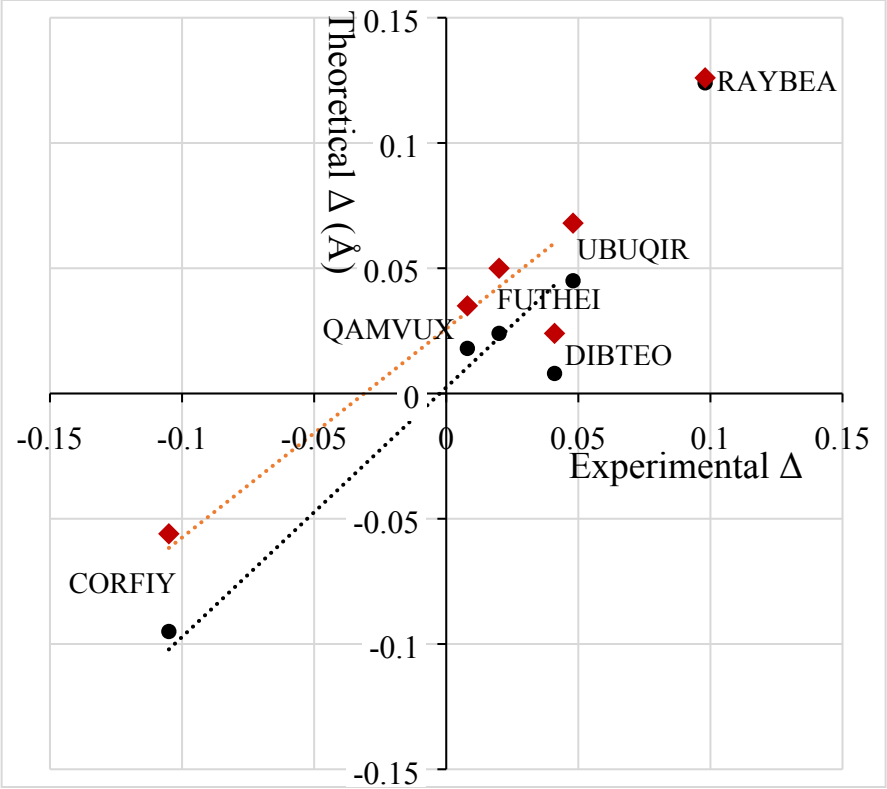


Figure S1. The correlation between experimental and theoretical Δ values (black circles and red diamonds based on UM05-2X/6-31+G(d,p) and UM06-2X/6-31+G(d,p), respectively). The CSD Refcode of the crystal structures were provided for each experimental data point. Correlation is based on data in Table S3.

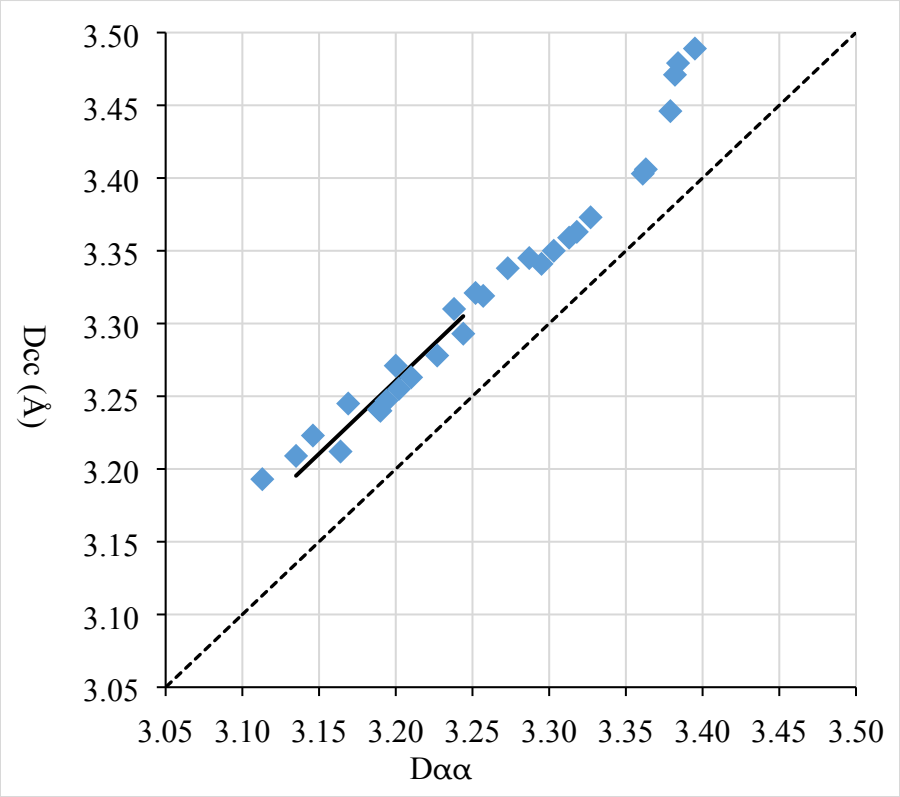
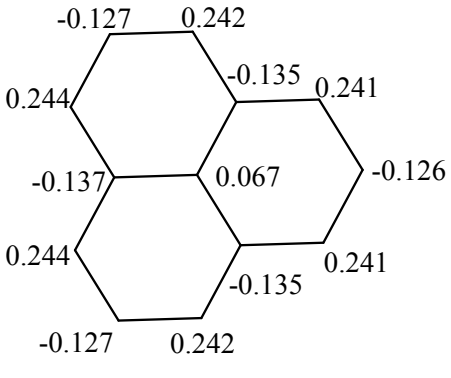


Figure S2. The trend line for the Haddon's compounds calculated from 29 structures.

