Ab initio and DFT Treatment of the Structures of Three Isomers of $C_{60}S$

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Abstract

Three isomers of $C_{60}S$ ($C_{60}S^{2-}$, [5,6]-closed $C_{60}S$, and [6,6]-closed $C_{60}S$) have been treated by *ab initio* and density functional theories. Using the B3LYP/DH(d) method with explicit diffuse functions for sulfur, the [6,6] isomer was calculated to be 18.33 kcal mol^{-1} more stable than the [5,6] isomer. Electron affinities for the three isomers were calculated—the [5,6]-closed C60S had the highest electron affinities of the three at 3.32 eV. Vibrational frequency and proton affinities calculations are underway.

Introduction

Over the past 15 years, fullerene sulfur complexes have received considerable attention. Not long after the preparation of [6,6]-closed $C_{60}O$ [1], the search for sulfur derivatives arose. In subsequent studies the preparations of $C_{60}S_8$ and $C_{60}S_{16}$ were reported. It was determined that the interactions between the C_{60} and sulfur consisted mainly of weak van der Waals interactions—a structure in which the C_{60} cages were surrounded by unbound crown-shaped sulfur rings (S_8)[2-3].

However, in high-pressure Raman studies of $C_{60}S_{16}$ [4], it has been proposed that the crown S_8 rings break down and form covalent C-S bonds with the C_{60} cage. The covalent bonding of sulfur directly to C_{60} has been reported in the thermolysis preparation of $C_{120}OS$ [5]. A plausible synthesis for $C_{60}S$, however, has yet to be determined [6]. While $C_{60}S$ has yet to be synthesized, computational results for the [6,6]$C_{60}S$ and [5,6]$C_{60}S$ bridged systems have been

reported at the semi-empirical MNDO [6] and AM1 [7] levels. A mechanism for the rearrangement between the isomers has also been reported at the semi-empirical AM1 level [8].

With the onslaught of modern technology, the ability to perform *ab inito* calculations on large systems is becoming readily available. As a result, the focus of this study was to computationally explore, using *ab initio* and DFT methods, three possible isomers of $C_{60}S$: $C_{60}S^{2-}$, [5,6]-closed $C_{60}S$ where the sulfur is bridged between a five and a six-membered ring, and [6,6]-closed $C_{60}S$ where the sulfur atom is bridged between two six-membered rings. The goal was to better understand the electronic properties and the specific structures of the molecules.

Calculation Details

All calculations were preformed using the G.A.M.E.S.S. suite of codes [9] running on one of four HPC machines: Compaq SC-45, SGI Origin 3900, SGI Altix BX2, or HP Opteron XC. All graphical modeling and calculations of bond lengths and angles were preformed using MOLEKEL 4.0 [10].

Three compounds in which a sulfur atom was bound to a C_{60} cage were studied: $C_{60}S^{2-}$, [5,6]$C_{60}S$ and [6,6]$C_{60}S$. The triplet state of each molecule as well as the protonated [6,6]$C_{60}SH^{-1}$ and [5,6]$C_{60}SH^{-1}$ were also considered. Initial gas phase geometries for each of the compounds were calculated at the AM1 semi-empirical level—AM1 provided a computationally inexpensive starting point. Next, the geometries and energies were optimized at the Hartree-Fock level using the Dunning-Hay basis set with an explicit diffuse function applied to the sulfur atom, HF/DH(d)+S(d,p). The calculations were then taken to the Density Function Theory level and final geometries, molecular energies, electron affinities and proton affinities for the three $C_{60}S$

systems were calculated at the B3LYP/DH(d)+S(d,p) level, both using a coarse DFT grid (theta=12, phi=24) and a fine DFT grid (theta=36, phi=72). Semi-numerical frequency calculations are currently being preformed at the B3LYP/DH(d)+S(d,p) level to ensure energy minima.

Results and Discussion

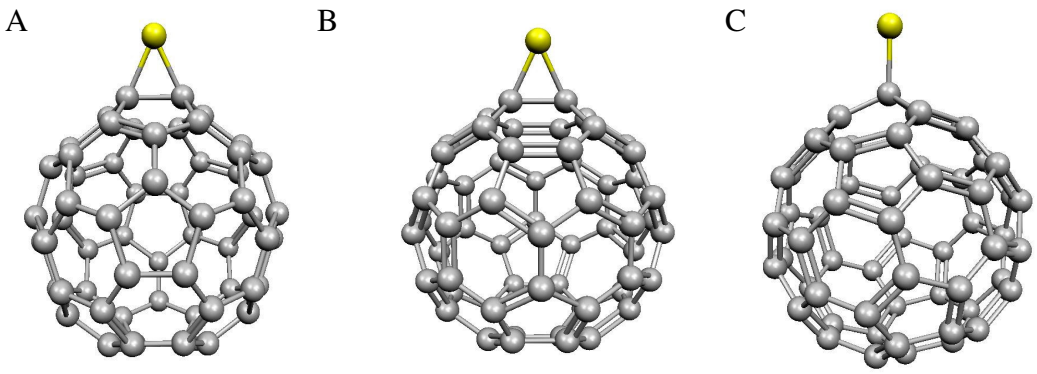

Figure 1. B3LYP/DH(d)+S(d,p) optimized structures of A) closed-[5,6]C_{60}S, B) closed-[6,6]C_{60}S, C) $C_{60}S^{2-}$.

