

Encapsulation and convex-face thiozonolysis of triatomic sulfur (S_3) with carbon nanotubes

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Nanotubes are a class of host cavities increasingly used to encapsulate unstable molecules, yet none have been exploited to host reactive sulfur species, such as thiozone (S_3). In this paper, density functional theory and (ONIOM) calculations were used to compute single-walled carbon nanotube (SWNT)–thiozone combinations for the inclusion of S_3 into the hollow nanotube space and to rationalize when 1,2,3-thiozonide formation can take place. Nanotube diameter selectivity for the isomerization of the C_{2v} form of S_3 to the D_{3h} form proved to be elusive. Acyclic C_{2v} S_3 was ~ 6 kcal/mol more stable than cyclic D_{3h} S_3 whether it was free or encapsulated within an SWNT. 1,2,3-Thiozonide formation took place on the convex side of nanotubes of low tube radii, such as the armchair (4,4) and (5,5) SWNTs. In terms of the reaction mode of C_{2v} S_3 , the 1,3-dipolar addition reaction was preferred compared with the [2 + 2] cycloaddition and chelotrope paths. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: carbon nanotubes; ONIOM; thiozonide; thiozone confinement

INTRODUCTION

In this paper, our goal was to compute various carbon nanotube–thiozone combinations for the inclusion of thiozone (S_3) into a hollow nanotube space to rationalize when 1,2,3-thiozonide formation can take place and to examine the thiozonolysis mechanism. C_{2v} symmetric S_3 (**1**) has been detected by UV–visible, microwave, and infrared spectroscopy^[1–5] and has been observed in the atmospheres of Venus and Io because of volcanic activity (Scheme 1).^[6–9] The D_{3h} form of S_3 (**2**) has thus far eluded experimental observation. There is rather sparse use of S_3 in organic synthesis^[10] because of its instability compared with cyclic S_8 ,^[11–15] even though its generation is seemingly straightforward in the disproportionation of S_2O .^[16] Previous papers also suggested the facile production of S_3 in the decomposition of natural product benzopentasulfanes.^[17–20]

Although nanotubes have not yet been used to encapsulate sulfur allotropes such as thiozone,^[21–24] literature nanotube calculations have revealed convex-surface diameter-dependent reactions with higher reactivity for the lower radii nanotubes.^[25–33] For example, density functional theory (DFT) calculations on singlet oxygen with ($n,0$) zigzag SWNTs showed an increased exothermicity with nanotubes of reduced diameters, and that type (metallic, chiral, non-metallic) did not play a role in this diameter–reactivity relationship.^[34,35] Recent DFT calculations using GGA-PW91/DNP to model the addition of methylamine to C_{60} , C_{50} , (5,5) SWNT, and (10,10) SWNT revealed a similar curvature dependence,^[36] although the addition of benzenediazonium salts to SWNTs was controlled by the optical band gap of the tube rather than the pyramidalization of the carbon atoms.^[37] DFT (ONIOM) methods have showed that the 1,3-dipolar cycloadditions of formozomethine ylide and fulminic acid took place only on the smallest-diameter SWNTs.^[29–33]

For a theoretical project, we considered armchair, zigzag, and chiral singlet-walled carbon nanotube (SWNT) hosts and possible interior and exterior reactions of S_3 (Fig. 1). Here, we

describe three classes of S_3 calculations: (i) free and (ii) SWNT-encapsulated S_3 (including a qualitative model that predicts an inner nanotube storage capacity of thiozone) and (iii) S_3 sulfuration of convex aromatic surfaces producing 1,2,3-thiozonide structures reminiscent of organic trisulfanes^[38] and molozonides.^[25–28] For simplicity, our study neglected possible S_3 reactions at nanotube end caps, regions around the rim,^[39] such as the COOH functionality introduced onto SWNTs or defect sites.^[40–44] (Scheme 2 illustrates how the nomenclature of carbon nanotubes is related to an unfolded graphene sheet, in which armchair nanotubes result when the m and n integers are equal, zigzag nanotubes take the form ($n,0$), and chiral nanotubes result when $m \neq n \neq 0$)^[45,46]

COMPUTATIONAL METHODS

Geometry optimizations were performed with the Gaussian 09 program package (Gaussian, Inc., Wallingford, CT, USA)^[47] using standard protocols^[48,49] and the M06-2X,^[50] B3P86,^[51–53] or