IV. Spin densities

The significant spin density on the α-position carbon indicates that these π dimers possess strong and very similar diradical character as shown in Sigure S3 and Table S4.

1



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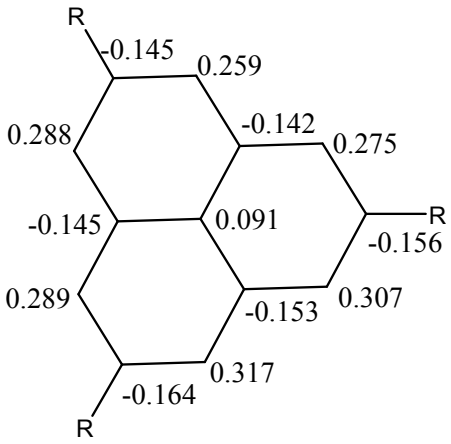

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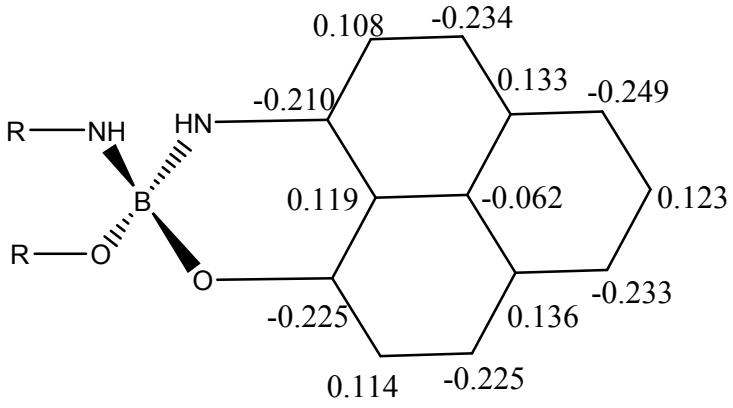
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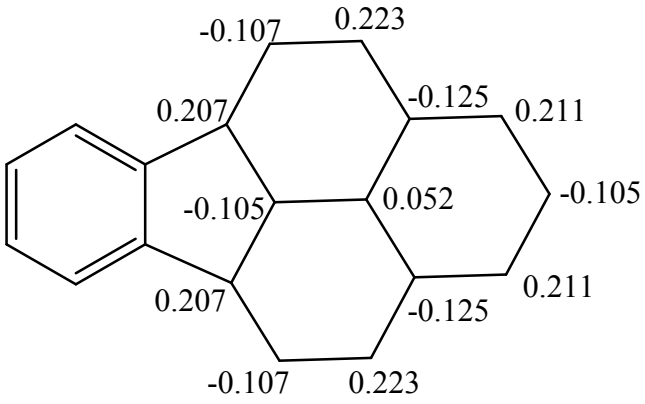
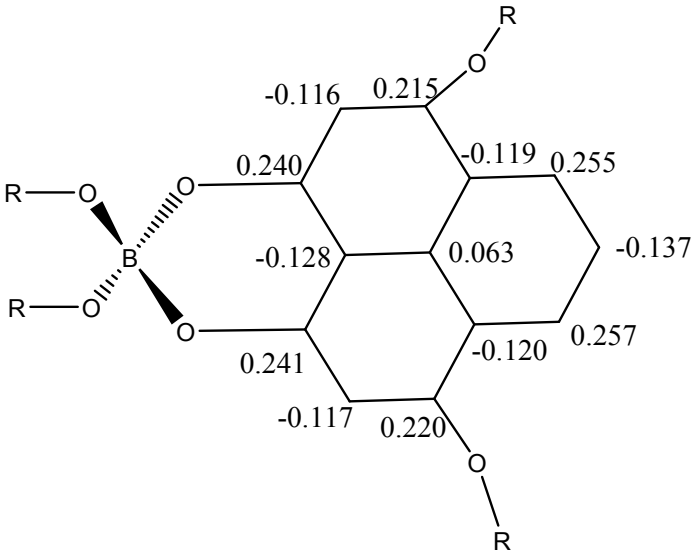
-0.234
0.133
-0.249
-0.210
HN
R—NH
B
0.119
-0.062
0.123
R—O
O
-0.233
-0.225
0.136
0.114
-0.225

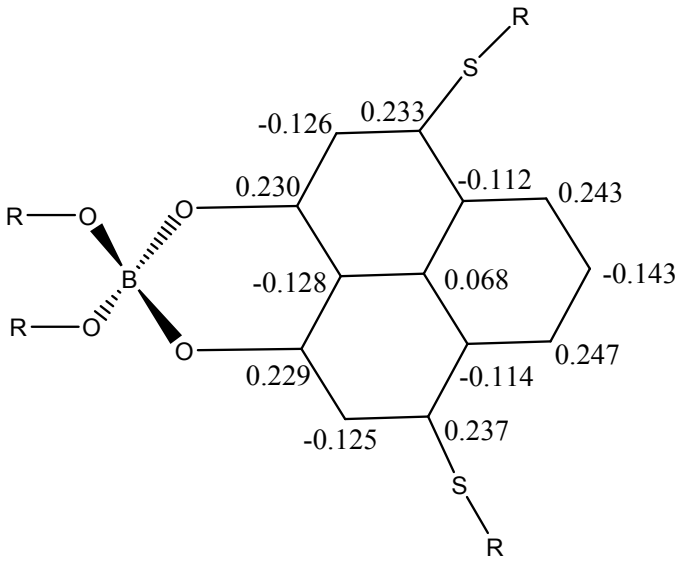
4


-0.107
0.223
0.207
-0.125
0.211
-0.105
0.052
-0.105
0.211
0.207
-0.125
-0.107
0.223

5(O)


R
O
-0.116
0.215
-0.119
0.255
0.240
O
R—O
B
-0.128
0.063
-0.137
R—O
O
0.257
-0.120
0.241
-0.117
0.220
O
R

5(S)