Three isomers of C_{60}S were considered (Figure 1): 1) with the sulfur bridging the C-C bond between five and six-membered rings [5,6], 2) with the sulfur bridging the C-C bond between two six-membered rings [6,6], and 3) with the sulfur dianion (S^{2-}). The most stable isomer appears to be [6,6]C_{60}S. At the B3LYP/DH(d)+S(d,p) level the [6,6] isomer is more stable than the [5,6] isomer by 18.33 kcal mol^{-1}. Table 1 summarizes the molecular energies for the three isomers and their different electron states at the applied theory levels. Cartesian coordinates for the optimized geometries at the fine grid B3LYP/DH(d)+S(d,p) level are included in Appendix A: Cartesian Coordinates.

Table 1: Molecular Energies (In Hartrees) of C60S Compounds

	HF/DH(d) + S(d,p)	B3LYP/DH(d) + S(d,p) Coarse Grid	B3LYP/DH(d) + S(d,p) Fine Grid
$C_{60}S^{2-}$	-2669.618248	-2683.218165	-2683.237395
[5,6]$C_{60}S$	-2669.565309	-2683.105609	-2683.126196
[6,6]$C_{60}S$	-2669.605281	-2683.136646	-2683.155404
$C_{60}S^{2-}$ (Triplet)	---	-2683.223882	-2683.226169
[5,6]$C_{60}S$ (Triplet)	---	-2683.086251	-2683.098384
[6,6]$C_{60}S$ (Triplet)	---	-2683.086512	-2683.094078
$C_{60}SH^{-}$ (In Petagon)	---	-2670.249814	In Progress
$C_{60}SH^{-}$ (On Hexagon)	---	In Progress	In Progress
[5,6]$C_{60}S^{-}$	---	-2683.227663	In Progress
[6,6]$C_{60}S^{-}$	---	-2683.247479	-2683.2499389

Table 1: This table is a summary of the calculated molecular energies for each of the compounds at different levels of theory. Only the initial singlet compounds were treated at the HF/DH(d)+S(d,p) level. Triplet states, protonated compounds and ionized compounds were built from B3LYP/DH(d)+S(d,p) geometries.

The geometry of the [6,6]$C_{60}S$ supports it as the most stable neutral isomer. The crucial C-C bond over which the sulfur atom is bridged was calculated to be 1.541 Å, while in the [5,6] isomer this C-C bond was 1.592 Å, as shown in Table 2. Since the difference in the length of this C-C bond is only 0.051 Å between the two isomers, it is valid to assume that both isomers probably coexist, especially at elevated temperatures. Although the $C_{60}S^{2-}$ exhibits slightly less strain on the C-C bonds than either of the two other isomers, its ability to exist stably is unlikely due to the -2 charge.

Interestingly, the excited triplet state of [6,6] $C_{60}S$ seems to be less strained over the bridged C-C bond, with a length of 1.530 Å, when compared to that of the neutral [6,6] $C_{60}S$ at 1.541 Å. This may in part be due to the great ability of C_{60} to stabilize charge—it is well known that C_{60} can stably exist as C_{60}^{6-}. This bond length of 1.530 Å is only slightly longer than the longest C-C bond found in $C_{60}S^{2-}$ which would suggest minimal strain on the C_{60} cage and possibly a more energetically favorable excited state. The molecular energy of the triplet

[6,6]$C_{60}S$, however, is 38.48 kcal mol^{-1} higher in energy than the singlet state. Therefore, the singlet state is most likely preferred.

Table 2: Bond Distances and Angles at B3LYP/DH(d) + S(d,p) Fine Grid theory level

Compound	Bond	Distance (Å)	Bond	Angle (°)
$C_{60}S^{2-}$				
	C-C	1.393 - 1.529	S-C-C (to Hexagon)	116.2
	C-S	1.865	S-C-C (to Pentagon)	109.5
[5,6]$C_{60}S$				
	C-C	1.387 - 1.592	C-S-C	51.1
	C-C (bound to S)	1.592		
	C-S	1.846		
[6,6]$C_{60}S$				
	C-C	1.387 - 1.541	C-S-C	49.6
	C-C (bound to S)	1.541		
	C-S	1.836		
[5,6]$C_{60}S^{1-}$				
	C-C	In Progress	C-S-C	In Progress
	C-C (bound to S)	In Progress		
	C-S	In Progress		
[6,6]$C_{60}S^{1-}$				
	C-C	1.390 – 1.532	C-S-C	48.9
	C-C (bound to S)	1.532		
	C-S	1.850		
$C_{60}SH^{1-}$(on hexagon)				
	C-C	In Progress	S-C-C (to Hexagon)	In Progress
	C-S	In Progress	S-C-C (to Pentagon)	In Progress
	S-H	In Progress	C-S-H	In Progress
$C_{60}SH^{1-}$(in pentagon)				
	C-C	In Progress	S-C-C (to Hexagon)	In Progress
	C-S	In Progress	S-C-C (to Pentagon)	In Progress
	S-H	In Progress	C-S-H	In Progress
$C_{60}S^{2-}$ Triplet				
	C-C	1.396 – 1.531	S-C-C (to Hexagon)	99.8
	C-S	1.863	S-C-C (to Pentagon)	116.8
[5,6]$C_{60}S$ Triplet				
	C-C	1.387 – 1.536	C-S-C	48.6
	C-C (bound to S)	1.536		
	C-S	1.867		
[6,6]$C_{60}S$ Triplet				
	C-C	1.395 – 1.530	C-S-C	49.2
	C-C (bound to S)	1.530		
	C-S	1.838		

Table 2: Unique bond lengths and angles for each of the three studied isomers of $C_{60}S$.