Scheme 1. Cyclic and acyclic forms of thiozone

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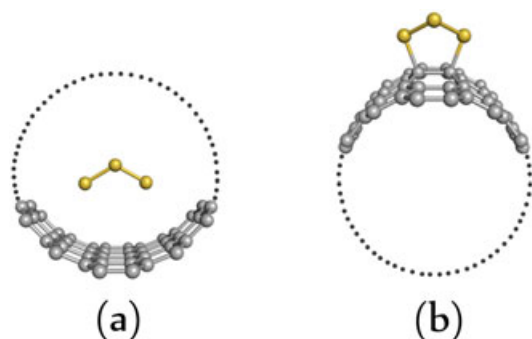
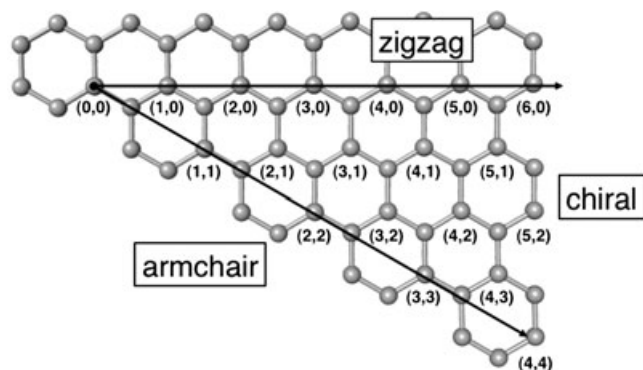


Figure 1. Schematic of (a) **1** encapsulated inside a single-walled carbon nanotube (SWNT) and (b) an SWNT 1,2,3-thiozonide



Scheme 2. Nomenclature of single-walled carbon nanotubes derived from a graphene segment with indexed lattice points (adapted from Dresselhaus *et al.*^[45])

SVWN^[54,55] functionals with either basis set “a” [6-31G(d)], “b” [6-311 + G(3d)], or “c” (STO-3G). Calculations were also conducted at the ONIOM(B3P86/a or b:SVWN/c) levels.^[56,57] Geometries were optimized to minima or maxima on the potential energy surface, and the IRC calculations were performed on the transition-state structures. All calculated values included thermal corrections for enthalpy.

RESULTS AND DISCUSSION

Calculated structures of thiozone

Here, we summarize data on thiozone. Table 1 gives the calculated properties and energetics of S_3 obtained from various theoretical methods. Except for SCF/DZ + P and M06-2X/cc-type, all calculations employed in Table 1 favor the C_{2v} form of S_3 to the D_{3h} form by 2.8 to 7.9 kcal/mol.^[59–65] Reaching **2** from **1** is a high-barrier process (24.8 to 36.9 kcal/mol); as reported before,^[66] the cyclization is symmetry forbidden attributed to the gain of a σ bond in **2** and the loss of a π bond in **1**. Ruedenberg *et al.* computed that the interconversion of **1** and **2** occurred via a C_{2v} transition state that lied in the vicinity of a conical intersection.^[67,68] To our surprise, the M06-2X method was not reliable; the near-isoenergetic S_3 values predicted make it difficult to justify the use of this method to make predictions for new nanotube–thiozone combinations in the paper. Even the inclusion of tight d polarization basis set functions on the M06-2X calculations did not produce relative energies similar to the coupled-cluster and CI calculations or bond lengths similar to the FT-microwave structure. On the other hand, the B3P86/6-311 + G (2d) calculations provided reasonable energetics and a good

Table 1. Calculated properties and energetics of the open C_{2v} and cyclic D_{3h} forms of S_3 ^{a,b,c}