6

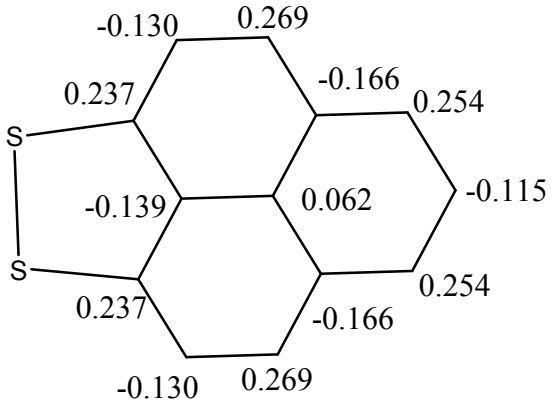


Figure S3. Spin density obtained at the UM05-2X/6-31+G(d,p) level.

Table S4. Computed spin densities at the UM05-2X/6-31+G(d,p) level

Species	CSD Refcode	Spin density on α-carbon[a]
1_2		0.242
2_2	CORFIY	0.289
3_2	UBUQIR	0.230[b]
4_2	RAYBEA	0.214 [b]
5_2 (O)	FUTHEI	0.238 [b]
5_2 (S)	QAMVUX	0.237 [b]
6_2	DIBTEO	0.253
7_2		0.233
8_2		0.254

[a]Value refers to the average over six α-carbons in one monomer at the equilibrium geometry of the dimer. [b]Calculations were done on simplified model dimers as listed in Chart S1.

V. Geometries of the optimized structures.

1_2: UM05-2X/6-31+G(d,p), --1001.59508979 Hartrees

C	0.000085000	0.000049000	1.580390000
C	-0.000085000	-0.000049000	-1.580310000
C	-1.233657000	-0.712252000	-1.574320000
C	1.233658000	0.712253000	1.574390000
C	-1.206705000	-2.126482000	-1.561229000
C	2.444940000	-0.018196000	1.561167000
C	-2.444940000	0.018203000	-1.561229000
C	1.206712000	2.126478000	1.561167000
C	-0.000058000	-2.815675000	-1.579031000
C	2.438477000	-1.407774000	1.578762000
C	-2.438475000	1.407787000	-1.579031000
C	0.000071000	2.815670000	1.578762000
C	-1.206885000	2.126664000	1.562200000
C	-1.238305000	2.108529000	-1.562290000
C	1.238302000	-2.108525000	1.562200000
C	1.206887000	-2.126668000	-1.562290000
C	-1.233252000	0.712334000	1.574807000
C	-0.000271000	1.424194000	-1.574718000
C	0.000273000	-1.424194000	1.574807000
C	1.233253000	-0.712332000	-1.574718000
C	-2.444877000	-0.017909000	1.561706000
C	1.237939000	2.108370000	-1.561439000
C	-1.237948000	-2.108371000	1.561706000
C	2.444872000	0.017901000	-1.561439000
C	-2.437783000	-1.407455000	1.578027000
C	2.437778000	1.407452000	-1.577720000
H	-2.146026000	-2.666952000	-1.560739000
H	3.382659000	0.525049000	1.560485000
H	-3.382661000	-0.525037000	-1.560739000
H	2.146035000	2.666944000	1.560485000
H	-0.000216000	-3.899054000	-1.578909000
H	3.376794000	-1.949320000	1.578435000
H	-3.376788000	1.949340000	-1.578909000
H	0.000236000	3.899050000	1.578435000
H	-2.146388000	2.666611000	1.561701000
H	-1.236163000	3.192137000	-1.561855000
H	1.236159000	-3.192133000	1.561701000

H	2.146390000	-2.666617000	-1.561855000
H	-3.382661000	0.525079000	1.561397000
H	1.236577000	3.192009000	-1.560881000
H	-1.236598000	-3.192010000	1.561397000
H	3.382649000	-0.525098000	-1.560881000
H	-3.376111000	-1.949199000	1.577142000
H	3.376106000	1.949195000	-1.576737000