It is also worthwhile to consider the possible stability of these compounds by looking at the heat of reaction. Treatment of (1/8)E S_8 + E C_{60} → E $C_{60}S$ (where E is the molecular energy) at the B3LYP/DH(d)+S(d,p) level resulted in the following heats of reaction shown in Table 3.

Table 3: Heat of Reaction

Product	Heat of Reaction (kcal mol^{-1})
[6,6]$C_{60}S$	8.3900485
[5,6]$C_{60}S$	26.7183313
$C_{60}S^{2-}$	-43.060042

Table 3: Calculated heat of reactions for the three isomers of $C_{60}S$.

These results show that upon reaction with S^{2-}, C_{60} would most likely favor $C_{60}S^{2-}$ as a product. This may be a preliminary indication that when an S atom covalently bonds to C_{60} the $C_{60}S^{2-}$ isomer is an intermediate in the formation of [6,6]$C_{60}S$ or [5,6]$C_{60}S$. As previously stated, at higher temperatures a mixture of isomers would likely exist. This is demonstrated by the difference in the heat of reaction of the three products. $C_{60}S^{2-}$ is 69.78 kcal mol^{-1} more stable than [6,6]$C_{60}S$ and [6,6]$C_{60}S$ is 18.33 kcal mol^{-1} more stable than [5,6]$C_{60}S$. Elevating the temperature of the reaction would provide the energy needed for the formation of all three isomers.

If indeed, the bridged isomers were formed at higher temperatures the following electrons affinities would be expected (Table 4). Both bridged compounds appear to be fairly strong oxidizing agents. They both also exhibit moderately higher vertical electron affinities than either of the components S^- or C_{60}. Br^- and I^- electron affinities are provided for comparison. What is interesting is how the electron affinity of [6,6]$C_{60}S$ increased by 0.543 eV after allowing the geometry to relax, but the electron affinity for [5,6]$C_{60}S$ decreased by 0.477 eV after geometry relaxation. The immediate addition of an electron seems to affect the two isomers differently. After geometry relaxation, however, the electron affinities of both isomers become more similar.

It should be noted that these calculations were preformed using the energies as calculated at the coarse grid B3LYP/DH(d)+S(d,p) level—fine grid energy is still being calculated for [5,6]C60S.

Table 4: Vertical Electron Affinities (Coarse Grid)

Compound	Electron Affinity (eV)
$[5,6]C_{60}S$	3.797
$[6,6]C_{60}S$	2.477
C_{60}	2.683 [11]
Br^-	3.363 [12]
I^-	3.063 [12]
S^-	2.07 [12]

Table 4: Electrons affinities calculated without allowing the geometry to relax.

Table 5: Adiabatic Electron Affinities (Coarse Grid)

Compound	Electron Affinity (eV)
$[5,6]C_{60}S$	3.32
$[6,6]C_{60}S$	3.02

Table 5: Electron affinities calculated after allowing geometry to relax.

Protonization energies are also being calculated for two conformations of $C_{60}SH^{1-}$: with the H atom oriented over the C-C bond between two six-membered rings (on Hexagon), and with the H atom oriented toward the middle of a five-membered ring (in Pentagon). At the present time these calculations have been completed only at the HF/DH(d)+S(d,p) level. Therefore, inclusion of the data would not allow for any meaningful comparisons. The major difficulty plaguing these calculations is the fact that upon searching for an SCF energy minimum, the calculation falls upon an oscillation point with a magnitude of approximately 84 hartrees. This ultimately results in a non-convergent SCF.

Often with an oscillation of this magnitude the problem is that the two orbitals are extremely close in energy. In each cycle the populations switch between Orbital A and Orbital B, occupying one then the other. The case could be that an improper wavefunction was applied to the calculation. This is most likely not the case, since the calculations have converged at the HF level of theory. This problem is currently being addressed.

Table 6: Proton Affinity

Compound	Proton Affinity
[5,6]$C_{60}S$	In Progress
[6,6]$C_{60}S$	In Progress

Table 6: Calculated proton affinities for the two bridged C60S isomers.

Finally, in order to confirm energy minima, semi-numerical frequency calculations are being preformed using a fine grid B3LYP/DH(d)+S(d,p) method. The major difficulty in performing semi-numerical frequency calculations is their demand for computer resources. To put this in perspective, a semi-numerical frequency calculation on S_8 submitted across 32 processors with 32 GB of RAM takes approximately six hours to complete. At this point the frequency calculation, for any of the forms of C60S recorded in Table 1, closest to being finished has been running for approximately 8 weeks on 64 processors with 64 GB of RAM.

Unfortunately, frequency calculations may be some of the most important data points. Not only does a frequency calculation provide computational data points against which experimental IR spectra can be compared, but they also verify energy minima by displaying imaginary frequencies which may be the result of local rather than global energy minima. These frequency calculations are currently running on the aforementioned HPC machines. The hope is to have final frequency data for all the forms of $C_{60}S$ within the next month.

Conclusions

While there has not been a successful synthesis of the $C_{60}S$, computationally the molecule appears to be stable as at least two different bridged isomers. The closed-[6,6]$C_{60}S$ isomer appears to be the most stable, although heat of reaction data suggests that a mixture of all three isomers likely exists at elevated temperatures. Both closed isomers exhibit fairly strong oxidation potential most closely related to I^- and Br^-. Currently work is continuing on calculating the

proton affinity for each of the closed isomers as well as calculating the frequency data for all the aforementioned forms of $C_{60}S$.