Method	C_{2v} 1		D_{3h} 2	Barrier height ^a	Rel. energy of $D_{3h}-C_{2v}$ ^a 2 1	Ref.
	S1–S2 (Å)	S1–S2–S3 (°)	S1–S2 (Å)			
Experiment	(1.917)	(117.4)	—	—	—	McCarthy <i>et al.</i> ^[58]
SCF/DZ + P	1.907	117.2	2.083	—	–9.3	Rice <i>et al.</i> ^[59]
B3LYP/cc-pVTZ	1.960	117.5	2.127	—	7.4	Millefiori and Alparone ^[60]
B3LYP/LanL2DZG(d)	1.956	117.5	2.130	24.8	7.9	Goddard <i>et al.</i> ^[61]
B3P86/6-311 + G(2d)	1.927	118.1	2.097	26.4	6.6	Goddard <i>et al.</i> ^[61]
M06-2X/b	1.936	118.0	2.102	28.9	2.8	This work
M06-2X/cc-pV5Z	1.900	117.6	2.063	—	–1.3	This work
M06-2X/cc-pV(Q + d)Z	1.896	117.7	2.062	29.4	–0.9	This work
M06-2X/cc-pV(5 + d)Z	1.896	117.7	2.062	30.1	–0.9	This work
MRCI + Q/ANO6532	1.937	117.8	2.094	36.9	6.8	Koch <i>et al.</i> ^[62]
CCSD(T)/ANO6532	1.932	117.3	2.093	—	5.6	Koch <i>et al.</i> ^[62]
CCSD(T)/cc-pV5Z	1.918	117.3	2.077	—	4.8	Francisco <i>et al.</i> ^[63]
CASPT2/ANO-QZP	1.924	117.3	2.083	—	6.7	Azizi <i>et al.</i> ^[64]
MR-ccCA-AQCC(S_DT)	—	—	—	—	5.3	Oyedepo and Wilson ^[65]

^aEnergies in kcal/mol.

^bExperimental values in parentheses.

^cThe computed S1–S2–S3 angle in D_{3h} S_3 was 60° in all cases.

geometry when compared with the available experimental structure for $C_{2v} S_3$. The B3P86/6-311+G(2d) computed S1–S2 bond length had a 0.01 Å discrepancy and S1–S2–S3 bond angle 0.7° discrepancy to the experimental structure.^[58]

Nanotube-encapsulated thiozone

Here, we investigated thiozone within the SWNT interiors. ONIOM calculations were carried out where the treatment separated the dinaphtho[2,1,8,7-*hijk*:2',1',8',7'-*stuv*]ovalene and the S_3 unit from the rest of the nanotube (Fig. 2). The junction between B3P86 and SVWN was at the remaining carbon atoms around the perimeter of the ovalene unit: for example, the 78 carbon atoms for the armchair (4,4) SWNT, the 198 carbon atoms for armchair (8,8) SWNT, and the 150 carbon atoms for

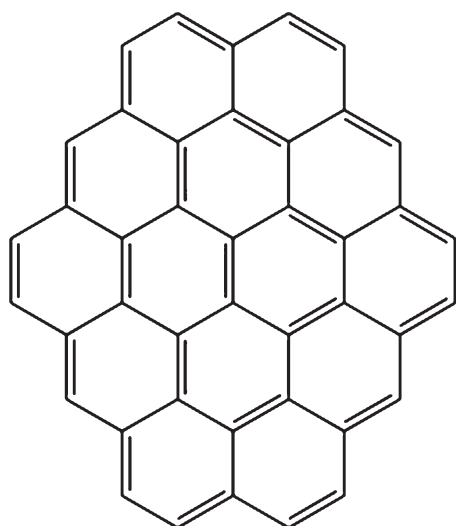


Figure 2. The dinaphtho[2,1,8,7-*hijk*:2',1',8',7'-*stuv*]ovalene unit used in the B3P86 portion of the ONIOM calculations

graphene. The ONIOM ground-state structures and energetics of encapsulated **1** and **2** are listed in Table 2.

We find that **1** is more stable than **2** within the SWNTs. The opposite was never found. Expected nanotube polarization effects^[69] to stabilize confined dipolar **1** had essentially no detectable effect. Although the smallest diameter nanotube analyzed was the (4,4), and with a diameter of 5.4 Å, the C and S atomic radii^[70] was judged to be too small to encapsulate **2**. The S1–S2–S3 bond angle was more linear for **1**@(4,4) SWNT compared with free **1**. For **1**@(5,5) SWNT, the $C_{2v} S_3$ molecule was aligned parallel to the tube, it along the z-axis, not perpendicular to the x-axis or y-axis (Fig. 3). The S_3 molecule can adopt the different orientations within the (5,5), (6,6), (7,7), and (8,8) SWNTs. Because the rotation depended on the space available for the S_3 molecule, C_2 rotation is facile within the (7,7), and (8,8) SWNTs along the z-axis or x-axis, in contrast to the (5,5) SWNT (~40–50 kcal/mol) and the (6,6) SWNT (~20 kcal/mol) (Fig. 4). The computations yielded no addition of S_3 to the inner wall of nanotubes undoubtedly because of the acute inverse pyramidalization that would be necessary to produce a thiozonide. Even along the z-axis, the thiozone does not react with the flat surface. An open-shell stepwise pathway to a biradical intermediate was sought, but no structure optimized to a C–S bonded compound or to a three-membered ring SWNT-1-persulfide structure with a linear sulfur linkage. DFT calculations also indicate that alkyl radicals do not react with the inner walls of carbon nanotubes because of the high-energy cost to produce a “negative” distortion of the tube geometries.^[71]