2_2: UM05-2X/6-31+G(d,p), -1945.06882951 Hartrees

C	-0.212448000	0.105015000	1.602192000
C	-1.436878000	0.788126000	1.391445000
C	-2.626741000	0.029473000	1.252403000
C	-2.628119000	-1.360578000	1.348440000
C	-1.404083000	-2.018459000	1.517899000
C	-0.186281000	-1.314002000	1.660501000
C	1.046430000	-1.960461000	1.913950000
C	2.228779000	-1.244463000	2.136751000
C	2.187916000	0.144745000	2.035473000
C	0.980694000	0.841611000	1.789244000
C	0.922585000	2.255226000	1.788800000
C	-0.276344000	2.944701000	1.623369000
C	-1.437596000	2.200621000	1.384108000
C	-3.925885000	-2.175891000	1.335408000
C	3.506604000	-1.988387000	2.540276000
C	-0.356347000	4.471501000	1.731188000
C	-3.890567000	-3.232261000	0.221017000
C	-4.080136000	-2.883123000	2.693827000
C	-5.163115000	-1.299704000	1.114486000
C	3.249680000	-2.743890000	3.856236000
C	3.910333000	-2.994244000	1.452555000
C	4.687850000	-1.039033000	2.765967000
C	-1.384569000	4.853802000	2.810092000
C	-0.790807000	5.071781000	0.386071000
C	0.985695000	5.099361000	2.123165000
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H	-2.385070000	2.704597000	1.233418000
H	-3.552408000	0.571143000	1.112504000
H	-1.374847000	-3.099546000	1.592377000
H	1.045640000	-3.042570000	1.979132000
H	3.081444000	0.734467000	2.192006000
H	-4.802166000	-3.835430000	0.252076000
H	-3.827456000	-2.754398000	-0.759054000
H	-3.036823000	-3.903413000	0.329226000
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H	-5.108877000	-0.765239000	0.162959000
H	-6.052964000	-1.933253000	1.094375000
H	2.951468000	-2.048007000	4.643636000
H	2.458881000	-3.487663000	3.744243000
H	4.159853000	-3.260623000	4.173887000
H	3.125700000	-3.731893000	1.282036000
H	4.112114000	-2.480492000	0.509695000
H	4.815721000	-3.527617000	1.755266000
H	5.566521000	-1.622255000	3.050836000
H	4.935042000	-0.483414000	1.858326000
H	4.483719000	-0.326450000	3.568274000
H	-1.427992000	5.941756000	2.913014000
H	-2.385455000	4.499548000	2.558582000
H	-1.104609000	4.424612000	3.774788000
H	-0.075387000	4.814208000	-0.398872000
H	-1.773305000	4.702427000	0.090397000
H	-0.845354000	6.161548000	0.461194000
H	1.339743000	4.719575000	3.084457000
H	1.755254000	4.915201000	1.370548000
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C	0.212448000	-0.105015000	-1.602192000
C	1.436878000	-0.788126000	-1.391445000
C	2.626741000	-0.029473000	-1.252403000
C	2.628119000	1.360578000	-1.348440000
C	1.404083000	2.018459000	-1.517899000
C	0.186281000	1.314002000	-1.660501000
C	-1.046430000	1.960461000	-1.913950000
C	-2.228779000	1.244463000	-2.136751000
C	-2.187916000	-0.144745000	-2.035473000
C	-0.980694000	-0.841611000	-1.789244000
C	-0.922585000	-2.255226000	-1.788800000
C	0.276344000	-2.944701000	-1.623369000
C	1.437596000	-2.200621000	-1.384108000
C	3.925885000	2.175891000	-1.335408000
C	-3.506604000	1.988387000	-2.540276000
C	0.356347000	-4.471501000	-1.731188000
C	3.890567000	3.232261000	-0.221017000
C	4.080136000	2.883123000	-2.693827000
C	5.163115000	1.299704000	-1.114486000
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C	1.384569000	-4.853802000	-2.810092000
C	0.790807000	-5.071781000	-0.386071000

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H	1.374847000	3.099546000	-1.592377000
H	-1.045640000	3.042570000	-1.979132000
H	-3.081444000	-0.734467000	-2.192006000
H	4.802166000	3.835430000	-0.252076000
H	3.827456000	2.754398000	0.759054000
H	3.036823000	3.903413000	-0.329226000
H	4.095020000	2.152039000	-3.505313000
H	5.015793000	3.449150000	-2.716751000
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H	5.289341000	0.570843000	-1.918270000
H	5.108877000	0.765239000	-0.162959000
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H	0.845354000	-6.161548000	-0.461194000
H	-1.339743000	-4.719575000	-3.084457000
H	-1.755254000	-4.915201000	-1.370548000
H	-0.860433000	-6.180969000	-2.213893000

3_2: UM05-2X/6-31+G(d,p), -1803.69908505 Hartrees

B	-0.110428000	0.716086000	-4.682656000
O	0.607124000	1.589761000	-3.799665000
C	1.044544000	1.206711000	-2.572513000
C	1.769930000	2.122253000	-1.810617000
H	1.931787000	3.113056000	-2.216820000
C	2.244077000	1.767541000	-0.558675000
H	2.796738000	2.487137000	0.033996000
C	2.034603000	0.468885000	-0.030213000
C	2.497649000	0.079253000	1.247320000
H	3.047281000	0.797239000	1.845422000

C	2.256515000	-1.200759000	1.732457000
H	2.601375000	-1.474027000	2.721521000
C	1.524306000	-2.115257000	0.982919000
H	1.311430000	-3.101143000	1.380017000
C	1.042010000	-1.775271000	-0.300066000
C	0.283167000	-2.668970000	-1.097385000
H	0.075726000	-3.660395000	-0.711874000
C	-0.180124000	-2.306857000	-2.350544000
H	-0.752046000	-3.012828000	-2.944069000
C	0.062911000	-1.026083000	-2.864553000
C	0.808998000	-0.098871000	-2.090078000
C	1.300268000	-0.470011000	-0.809857000
N	-0.357053000	-0.635091000	-4.116674000
O	-1.424354000	1.381829000	-5.080639000
C	-1.666608000	1.934694000	-6.226040000
C	0.388374000	1.182987000	-7.162198000
C	-0.817639000	1.896578000	-7.305938000
N	0.707972000	0.617810000	-6.030146000
B	0.110428000	-0.716086000	4.682656000
O	-0.607124000	-1.589761000	3.799665000
C	-1.044544000	-1.206711000	2.572513000
C	-1.769930000	-2.122253000	1.810617000
H	-1.931787000	-3.113056000	2.216820000
C	-2.244077000	-1.767541000	0.558675000
H	-2.796738000	-2.487137000	-0.033996000
C	-2.034603000	-0.468885000	0.030213000
C	-2.497649000	-0.079253000	-1.247320000
H	-3.047281000	-0.797239000	-1.845422000
C	-2.256515000	1.200759000	-1.732457000
H	-2.601375000	1.474027000	-2.721521000
C	-1.524306000	2.115257000	-0.982919000
H	-1.311430000	3.101143000	-1.380017000
C	-1.042010000	1.775271000	0.300066000
C	-0.283167000	2.668970000	1.097385000
H	-0.075726000	3.660395000	0.711874000
C	0.180124000	2.306857000	2.350544000
H	0.752046000	3.012828000	2.944069000
C	-0.062911000	1.026083000	2.864553000
C	-0.808998000	0.098871000	2.090078000
C	-1.300268000	0.470011000	0.809857000
N	0.357053000	0.635091000	4.116674000
O	1.424354000	-1.381829000	5.080639000
C	1.666608000	-1.934694000	6.226040000
C	-0.388374000	-1.182987000	7.162198000
C	0.817639000	-1.896578000	7.305938000
N	-0.707972000	-0.617810000	6.030146000