While this study brushes the surface of the characterization of $C_{60}S$ at a decent theory level, there is still a need to computationally explore, at an electron correlated theory level, a plausible mechanism of isomer rearrangement as well a mechanism of $C_{60}S$ formation. In its finished state this current report will be able to serve as a comparison for any attempts to synthesize this elusive compound.

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References

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[12] Values for electron affinities were taken from the 58th edition of CRC.

Appendix A: Cartesian Coordinates

$C_{60}S^{2-}$ B3LYP/DH(d)+S(d,p)

C	-0.0085200297	-0.7159922782	-3.4780183383
C	-0.0085200297	-0.7159922782	3.4780183383
C	-0.0106389959	0.6886085927	-3.4715691038
C	-0.0106389959	0.6886085927	3.4715691038
C	-1.1849674677	-1.4592191866	-3.0586793318
C	-1.1849674677	-1.4592191866	3.0586793318
C	1.1781948384	-1.4396616353	-3.0369074367
C	1.1781948384	-1.4396616353	3.0369074367
C	-1.1970252874	1.4203696247	-3.0173549831
C	-1.1970252874	1.4203696247	3.0173549831
C	1.1583854820	1.4189497884	-3.0287079357
C	1.1583854820	1.4189497884	3.0287079357
C	-2.3166667187	-0.7457713197	-2.6041691254
C	-2.3166667187	-0.7457713197	2.6041691254
C	2.3135754042	-0.7281526952	-2.6100268871
C	2.3135754042	-0.7281526952	2.6100268871
C	-2.3495156403	0.6968311859	-2.6176439520
C	-2.3495156403	0.6968311859	2.6176439520
C	2.3128563953	0.7217881981	-2.6147227527
C	2.3128563953	0.7217881981	2.6147227527
C	-0.7217883062	-2.6143412195	-2.3085625615
C	-0.7217883062	-2.6143412195	2.3085625615
C	0.7391374917	-2.6207500204	-2.3153001073
C	0.7391374917	-2.6207500204	2.3153001073
C	-0.7681153571	2.6009234473	-2.3261252535
C	-0.7681153571	2.6009234473	2.3261252535
C	0.7005349674	2.5936062987	-2.3053555360
C	0.7005349674	2.5936062987	2.3053555360
C	-3.0461290151	-1.2111445090	-1.4292222333
C	-3.0461290151	-1.2111445090	1.4292222333
C	3.0407673542	-1.1792986563	-1.4270798808
C	3.0407673542	-1.1792986563	1.4270798808
C	-3.0681148687	1.1397222768	-1.4306020829
C	-3.0681148687	1.1397222768	1.4306020829
C	3.0238393355	1.1744585223	-1.4378875701
C	3.0238393355	1.1744585223	1.4378875701
C	-1.4183459830	-3.0658606152	-1.1777177254
C	-1.4183459830	-3.0658606152	1.1777177254
C	1.4394961538	-3.0518505135	-1.1757418565
C	1.4394961538	-3.0518505135	1.1757418565
C	-1.4484175365	3.0139165090	-1.1506331610
C	-1.4484175365	3.0139165090	1.1506331610
C	1.3890698397	3.0317820050	-1.1770415195
C	1.3890698397	3.0317820050	1.1770415195
C	-2.6028542721	-2.3399494873	-0.7271250415
C	-2.6028542721	-2.3399494873	0.7271250415
C	2.6154240369	-2.3192681411	-0.7284696198
C	2.6154240369	-2.3192681411	0.7284696198
C	-2.6398710549	2.2691457943	-0.7248929343
C	-2.6398710549	2.2691457943	0.7248929343
C	2.5399636990	2.2895692512	-0.7283666498
C	2.5399636990	2.2895692512	0.7283666498
C	-3.5130094489	-0.0402604581	-0.7004708754
C	-3.5130094489	-0.0402604581	0.7004708754
C	3.4806816254	0.0001372376	-0.6997674900
C	3.4806816254	0.0001372376	0.6997674900
C	-0.6860436086	-3.5003735131	0.0000000000
C	0.7227211988	-3.5190289542	0.0000000000
C	-0.7606732546	3.4916493684	0.0000000000
C	0.7332360420	3.7537063264	0.0000000000
S	1.2539950002	5.5450295139	0.0000000000

[5,6]-closed $C_{60}S$ B3LYP/DH(d)+S(d,p)