In the absence of molecular-dynamics simulations of S_3 molecules within the nanotubes, we speculate a qualitative picture based on the previous static computed structures. Because of the large radii, undoubtedly many S_3 molecules can reside within the (6,6), (7,7), and (8,8) SWNTs, which could oligomerize to other sulfur allotropes or plug the nanotubes. The coupling product cyclic S_6 does not fit within the (5,5) SWNT; however, there was sufficient but limited space for cyclic S_8

Table 2. Calculated properties and energetics of **1** and **2** encapsulated in nanotubes^{a,b,c}

SWNT	1		2		Rel. energy S_3 $D_{3h}-C_{2v}$ ^a 2 1	Nanotube diameter (Å) ^d
	S1–S2 (Å)	S1–S2–S3 (°)	S1–S2 (Å)	S1–S2–S3 (°)		
(4,4) ^c	1.933	121.2	—	—	—	5.4
(5,5)	1.934	116.6	2.056	59.5	13.2	6.8
(6,4)	1.932	116.9	2.060	59.7	8.9	6.8
(9,0)	1.928	117.6	2.064	60.2	9.8	7.1
(8,2)	1.934	117.3	2.067	60.3	10.1	7.2
(7,4)	1.927	117.6	2.073	59.8	7.2	7.6
(6,6)	1.926	117.7	2.089	59.5	7.2	8.2
(7,7)	1.927	118.0	2.091	60.0	7.6	9.5

^aEnergies in kcal/mol; length of the nanotube = 1.2 nm.

^bCalculated by ONIOM(B3P86/b:SVWN/c)//ONIOM(B3P86/a:SVWN/c).

^c $D_{3h} S_3$: S2–S3 = 1.92 Å; S2–S3–S1 = 67.3°.

^dNanotube diameters taken from Lawler *et al.*^[80].

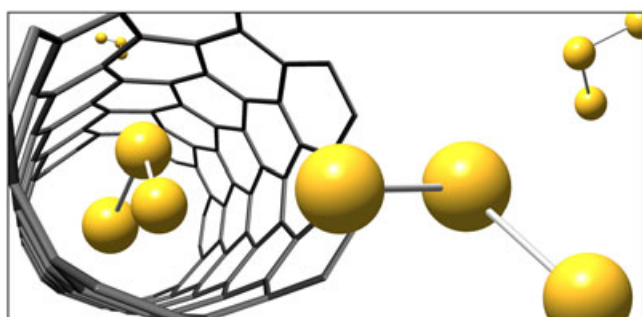


Figure 3. The S_3 molecule preferentially lies along the z-axis of the armchair (5,5) single-walled carbon nanotube, which is flat. There was a high energy ($\sim 40\text{--}50$ kcal/mol) for the rotation of S_3 within this nanotube

within the (6,6) SWNT (Fig. 5). *Catena*-sulfur could form,^[72,73] and our ONIOM inner-tube S_3 dimerization results agree with the previous assessment for a triplet S_6 chain product^[74–77] whose egress or translational motion would likely be restricted by reptation.^[78] A previous study reported that the intercalation of CdI_2 and molten elemental sulfur guests led to a $CdS@SWNT$ composite but in larger diameter tubes, 1–1.4 nm,^[79] than those studied here.

Whereas the encapsulated thiozone does not react with the interior of the nanotube, there is theoretical evidence for the thiozonolysis of the exterior nanotube surface.