H	-0.947755000	-1.288192000	-4.604351000
H	1.583526000	0.115214000	-5.989206000
H	-1.583526000	-0.115214000	5.989206000
H	0.947755000	1.288192000	4.604351000
H	-2.631475000	2.431472000	-6.287359000
H	-1.082662000	2.368507000	-8.237789000
H	1.067352000	1.079926000	-8.003020000
H	-1.067352000	-1.079926000	8.003020000
H	1.082662000	-2.368507000	8.237789000
H	2.631475000	-2.431472000	6.287359000

4$_2$: UM05-2X/6-31+G(d,p), -2385.52247035 Hartrees

C	-0.556918000	3.769082000	0.714505000
C	-0.079614000	4.872136000	1.423595000
C	0.434982000	5.953025000	0.695736000
C	0.434982000	5.953025000	-0.695736000
C	-0.079614000	4.872136000	-1.423595000
C	-0.556918000	3.769082000	-0.714505000
C	-0.988938000	2.435013000	-1.173226000
C	-1.148288000	1.787661000	-2.404923000
H	-0.970382000	2.303253000	-3.339175000
C	-1.501825000	0.438582000	-2.429478000
H	-1.606958000	-0.060750000	-3.385969000
C	-1.733229000	-0.317067000	-1.245509000
C	-2.046000000	-1.693792000	-1.216733000
H	-2.141906000	-2.241526000	-2.147843000
C	-2.216891000	-2.353005000	0.000000000
H	-2.434238000	-3.414931000	0.000000000
C	-2.046000000	-1.693792000	1.216733000
H	-2.141906000	-2.241526000	2.147843000
C	-1.733229000	-0.317067000	1.245509000
C	-1.501825000	0.438582000	2.429478000
H	-1.606958000	-0.060750000	3.385969000
C	-1.148288000	1.787661000	2.404923000
H	-0.970382000	2.303253000	3.339175000
C	-0.988938000	2.435013000	1.173226000
C	-1.227629000	1.690007000	0.000000000
C	-1.588030000	0.344613000	0.000000000
C	-0.083076000	4.921992000	2.909055000
C	-1.287652000	4.876603000	3.618306000
H	-2.219030000	4.789594000	3.070625000
C	-1.290573000	4.939237000	5.008754000
H	-2.230178000	4.906195000	5.546617000
C	-0.088727000	5.048023000	5.707607000
H	-0.091536000	5.095220000	6.789631000
C	1.114976000	5.100825000	5.008604000

H	2.051982000	5.186304000	5.545219000
C	1.116755000	5.042378000	3.616166000
H	2.051888000	5.078646000	3.068186000
C	-0.083076000	4.921992000	-2.909055000
C	1.116755000	5.042378000	-3.616166000
H	2.051888000	5.078646000	-3.068186000
C	1.114976000	5.100825000	-5.008604000
H	2.051982000	5.186304000	-5.545219000
C	-0.088727000	5.048023000	-5.707607000
H	-0.091536000	5.095220000	-6.789631000
C	-1.290573000	4.939237000	-5.008754000
H	-2.230178000	4.906195000	-5.546617000
C	-1.287652000	4.876603000	-3.618306000
H	-2.219030000	4.789594000	-3.070625000
C	-0.434982000	-5.953025000	0.695736000
C	-0.434982000	-5.953025000	-0.695736000
C	0.556918000	-3.769082000	0.714505000
C	0.079614000	-4.872136000	1.423595000
C	0.079614000	-4.872136000	-1.423595000
C	0.556918000	-3.769082000	-0.714505000
C	0.988938000	-2.435013000	-1.173226000
C	1.148288000	-1.787661000	-2.404923000
H	0.970382000	-2.303253000	-3.339175000
C	1.501825000	-0.438582000	-2.429478000
H	1.606958000	0.060750000	-3.385969000
C	1.733229000	0.317067000	-1.245509000
C	2.046000000	1.693792000	-1.216733000
H	2.141906000	2.241526000	-2.147843000
C	2.216891000	2.353005000	0.000000000
H	2.434238000	3.414931000	0.000000000
C	2.046000000	1.693792000	1.216733000
H	2.141906000	2.241526000	2.147843000
C	1.733229000	0.317067000	1.245509000
C	1.501825000	-0.438582000	2.429478000
H	1.606958000	0.060750000	3.385969000
C	1.148288000	-1.787661000	2.404923000
H	0.970382000	-2.303253000	3.339175000
C	0.988938000	-2.435013000	1.173226000
C	1.227629000	-1.690007000	0.000000000
C	1.588030000	-0.344613000	0.000000000
C	0.083076000	-4.921992000	2.909055000
C	1.287652000	-4.876603000	3.618306000
H	2.219030000	-4.789594000	3.070625000
C	1.290573000	-4.939237000	5.008754000
H	2.230178000	-4.906195000	5.546617000
C	0.088727000	-5.048023000	5.707607000