C	-0.0102791633	-0.7097525383	-3.4980829198
C	-0.0102791633	-0.7097525383	3.4980829198
C	-0.0089072880	0.6916132562	-3.4856378776
C	-0.0089072880	0.6916132562	3.4856378776
C	-1.1886458401	-1.4371615313	-3.0432373775
C	-1.1886458401	-1.4371615313	3.0432373775
C	1.1674473659	-1.4341838165	-3.0497331856
C	1.1674473659	-1.4341838165	3.0497331856
C	-1.1857818406	1.4156248256	-3.0309387421
C	-1.1857818406	1.4156248256	3.0309387421
C	1.1668797281	1.4180853512	-3.0350803012
C	1.1668797281	1.4180853512	3.0350803012
C	-2.3194767034	-0.7398357981	-2.6093780761
C	-2.3194767034	-0.7398357981	2.6093780761
C	2.2975216408	-0.7285947785	-2.6152617319
C	2.2975216408	-0.7285947785	2.6152617319
C	-2.3196743900	0.7170215928	-2.6048152534
C	-2.3196743900	0.7170215928	2.6048152534
C	2.2916121954	0.7235250789	-2.6033940155
C	2.2916121954	0.7235250789	2.6033940155
C	-0.7338641715	-2.6146369411	-2.3143491863
C	-0.7338641715	-2.6146369411	2.3143491863
C	0.7227833457	-2.6074277455	-2.3186181120
C	0.7227833457	-2.6074277455	2.3186181120
C	-0.7372491403	2.5889301392	-2.2939388319
C	-0.7372491403	2.5889301392	2.2939388319
C	0.7126948947	2.6040859818	-2.2921556377
C	0.7126948947	2.6040859818	2.2921556377
C	-3.0454465533	-1.1889754524	-1.4274307930
C	-3.0454465533	-1.1889754524	1.4274307930
C	3.0205422682	-1.1578159403	-1.4349724120
C	3.0205422682	-1.1578159403	1.4349724120
C	-3.0516326037	1.1659908926	-1.4279155876
C	-3.0516326037	1.1659908926	1.4279155876
C	3.0458349595	1.1779297590	-1.4395024624
C	3.0458349595	1.1779297590	1.4395024624
C	-1.4272896930	-3.0436527771	-1.1785445034
C	-1.4272896930	-3.0436527771	1.1785445034
C	1.4264393094	-3.0234445555	-1.1798215336
C	1.4264393094	-3.0234445555	1.1798215336
C	-1.4481579523	3.0314275601	-1.1726791607
C	-1.4481579523	3.0314275601	1.1726791607
C	1.4111494742	3.0525155942	-1.1810126097
C	1.4111494742	3.0525155942	1.1810126097
C	-2.6086692187	-2.3197872385	-0.7267321333
C	-2.6086692187	-2.3197872385	0.7267321333
C	2.5927248572	-2.2811287833	-0.7344151782
C	2.5927248572	-2.2811287833	0.7344151782
C	-2.6255879829	2.3005585435	-0.7282372143
C	-2.6255879829	2.3005585435	0.7282372143
C	2.7373425528	2.4577155505	-0.7957929912
C	2.7373425528	2.4577155505	0.7957929912
C	-3.4965418448	-0.0135065048	-0.7015296874
C	-3.4965418448	-0.0135065048	0.7015296874
C	3.4703007553	0.0482709743	-0.7174335585
C	3.4703007553	0.0482709743	0.7174335585
C	-0.6960744917	-3.4885547229	0.0000000000
C	0.7028325822	-3.4758175407	0.0000000000
C	-0.7196924365	3.4744266586	0.0000000000
C	0.6905957012	3.4712231069	0.0000000000
S	4.0102007225	3.5319411003	0.0000000000

[6,6]-closed $C_{60}S$ B3LYP/DH(d)+S(d,p)

C	0.0076383625	-0.7015876108	-3.4782106185
C	0.0076383625	-0.7015876108	3.4782106185
C	0.0202950203	0.6964112348	-3.4660658130
C	0.0202950203	0.6964112348	3.4660658130
C	-1.1781221259	-1.4228565406	-3.0338979572
C	-1.1781221259	-1.4228565406	3.0338979572
C	1.1801460427	-1.4442050632	-3.0338983597
C	1.1801460427	-1.4442050632	3.0338983597
C	-1.1522623000	1.4349459211	-3.0202553182
C	-1.1522623000	1.4349459211	3.0202553182
C	1.2060316368	1.4135976284	-3.0202567522
C	1.2060316368	1.4135976284	3.0202567522
C	-2.3073323269	-0.7160536141	-2.6046290159
C	-2.3073323269	-0.7160536141	2.6046290159
C	2.3219676950	-0.7579625855	-2.6046296631
C	2.3219676950	-0.7579625855	2.6046296631
C	-2.2966068097	0.7390620473	-2.6012235463
C	-2.2966068097	0.7390620473	2.6012235463
C	2.3375900965	0.6971087530	-2.6012241559
C	2.3375900965	0.6971087530	2.6012241559
C	-0.7386787490	-2.6033070947	-2.3091512963
C	-0.7386787490	-2.6033070947	2.3091512963
C	0.7193994622	-2.6165006422	-2.3091473201
C	0.7193994622	-2.6165006422	2.3091473201
C	-0.7017424744	2.6091503566	-2.2984941107
C	-0.7017424744	2.6091503566	2.2984941107
C	0.7768452044	2.5957666703	-2.2984958599
C	0.7768452044	2.5957666703	2.2984958599
C	-3.0407791727	-1.1639924336	-1.4284221165
C	-3.0407791727	-1.1639924336	1.4284221165
C	3.0471845750	-1.2191081953	-1.4284234227
C	3.0471845750	-1.2191081953	1.4284234227
C	-3.0158128351	1.1888744680	-1.4287956266
C	-3.0158128351	1.1888744680	1.4287956266
C	3.0648217143	1.1338248826	-1.4287956274
C	3.0648217143	1.1338248826	1.4287956274
C	-1.4423042514	-3.0336547323	-1.1777926644
C	-1.4423042514	-3.0336547323	1.1777926644
C	1.4151186888	-3.0595165961	-1.1777902951
C	1.4151186888	-3.0595165961	1.1777902951
C	-1.4048253342	3.0491960545	-1.1868513571
C	-1.4048253342	3.0491960545	1.1868513571
C	1.4877796810	3.0230114921	-1.1868531740
C	1.4877796810	3.0230114921	1.1868531740
C	-2.6153604353	-2.2993458641	-0.7283838970
C	-2.6153604353	-2.2993458641	0.7283838970
C	2.6012789308	-2.3465729693	-0.7283838513
C	2.6012789308	-2.3465729693	0.7283838513
C	-2.5577614471	2.3143751577	-0.7285008240
C	-2.5577614471	2.3143751577	0.7285008240
C	2.6272189341	2.2674307029	-0.7285000201
C	2.6272189341	2.2674307029	0.7285000201
C	-3.4794593381	0.0163040106	-0.6989161537
C	-3.4794593381	0.0163040106	0.6989161537
C	3.5071639554	-0.0469514871	-0.6989163805
C	3.5071639554	-0.0469514871	0.6989163805
C	-0.7172583839	-3.4890231659	0.0000000000
C	0.6819448035	-3.5016799948	0.0000000000
C	-0.7232475186	3.6669192280	0.0000000000
C	0.8174934796	3.6529706839	0.0000000000
S	0.0622028193	5.3259253469	0.0000000000