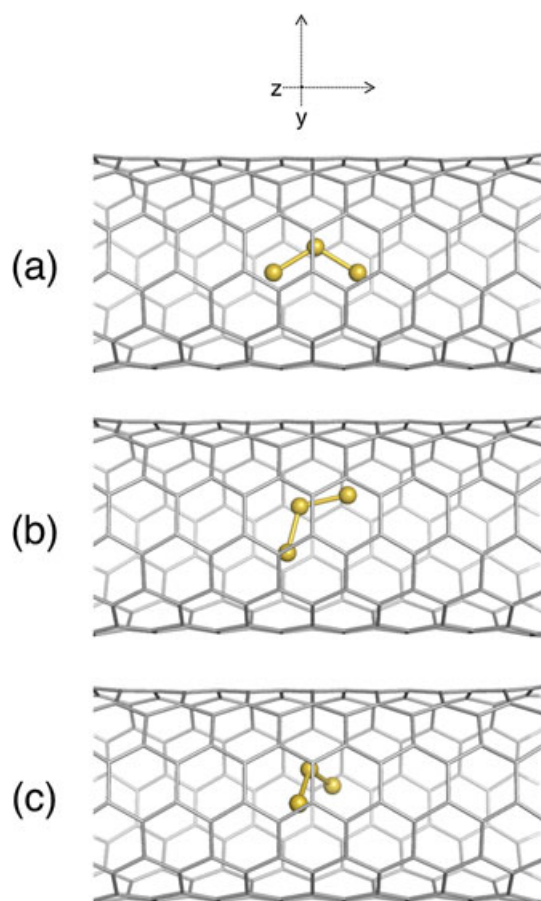


Figure 4. Side-on view of rotation **1** within the (6,6) single-walled carbon nanotube. Conformer (c) was less stable by ~ 20 kcal/mol compared with (a) or (b)

Mode of attack of thiozone

Any claim that a nanotube can host thiozone requires an inert interior and that the exterior reactivity can in principle be controlled. Here, we investigate an exterior sulfuration reaction. Because C_{60} has greater curvature than any nanotube studied here, it served as a model compound to examine thiozonation paths (Figs. 6 and 7). Figure 6 shows three routes for the addition of **1** to C_{60} ; they include the 1,3-dipolar addition to form 3',4',5'-trithiacyclopenta[1,9](C_{60})[5,6]fullerene **5** (path A), the [2+2] cycloaddition to form the 3',4'-dithiacyclobuta-1-sulfide [1,9](C_{60})[5,6]fullerene **6** (path B), and the chelotrope addition to form the 3'-thiacyclopropa-1,1-disulfide[1,9](C_{60})[5,6]fullerene **7** (path C). Path A involves symmetrical formation of the C1–S1 and C2–S3 bonds of **TS4/5** to give thiozonide **5**. The $C_{60}S_3$ thiozonide **5** has C_s symmetry and C1–S1 and C2–S3 bond lengths of 1.87 Å (Fig. 7). Path B involves formation of the C1–S1 and C2–S2 bonds of **TS4/6** to give 1,2-dithietane-1-sulfide **6**. Dithietane **6** has a branched $S_2=S_3$ bond that is 1.92 Å in length. Path C involves formation of the C1–S2 and C2–S2 bonds of **TS4/7** to give C_{2v} symmetric thiirane-1,1-disulfide **7**. Compound **7** has S1–S2 and S2–S3 bond lengths of 1.94 Å and a structure analogous to a thiirane sulfone.^[81]

As expected, the 1,3-dipolar addition of S_3 at the 6,6 site was preferred compared with the [2+2] cycloaddition and chelotrope paths. The computed barriers of paths A–C were 5.6 kcal/mol, 28.0 kcal/mol, and 42.6 kcal/mol, respectively. Path A was exothermic by 21.2 kcal/mol. In contrast, path B was endothermic by 1.4 kcal/mol, and path C was endothermic by 29.7 kcal/mol. Unlike the endergonic 1,3-dipolar cycloaddition of azomethine ylide to various nanostructures,^[82] at 298 K, the ΔG_{rxn} of path A was -5.9 kcal/mol suggesting that the trisulfane product may be stable at room temperature. The results are understandable in terms of a 1,3-dipole process (of Huisgen known for 50 years) for species such as ozone.^[83] In this regard, there is some similarity to the fullerene/ozone system, previous PBE/TZ calculations showed the addition of ozone to C_{60} at the 6,6 site to be exothermic by 31.5 kcal/mol and to C_{70} at the *a,b* site to be exothermic by 30.6 kcal/mol.^[84–86] The 1,2,3-trithiane ring of $C_{60}S_3$ **5** has an envelope conformation with a