H	0.091536000	-5.095220000	6.789631000
C	-1.114976000	-5.100825000	5.008604000
H	-2.051982000	-5.186304000	5.545219000
C	-1.116755000	-5.042378000	3.616166000
H	-2.051888000	-5.078646000	3.068186000
C	0.083076000	-4.921992000	-2.909055000
C	-1.116755000	-5.042378000	-3.616166000
H	-2.051888000	-5.078646000	-3.068186000
C	-1.114976000	-5.100825000	-5.008604000
H	-2.051982000	-5.186304000	-5.545219000
C	0.088727000	-5.048023000	-5.707607000
H	0.091536000	-5.095220000	-6.789631000
C	1.290573000	-4.939237000	-5.008754000
H	2.230178000	-4.906195000	-5.546617000
C	1.287652000	-4.876603000	-3.618306000
H	2.219030000	-4.789594000	-3.070625000
H	0.812330000	6.813711000	-1.235826000
H	0.812330000	6.813711000	1.235826000
H	-0.812330000	-6.813711000	-1.235826000
H	-0.812330000	-6.813711000	1.235826000

5_2(O): UM05-2X/6-31+G(d,p), -2341.22736648 Hartrees

B	0.262127000	4.572832000	0.404054000
O	-1.010574000	3.938686000	0.361008000
C	-1.139418000	2.640816000	0.738508000
C	-2.407369000	2.073388000	0.801984000
H	-3.249998000	2.685520000	0.517443000
C	-2.542619000	0.744915000	1.188464000
C	-1.416520000	-0.051447000	1.548950000
C	-1.530558000	-1.401617000	1.945160000
H	-2.508730000	-1.860331000	1.977386000
C	-0.393153000	-2.127138000	2.284155000
H	-0.495350000	-3.165397000	2.574211000
C	0.874266000	-1.559318000	2.217204000
H	1.753862000	-2.138392000	2.461311000
C	1.026321000	-0.211968000	1.822017000
C	2.295949000	0.428102000	1.729627000
C	2.421443000	1.756102000	1.338516000
H	3.378171000	2.248863000	1.251048000
C	1.283167000	2.481674000	1.004041000
C	0.005441000	1.901501000	1.083365000
C	-0.128457000	0.547260000	1.486679000
O	1.414596000	3.776300000	0.615530000
O	0.442337000	5.332043000	-0.899932000
C	0.207633000	6.586856000	-1.019224000
C	-0.018348000	6.861693000	1.319410000

C	-0.075290000	7.424399000	0.048478000
O	0.202965000	5.622279000	1.530532000
B	-0.262127000	-4.572832000	-0.404054000
O	1.010574000	-3.938686000	-0.361008000
C	1.139418000	-2.640816000	-0.738508000
C	2.407369000	-2.073388000	-0.801984000
H	3.249998000	-2.685520000	-0.517443000
C	2.542619000	-0.744915000	-1.188464000
C	1.416520000	0.051447000	-1.548950000
C	1.530558000	1.401617000	-1.945160000
H	2.508730000	1.860331000	-1.977386000
C	0.393153000	2.127138000	-2.284155000
H	0.495350000	3.165397000	-2.574211000
C	-0.874266000	1.559318000	-2.217204000
H	-1.753862000	2.138392000	-2.461311000
C	-1.026321000	0.211968000	-1.822017000
C	-2.295949000	-0.428102000	-1.729627000
C	-2.421443000	-1.756102000	-1.338516000
H	-3.378171000	-2.248863000	-1.251048000
C	-1.283167000	-2.481674000	-1.004041000
C	-0.005441000	-1.901501000	-1.083365000
C	0.128457000	-0.547260000	-1.486679000
O	-1.414596000	-3.776300000	-0.615530000
O	-0.442337000	-5.332043000	0.899932000
C	-0.207633000	-6.586856000	1.019224000
C	0.018348000	-6.861693000	-1.319410000
C	0.075290000	-7.424399000	-0.048478000
O	-0.202965000	-5.622279000	-1.530532000
H	0.272628000	6.967718000	-2.035370000
H	-0.259724000	8.476467000	-0.095203000
H	-0.137019000	7.468965000	2.214076000
H	0.137019000	-7.468965000	-2.214076000
H	0.259724000	-8.476467000	0.095203000
H	-0.272628000	-6.967718000	2.035370000
O	-3.368282000	0.345793000	-2.071316000
C	-4.610616000	-0.310814000	-2.253931000
H	-4.521423000	-1.103617000	-3.001477000
H	-4.976904000	-0.733190000	-1.314840000
H	-5.302827000	0.450938000	-2.606187000
O	3.751299000	-0.117609000	-1.273201000
C	4.909128000	-0.910352000	-1.082055000
H	4.937734000	-1.322647000	-0.070276000
H	4.946129000	-1.723337000	-1.812598000
H	5.755953000	-0.244306000	-1.232892000
O	3.368282000	-0.345793000	2.071316000
C	4.610616000	0.310814000	2.253931000

H	4.976904000	0.733190000	1.314840000
H	4.521423000	1.103617000	3.001477000
H	5.302827000	-0.450938000	2.606187000
O	-3.751299000	0.117609000	1.273201000
C	-4.909128000	0.910352000	1.082055000
H	-4.946129000	1.723337000	1.812598000
H	-4.937734000	1.322647000	0.070276000
H	-5.755953000	0.244306000	1.232892000