$C_{60}S^{2-}$ TRIPLET B3LYP/DH(d)+S(d,p)

C	-0.0028966614	-0.7098480800	-3.4894010588
C	-0.0028966614	-0.7098480800	3.4894010588
C	-0.0013841364	0.6910615913	-3.4812578788
C	-0.0013841364	0.6910615913	3.4812578788
C	-1.1804025996	-1.4478488650	-3.0526028271
C	-1.1804025996	-1.4478488650	3.0526028271
C	1.1762338159	-1.4442307826	-3.0426993392
C	1.1762338159	-1.4442307826	3.0426993392
C	-1.1811302939	1.4250335936	-3.0292224460
C	-1.1811302939	1.4250335936	3.0292224460
C	1.1740934563	1.4184762796	-3.0312040072
C	1.1740934563	1.4184762796	3.0312040072
C	-2.3105216739	-0.7374913572	-2.6092358344
C	-2.3105216739	-0.7374913572	2.6092358344
C	2.3114500297	-0.7415181730	-2.6122443290
C	2.3114500297	-0.7415181730	2.6122443290
C	-2.3282045050	0.7090543855	-2.6175401048
C	-2.3282045050	0.7090543855	2.6175401048
C	2.3173851774	0.7102119142	-2.6132963254
C	2.3173851774	0.7102119142	2.6132963254
C	-0.7239685931	-2.6208277214	-2.3257542231
C	-0.7239685931	-2.6208277214	2.3257542231
C	0.7244170150	-2.6269632468	-2.3287728837
C	0.7244170150	-2.6269632468	2.3287728837
C	-0.7414894879	2.6028389356	-2.3287118682
C	-0.7414894879	2.6028389356	2.3287118682
C	0.7284152145	2.5954260788	-2.3121814521
C	0.7284152145	2.5954260788	2.3121814521
C	-3.0462001859	-1.1928029578	-1.4284960456
C	-3.0462001859	-1.1928029578	1.4284960456
C	3.0426928415	-1.1922443884	-1.4280606787
C	3.0426928415	-1.1922443884	1.4280606787
C	-3.0490380052	1.1472548341	-1.4292349564
C	-3.0490380052	1.1472548341	1.4292349564
C	3.0321021368	1.1513565161	-1.4330672484
C	3.0321021368	1.1513565161	1.4330672484
C	-1.4342550641	-3.0613480170	-1.1841458601
C	-1.4342550641	-3.0613480170	1.1841458601
C	1.4340311201	-3.0606668946	-1.1828996455
C	1.4340311201	-3.0606668946	1.1828996455
C	-1.4333494187	3.0153321255	-1.1675812967
C	-1.4333494187	3.0153321255	1.1675812967
C	1.4282078708	3.0280623823	-1.1848358050
C	1.4282078708	3.0280623823	1.1848358050
C	-2.5995907601	-2.3296896121	-0.7321508527
C	-2.5995907601	-2.3296896121	0.7321508527
C	2.5998600587	-2.3323266233	-0.7325922117
C	2.5998600587	-2.3323266233	0.7325922117
C	-2.6092511347	2.2805352835	-0.7294424529
C	-2.6092511347	2.2805352835	0.7294424529
C	2.5640736155	2.2822868451	-0.7323563947
C	2.5640736155	2.2822868451	0.7323563947
C	-3.5133314133	-0.0265631082	-0.7084493891
C	-3.5133314133	-0.0265631082	0.7084493891
C	3.4954618084	-0.0212318645	-0.7069630073
C	3.4954618084	-0.0212318645	0.7069630073
C	-0.6997084878	-3.4869072149	0.0000000000
C	0.7040106980	-3.4978324752	0.0000000000
C	-0.7294017880	3.4791429306	0.0000000000
C	0.7524779997	3.7238419251	0.0000000000
S	0.7649297836	5.5866554235	0.0000000000

[5,6]-closed $C_{60}S$ TRIPLET B3LYP/DH(d)+S(d,p)