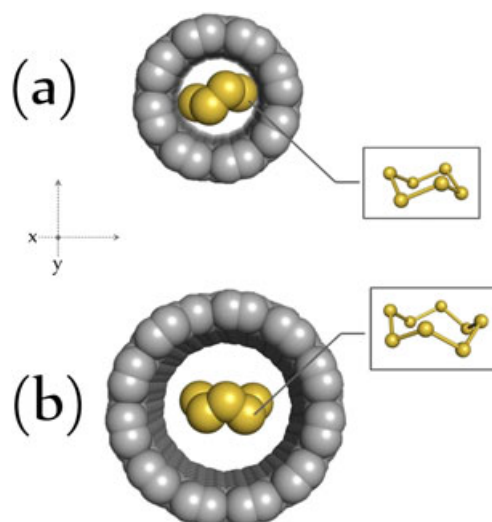


Figure 5. End-on view of (a) cyclic S_6 at (5,5) single-walled carbon nanotube (SWNT) and (b) cyclic S_8 at (6,6) SWNT

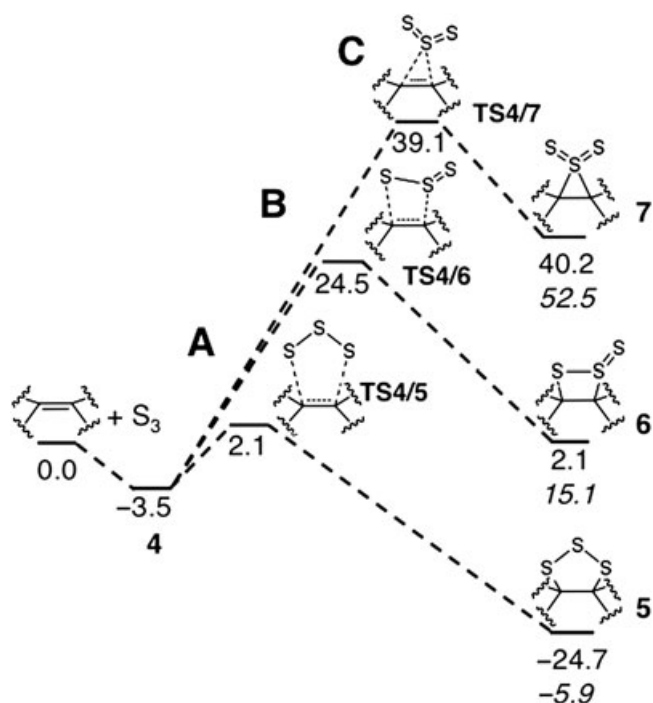


Figure 6. ONIOM(B3P86/b:SVWN/c)//ONIOM(B3P86/a:SVWN/c) computed energetics of the S_3 [60]fullerene sulfuration, which includes thermal corrections for enthalpy at 298 K (in kcal/mol). The values for free energy are in italics

pucker angle of 121.0° and a barrier to ring inversion of $\Delta H^\ddagger = 20.3$ kcal/mol at the B3P86/b level (Fig. 8A). 1,2,3-Trisulfane arenes, such as trithiolane (6b,12b-epitrithioacenaphtho[1,2-*a*]acenaphthylene) showed barriers to ring inversion of $\Delta H^\ddagger = 13.9$ kcal/mol by dynamic NMR analyses (Fig. 8B).^[87–89] The structural features of the enveloped-shaped **5** are similar to that of molozonides, and both reactions have large barriers for back dissociation of S_3 or O_3 . Harpp and Smith reported the S–S bond cleaving process of a trisulfide, which required phosphorus compounds to lead to sulfur extrusion.^[38]

Thiozonation of the convex face of single-walled carbon nanotubes

Next, ONIOM calculations were used to examine the exterior thiozonolysis of armchair (*n,n*) SWNTs ($n=4–8$) (Table 3 and Fig. 9). There were multiple reactive sites on the SWNTs; however, we selected a reaction where the orientation of the S1 and S3 atoms of S_3 were added at a 6,6 site orthogonal midway along the length of the nanotube. Not surprisingly, the smaller radii nanotubes enhanced the stability of the thiozonide product. Calculated values were also included for graphene and C_{60} . Only the 1,3-dipolar cycloaddition step was examined because the [2+2] route to the four-membered ring dithiacyclobutasulfide should be a high-energy process (*vide supra*). The ONIOM geometries of **5** and **9–12** were substantially different from **13** and **14**. In the former, the C–S bond distances were less than 2.0 Å; in the latter, they were ~ 4.0 Å.