5_2(S): UM05-2X/6-31+G(d,p), -3633.08283215 Hartrees

B	0.273558000	4.549217000	0.408357000
O	-0.998112000	3.916807000	0.332482000
C	-1.138593000	2.625214000	0.729469000
C	-2.409021000	2.070926000	0.801542000
H	-3.242613000	2.693458000	0.512040000
C	-2.572392000	0.752061000	1.214149000
C	-1.443198000	-0.054540000	1.563341000
C	-1.553881000	-1.407792000	1.953016000
H	-2.524515000	-1.884923000	1.986568000
C	-0.423858000	-2.141114000	2.290455000
H	-0.531140000	-3.181751000	2.569178000
C	0.842706000	-1.574683000	2.240312000
H	1.704535000	-2.178505000	2.492805000
C	1.012526000	-0.225256000	1.857527000
C	2.290774000	0.414104000	1.795581000
C	2.410200000	1.734646000	1.373746000
H	3.364756000	2.232878000	1.293098000
C	1.280232000	2.456183000	1.013375000
C	-0.000720000	1.880255000	1.089976000
C	-0.144049000	0.531576000	1.504702000
O	1.420445000	3.744035000	0.604211000
O	0.465007000	5.353578000	-0.864412000
C	0.174576000	6.599306000	-0.949156000
C	-0.072780000	6.797078000	1.394092000
C	-0.159432000	7.390700000	0.138184000
O	0.202786000	5.564794000	1.570536000
B	-0.273558000	-4.549217000	-0.408357000
O	0.998112000	-3.916807000	-0.332482000
C	1.138593000	-2.625214000	-0.729469000
C	2.409021000	-2.070926000	-0.801542000
H	3.242613000	-2.693458000	-0.512040000
C	2.572392000	-0.752061000	-1.214149000
C	1.443198000	0.054540000	-1.563341000
C	1.553881000	1.407792000	-1.953016000
H	2.524515000	1.884923000	-1.986568000
C	0.423858000	2.141114000	-2.290455000

H	0.531140000	3.181751000	-2.569178000
C	-0.842706000	1.574683000	-2.240312000
H	-1.704535000	2.178505000	-2.492805000
C	-1.012526000	0.225256000	-1.857527000
C	-2.290774000	-0.414104000	-1.795581000
C	-2.410200000	-1.734646000	-1.373746000
H	-3.364756000	-2.232878000	-1.293098000
C	-1.280232000	-2.456183000	-1.013375000
C	0.000720000	-1.880255000	-1.089976000
C	0.144049000	-0.531576000	-1.504702000
O	-1.420445000	-3.744035000	-0.604211000
O	-0.465007000	-5.353578000	0.864412000
C	-0.174576000	-6.599306000	0.949156000
C	0.072780000	-6.797078000	-1.394092000
C	0.159432000	-7.390700000	-0.138184000
O	-0.202786000	-5.564794000	-1.570536000
H	0.239351000	7.014508000	-1.951741000
H	-0.388522000	8.437383000	0.022910000
H	-0.209139000	7.376525000	2.304696000
H	0.209139000	-7.376525000	-2.304696000
H	0.388522000	-8.437383000	-0.022910000
H	-0.239351000	-7.014508000	1.951741000
C	-5.032812000	-0.674607000	-2.290167000
H	-4.815640000	-1.510722000	-2.953931000
H	-5.223750000	-1.023688000	-1.276115000
H	-5.908677000	-0.143342000	-2.660774000
C	5.291947000	-1.391191000	-1.060080000
H	5.189419000	-1.745603000	-0.035282000
H	5.125671000	-2.201539000	-1.769127000
H	6.294188000	-0.990024000	-1.205740000
C	5.032812000	0.674607000	2.290167000
H	5.223750000	1.023688000	1.276115000
H	4.815640000	1.510722000	2.953931000
H	5.908677000	0.143342000	2.660774000
C	-5.291947000	1.391191000	1.060080000
H	-5.125671000	2.201539000	1.769127000
H	-5.189419000	1.745603000	0.035282000
H	-6.294188000	0.990024000	1.205740000
S	3.689292000	-0.538702000	2.314552000
S	4.169640000	-0.008143000	-1.380247000
S	-3.689292000	0.538702000	-2.314552000
S	-4.169640000	0.008143000	1.380247000

6_2: UM05-2X/6-31+G(d,p), -2591.87628426 Hartrees

S	4.254251000	-0.780275000	1.056021000
C	2.534791000	-1.116427000	1.214418000

C	1.872659000	-1.264308000	2.436244000
H	2.412015000	-1.157283000	3.369210000
C	0.513818000	-1.539394000	2.444323000
H	-0.003584000	-1.648625000	3.389653000
C	-0.225662000	-1.699799000	1.240949000
C	-1.607916000	-1.981043000	1.213161000
H	-2.147997000	-2.079194000	2.147406000
C	-2.274680000	-2.131233000	0.000994000
H	-3.336744000	-2.343388000	0.001199000
C	-1.608165000	-1.981645000	-1.211278000
H	-2.148460000	-2.079843000	-2.145375000
C	-0.225850000	-1.700497000	-1.239585000
C	0.513307000	-1.540715000	-2.443219000
H	-0.004258000	-1.650369000	-3.388427000
C	1.872064000	-1.265187000	-2.435562000
H	2.411208000	-1.158495000	-3.368690000
C	2.534493000	-1.116868000	-1.213925000
C	1.839170000	-1.266209000	0.000334000
C	0.455296000	-1.558452000	0.000554000
S	4.254008000	-0.780568000	-1.056058000
S	-4.254150000	0.781196000	-1.057243000
C	-2.534474000	1.116622000	-1.215099000
C	-1.871993000	1.264981000	-2.436703000
H	-2.411169000	1.158726000	-3.369862000
C	-0.513018000	1.539462000	-2.444267000
H	0.004874000	1.647737000	-3.389443000
C	0.226126000	1.699423000	-1.240670000
C	1.608338000	1.981080000	-1.212428000
H	2.148574000	2.079700000	-2.146537000
C	2.274643000	2.131416000	-0.000094000
H	3.336596000	2.344153000	0.000113000
C	1.607842000	1.981307000	1.212050000
H	2.147775000	2.080120000	2.146312000
C	0.225651000	1.699642000	1.239851000
C	-0.513975000	1.539903000	2.443221000
H	0.003312000	1.649593000	3.388561000
C	-1.872867000	1.265049000	2.435103000
H	-2.412382000	1.158736000	3.368059000
C	-2.534833000	1.116558000	1.213265000
C	-1.839004000	1.265359000	-0.000826000
C	-0.455123000	1.557606000	-0.000544000
S	-4.254504000	0.781445000	1.054835000