C	-0.0033350795	-0.7034946623	-3.4814159975
C	-0.0033350795	-0.7034946623	3.4814159975
C	-0.0010755551	0.7079449264	-3.4748156316
C	-0.0010755551	0.7079449264	3.4748156316
C	-1.1692762765	-1.4262571760	-3.0329925427
C	-1.1692762765	-1.4262571760	3.0329925427
C	1.1774067485	-1.4310765688	-3.0283786561
C	1.1774067485	-1.4310765688	3.0283786561
C	-1.1893245654	1.4294606178	-3.0250739324
C	-1.1893245654	1.4294606178	3.0250739324
C	1.1580022169	1.4341608118	-3.0357285735
C	1.1580022169	1.4341608118	3.0357285735
C	-2.3134155274	-0.7307886006	-2.6001667170
C	-2.3134155274	-0.7307886006	2.6001667170
C	2.3023578071	-0.7334864752	-2.5917093255
C	2.3023578071	-0.7334864752	2.5917093255
C	-2.3195164293	0.7257121976	-2.6001416028
C	-2.3195164293	0.7257121976	2.6001416028
C	2.3025107209	0.7319692456	-2.5818420774
C	2.3025107209	0.7319692456	2.5818420774
C	-0.7199823888	-2.6106772424	-2.3061035714
C	-0.7199823888	-2.6106772424	2.3061035714
C	0.7333543659	-2.6176568723	-2.3095450269
C	0.7333543659	-2.6176568723	2.3095450269
C	-0.7525536637	2.6099951007	-2.2990349543
C	-0.7525536637	2.6099951007	2.2990349543
C	0.7006050004	2.6163762238	-2.2952494059
C	0.7006050004	2.6163762238	2.2952494059
C	-3.0346815630	-1.1815963286	-1.4289185540
C	-3.0346815630	-1.1815963286	1.4289185540
C	3.0357775907	-1.1847352335	-1.4236212636
C	3.0357775907	-1.1847352335	1.4236212636
C	-3.0567859759	1.1751169923	-1.4263289324
C	-3.0567859759	1.1751169923	1.4263289324
C	3.0297517576	1.1713915567	-1.4447562623
C	3.0297517576	1.1713915567	1.4447562623
C	-1.4204426501	-3.0445858511	-1.1767189852
C	-1.4204426501	-3.0445858511	1.1767189852
C	1.4357855186	-3.0523038283	-1.1777575242
C	1.4357855186	-3.0523038283	1.1777575242
C	-1.4633465022	3.0482497898	-1.1738387752
C	-1.4633465022	3.0482497898	1.1738387752
C	1.3902692551	3.0516962003	-1.1736215520
C	1.3902692551	3.0516962003	1.1736215520
C	-2.5976027253	-2.3159858042	-0.7244672571
C	-2.5976027253	-2.3159858042	0.7244672571
C	2.6108602032	-2.3269607074	-0.7262531931
C	2.6108602032	-2.3269607074	0.7262531931
C	-2.6386455649	2.3140689838	-0.7280992501
C	-2.6386455649	2.3140689838	0.7280992501
C	2.7080331098	2.4440257163	-0.7677587648
C	2.7080331098	2.4440257163	0.7677587648
C	-3.4945864789	-0.0052051188	-0.6997981267
C	-3.4945864789	-0.0052051188	0.6997981267
C	3.4643443302	0.0000525096	-0.7005745259
C	3.4643443302	0.0000525096	0.7005745259
C	-0.6915754849	-3.4980359804	0.0000000000
C	0.7068216684	-3.5044735674	0.0000000000
C	-0.7427107894	3.4978882756	0.0000000000
C	0.6678681996	3.4747322907	0.0000000000
S	4.0106210493	3.5390681742	0.0000000000

[6,6]-closed $C_{60}S$ TRIPLET B3LYP/DH(d)+S(d,p)

C	-0.0033350795	-0.7034946623	-3.4814159975
C	-0.0033350795	-0.7034946623	3.4814159975
C	-0.0010755551	0.7079449264	-3.4748156316
C	-0.0010755551	0.7079449264	3.4748156316
C	-1.1692762765	-1.4262571760	-3.0329925427
C	-1.1692762765	-1.4262571760	3.0329925427
C	1.1774067485	-1.4310765688	-3.0283786561
C	1.1774067485	-1.4310765688	3.0283786561
C	-1.1893245654	1.4294606178	-3.0250739324
C	-1.1893245654	1.4294606178	3.0250739324
C	1.1580022169	1.4341608118	-3.0357285735
C	1.1580022169	1.4341608118	3.0357285735
C	-2.3134155274	-0.7307886006	-2.6001667170
C	-2.3134155274	-0.7307886006	2.6001667170
C	2.3023578071	-0.7334864752	-2.5917093255
C	2.3023578071	-0.7334864752	2.5917093255
C	-2.3195164293	0.7257121976	-2.6001416028
C	-2.3195164293	0.7257121976	2.6001416028
C	2.3025107209	0.7319692456	-2.5818420774
C	2.3025107209	0.7319692456	2.5818420774
C	-0.7199823888	-2.6106772424	-2.3061035714
C	-0.7199823888	-2.6106772424	2.3061035714
C	0.7333543659	-2.6176568723	-2.3095450269
C	0.7333543659	-2.6176568723	2.3095450269
C	-0.7525536637	2.6099951007	-2.2990349543
C	-0.7525536637	2.6099951007	2.2990349543
C	0.7006050004	2.6163762238	-2.2952494059
C	0.7006050004	2.6163762238	2.2952494059
C	-3.0346815630	-1.1815963286	-1.4289185540
C	-3.0346815630	-1.1815963286	1.4289185540
C	3.0357775907	-1.1847352335	-1.4236212636
C	3.0357775907	-1.1847352335	1.4236212636
C	-3.0567859759	1.1751169923	-1.4263289324
C	-3.0567859759	1.1751169923	1.4263289324
C	3.0297517576	1.1713915567	-1.4447562623
C	3.0297517576	1.1713915567	1.4447562623
C	-1.4204426501	-3.0445858511	-1.1767189852
C	-1.4204426501	-3.0445858511	1.1767189852
C	1.4357855186	-3.0523038283	-1.1777575242
C	1.4357855186	-3.0523038283	1.1777575242
C	-1.4633465022	3.0482497898	-1.1738387752
C	-1.4633465022	3.0482497898	1.1738387752
C	1.3902692551	3.0516962003	-1.1736215520
C	1.3902692551	3.0516962003	1.1736215520
C	-2.5976027253	-2.3159858042	-0.7244672571
C	-2.5976027253	-2.3159858042	0.7244672571
C	2.6108602032	-2.3269607074	-0.7262531931
C	2.6108602032	-2.3269607074	0.7262531931
C	-2.6386455649	2.3140689838	-0.7280992501
C	-2.6386455649	2.3140689838	0.7280992501
C	2.7080331098	2.4440257163	-0.7677587648
C	2.7080331098	2.4440257163	0.7677587648
C	-3.4945864789	-0.0052051188	-0.6997981267
C	-3.4945864789	-0.0052051188	0.6997981267
C	3.4643443302	0.0000525096	-0.7005745259
C	3.4643443302	0.0000525096	0.7005745259
C	-0.6915754849	-3.4980359804	0.0000000000
C	0.7068216684	-3.5044735674	0.0000000000
C	-0.7427107894	3.4978882756	0.0000000000
C	0.6678681996	3.4747322907	0.0000000000
S	4.0106210493	3.5390681742	0.0000000000