The *abcd* dihedral angle change (used to gauge the magnitude of change in sp^3 character of the trisulfane product

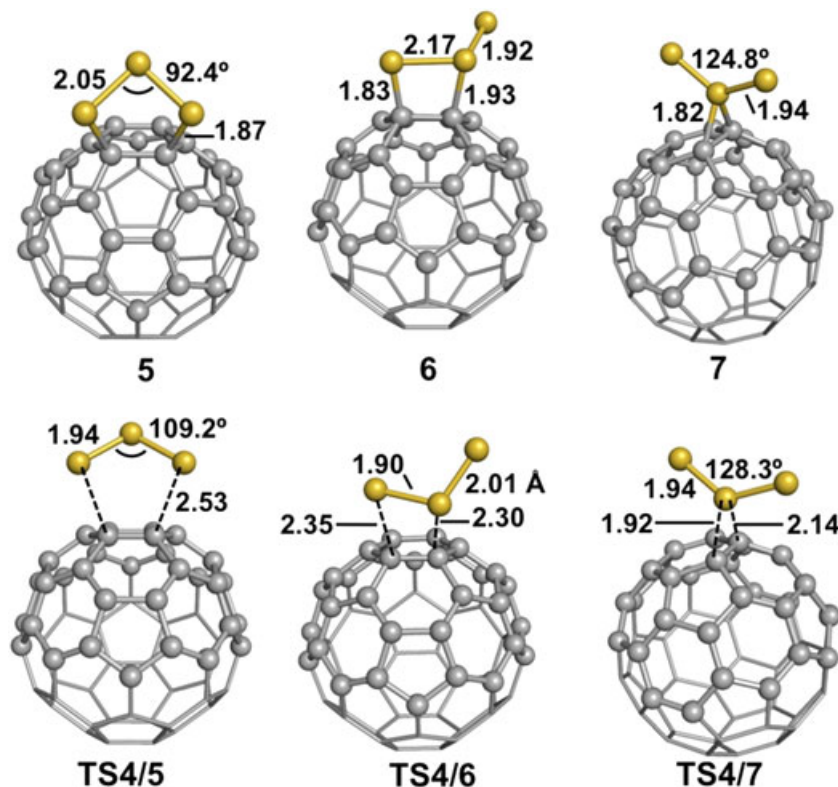


Figure 7. ONIOM(B3P86/a:SVWN/STO-3G) optimized geometries of minima and transition structures (bond distances are in Å, angles are in deg). The B3P86 layer is in ball-and-stick model, and the single-walled carbon nanotube layer is in tube model. The gray atoms are carbon, and the yellow atoms are sulfur

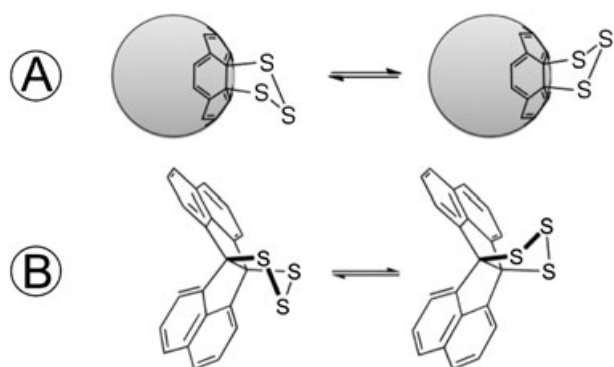


Figure 8. Ring-flipping inversion of $C_{60}S_3$ and trithiolane (6b,12b-epitrithioacenaphtho[1,2-a]acenaphthylene). The puckering angle is a measure of deviation of the ring from planarity as defined as the angle formed by the center sulfur and the midpoint of the plane made by the flanking two carbon–sulfur bonds

versus the sp^2 character of the initial all-carbon precursor) also showed a curvature-dependent thiozonation. Thiozonides were formed for **5**, **9–12**, and S_3 was physisorbed for **13** and **14**. Greater curvature of the arene host led to the enhanced stability of the thiozonide product. The thiozonation was exothermic for C_{60} and for the SWNTs of diameters less than ~ 6.8 Å and reagent $abcd$ dihedral angles less than $\sim 157^\circ$ in the series examined. For **13** and **14**, only weakly associated S_3 adducts were found.