7_2: UM05-2X/6-31+G(d,p), -1904.17802121 Hartrees

C	0.011505000	1.557870000	0.000008000
C	-0.011505000	-1.557870000	0.000008000

C	0.708077000	-1.551870000	-1.246944000
C	-0.707939000	1.551726000	1.247038000
C	-0.034351000	-1.507671000	-2.454531000
C	-2.125548000	1.529696000	1.207831000
C	2.125647000	-1.529875000	-1.207612000
C	0.034681000	1.508127000	2.454547000
C	-1.417847000	-1.501797000	-2.435748000
C	-2.800367000	1.541613000	0.000143000
C	2.800367000	-1.541613000	0.000143000
C	1.418146000	1.502369000	2.435600000
C	2.125548000	1.493846000	1.246705000
C	2.125548000	-1.529696000	1.207831000
C	-2.125647000	1.529875000	-1.207612000
C	-2.125412000	-1.493737000	-1.246954000
C	1.451182000	1.534675000	-0.000073000
C	0.707939000	-1.551726000	1.247038000
C	-0.708077000	1.551870000	-1.246944000
C	-1.451182000	-1.534675000	-0.000073000
C	2.125412000	1.493737000	-1.246954000
C	-0.034681000	-1.508127000	2.454547000
C	0.034351000	1.507671000	-2.454531000
C	-2.125548000	-1.493846000	1.246705000
C	1.417847000	1.501797000	-2.435748000
C	-1.418146000	-1.502369000	2.435600000
H	-1.959416000	-1.426613000	-3.374242000
H	-3.885224000	1.483849000	0.000186000
H	3.885224000	-1.483849000	0.000186000
H	1.959853000	1.427586000	3.374051000
H	1.959416000	1.426613000	-3.374242000
H	-1.959853000	-1.427586000	3.374051000
O	0.618663000	-1.478581000	3.655000000
H	-0.044533000	-1.455257000	4.351241000
O	2.839358000	-1.501656000	2.373312000
O	-3.491541000	-1.452276000	1.280866000
H	-3.762695000	-1.424178000	2.203375000
O	-3.491417000	-1.452618000	-1.281252000
O	0.619186000	-1.477885000	-3.654896000
O	2.839571000	-1.502060000	-2.373036000
O	-0.619186000	1.477885000	-3.654896000
O	-2.839571000	1.502060000	-2.373036000
H	-3.774297000	1.486666000	-2.146091000
O	-2.839358000	1.501656000	2.373312000
H	-3.774100000	1.486092000	2.146448000
O	-0.618663000	1.478581000	3.655000000
H	0.044533000	1.455257000	4.351241000
O	3.491417000	1.452618000	-1.281252000

O	3.491541000	1.452276000	1.280866000
H	3.762695000	1.424178000	2.203375000
H	-0.043940000	-1.454977000	-4.351213000
H	3.774297000	-1.486666000	-2.146091000
H	3.774100000	-1.486092000	2.146448000
H	-3.762477000	-1.424357000	-2.203784000
H	0.043940000	1.454977000	-4.351213000
H	3.762477000	1.424357000	-2.203784000

8$_2$: UM05-2X/6-31+G(d,p), -2787.65728119 Hartrees

C	-1.580000000	-0.003112000	0.000000000
C	1.580000000	0.003112000	0.000000000
C	1.577973000	-1.426240000	0.000000000
C	-1.577973000	1.426240000	0.000000000
C	1.546227000	-2.099508000	1.239061000
C	-1.546227000	2.099508000	1.239061000
C	1.546227000	-2.099508000	-1.239061000
C	-1.546227000	2.099508000	-1.239061000
C	1.554213000	-1.404971000	2.435848000
C	-1.554213000	1.404971000	2.435848000
C	1.554213000	-1.404971000	-2.435848000
C	-1.554213000	1.404971000	-2.435848000
C	-1.545230000	0.020842000	-2.440952000
C	1.545230000	-0.020842000	-2.440952000
C	-1.545230000	0.020842000	2.440952000
C	1.545230000	-0.020842000	2.440952000
C	-1.576909000	-0.717124000	-1.238681000
C	1.576909000	0.717124000	-1.238681000
C	-1.576909000	-0.717124000	1.238681000
C	1.576909000	0.717124000	1.238681000
C	-1.543355000	-2.127104000	-1.201185000
C	1.543355000	2.127104000	-1.201185000
C	-1.543355000	-2.127104000	1.201185000
C	1.543355000	2.127104000	1.201185000
C	-1.551113000	-2.814408000	0.000000000
C	1.551113000	2.814408000	0.000000000
F	-1.526337000	-4.143360000	0.000000000
F	-1.525795000	-2.841354000	2.325331000
F	-1.527569000	-0.596502000	3.620607000
F	-1.529314000	2.071090000	3.585585000
F	-1.530136000	3.430355000	1.291295000
F	-1.530136000	3.430355000	-1.291295000
F	-1.529314000	2.071090000	-3.585585000
F	-1.527569000	-0.596502000	-3.620607000
F	-1.525795000	-2.841354000	-2.325331000
F	1.530136000	-3.430355000	1.291295000

F	1.530136000	-3.430355000	-1.291295000
F	1.529314000	-2.071090000	-3.585585000
F	1.527569000	0.596502000	-3.620607000
F	1.525795000	2.841354000	-2.325331000
F	1.526337000	4.143360000	0.000000000
F	1.525795000	2.841354000	2.325331000
F	1.527569000	0.596502000	3.620607000
F	1.529314000	-2.071090000	3.585585000

VI. References and full list of authors of ref. 23.[3]

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