[6,6]-closed $C_{60}S^{-1}$ B3LYP/DH(d)+S(d,p)

C	0.0075517316	-0.7111596146	-3.4891950699
C	0.0075517316	-0.7111596146	3.4891950699
C	0.0203649695	0.7041773394	-3.4783868314
C	0.0203649695	0.7041773394	3.4783868314
C	-1.1709844305	-1.4235134702	-3.0346485930
C	-1.1709844305	-1.4235134702	3.0346485930
C	1.1729968387	-1.4447328166	-3.0346498004
C	1.1729968387	-1.4447328166	3.0346498004
C	-1.1449518557	1.4345136328	-3.0215731583
C	-1.1449518557	1.4345136328	3.0215731583
C	1.1987152214	1.4132982839	-3.0215750261
C	1.1987152214	1.4132982839	3.0215750261
C	-2.3040954624	-0.7186683351	-2.5972768113
C	-2.3040954624	-0.7186683351	2.5972768113
C	2.3186836215	-0.7605183863	-2.5972761577
C	2.3186836215	-0.7605183863	2.5972761577
C	-2.2924847238	0.7420328007	-2.5934078289
C	-2.2924847238	0.7420328007	2.5934078289
C	2.3335213864	0.7001536321	-2.5934073320
C	2.3335213864	0.7001536321	2.5934073320
C	-0.7369263998	-2.6111862269	-2.3072757822
C	-0.7369263998	-2.6111862269	2.3072757822
C	0.7175036687	-2.6243459642	-2.3072709314
C	0.7175036687	-2.6243459642	2.3072709314
C	-0.6985379421	2.6164588379	-2.2980852864
C	-0.6985379421	2.6164588379	2.2980852864
C	0.7737738135	2.6031320432	-2.2980870671
C	0.7737738135	2.6031320432	2.2980870671
C	-3.0401723937	-1.1670921524	-1.4309330898
C	-3.0401723937	-1.1670921524	1.4309330898
C	3.0465237284	-1.2221978795	-1.4309353593
C	3.0465237284	-1.2221978795	1.4309353593
C	-3.0183012120	1.1953411705	-1.4331413622
C	-3.0183012120	1.1953411705	1.4331413622
C	3.0674262091	1.1402453714	-1.4331401444
C	3.0674262091	1.1402453714	1.4331401444
C	-1.4445076319	-3.0411806129	-1.1764367182
C	-1.4445076319	-3.0411806129	1.1764367182
C	1.4171847864	-3.0670824853	-1.1764352211
C	1.4171847864	-3.0670824853	1.1764352211
C	-1.4067615878	3.0564380143	-1.1863242814
C	-1.4067615878	3.0564380143	1.1863242814
C	1.4898483106	3.0302189527	-1.1863257162
C	1.4898483106	3.0302189527	1.1863257162
C	-2.6195943613	-2.3127612179	-0.7244514806
C	-2.6195943613	-2.3127612179	0.7244514806
C	2.6052666734	-2.3600607900	-0.7244507367
C	2.6052666734	-2.3600607900	0.7244507367
C	-2.5605488599	2.3279715908	-0.7260782164
C	-2.5605488599	2.3279715908	0.7260782164
C	2.6302534734	2.2809765049	-0.7260778876
C	2.6302534734	2.2809765049	0.7260778876
C	-3.4669770577	0.0166188920	-0.6991133974
C	-3.4669770577	0.0166188920	0.6991133974
C	3.4946895929	-0.0464094614	-0.6991136048
C	3.4946895929	-0.0464094614	0.6991136048
C	-0.7176076001	-3.4991204826	0.0000000000
C	0.6821099368	-3.5117800075	0.0000000000
C	-0.7190821533	3.6653481666	0.0000000000
C	0.8133017495	3.6514753289	0.0000000000
S	0.0623578533	5.3427416876	0.0000000000