It can be noted that a low-energy path to cleavage of the S–S and C–S bonds in **5** was not found, **5** did not decompose to Criegee-like intermediates [thione ($R_2C=S$) and thiosulfine ($R_2C=S^+S^-$)], and $C_{60}S_3$ thiozonide **5** converts to the four-membered ring 1,2-dithietane-1-sulfide (**6**) in a high-energy process (53.6 kcal/mol). By comparison, fullerene molozonides are labile^[90] and decompose by Criegee carbonyl/carbonyl-*O*-oxide pairs.^[91] The carbonyl oxygen attacks the carbonyl-*O*-oxide carbon, leading to O_2 departure and sp^3 epoxide or sp^2

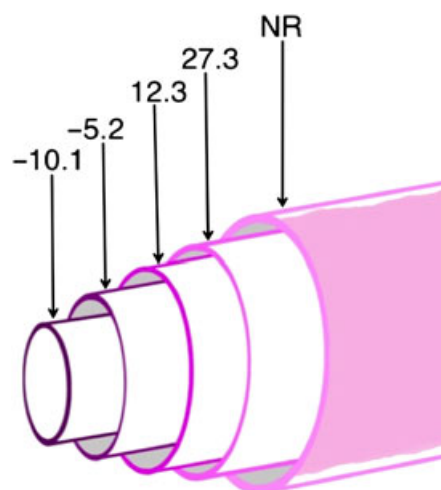


Figure 9. Schematic representation of the (n,n) single-walled carbon nanotubes ($n=4-8$) and the ΔH_{rxn} (kcal/mol) for the formation of thiozonides connected orthogonally along the x -axis or y -axis. Energetics were computed at the ONIOM(B3P86/b:SVWN/c)//ONIOM(B3P86/a:SVWN/c) level. NR=no reaction

oxidoannulene formation (such as the a,b -isomer and c,c -isomer, respectively, in C_{70}).

CONCLUSION

The calculations of free and nanotube-encapsulated thiozone predict the existence of both **1** and **2**, with the former having greater stability. There was no reactivity of S_3 with the nanotube interior itself. The (5,5) SWNT was unique among the thiozone-trapped CNTs; **1** was situated coaxially inside, although the difficulty of translational motion of S_3 (or the reptative motion of S_6 or S_9 chain products) was not computed. Larger-diameter SWNTs [(n,n) $n=(6-8)$] have hollow spaces to trap many S_3

Table 3. Calculated structural parameters of thiozonides or thiozone adducts of [60]fullerene, single-walled carbon nanotubes (SWNTs), and graphene^{a,b}

Thiozonide	C1–S1 (Å)	S1–S2–S3 (Å)	$abcd$ in reagent ($^\circ$)	$abcd$ in product ($^\circ$)
$C_{60}S_3$ 5	1.86	92.5	138.4	115.2
(4,4) SWNT S_3 9	1.91	93.0	156.4	130.3
(5,5) SWNT S_3 10	1.93	93.0	156.9	132.0
(6,6) SWNT S_3 11	1.94	92.9	160.8	133.2
(7,7) SWNT S_3 12	1.96	93.0	163.4	134.1
(8,8) SWNT S_3 13	3.96	117.6	165.3	—
graphene/ S_3 14	4.01	118.4	180.0	—

^aOptimized at the ONIOM(B3P86/a:SVWN/c) level. The B3P86/a portion of the ONIOM calculation included S_3 and the dinaphthovalene core, and SVWN/c was used on the remaining portion of the molecule.
^bLength of the SWNTs = 1.2 nm.

molecules, where there was restricted or insufficient space for cyclic S_6 in the (5,5) SWNT and cyclic S_8 in the (6,6) SWNT. Thiozonolysis was predicted to trisulfurate convex arene surfaces, such as the (4,4) and (5,5) SWNTs, because of greater convexity than the (6,6), (7,7), and (8,8) SWNTs. The 1,3-dipolar addition of S_3 was preferred compared with the [2+2] cycloaddition and chelotrope paths.

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REFERENCES

- [1] S. Thorwirth, M. C. McCarthy, C. A. Gottlieb, P. Thaddeus, H. Gupta, J. F. Stanton, *J. Chem. Phys.* **2005**, *123*, 1.
- [2] P. L. Burrow, J. W. Birks, *Anal. Chem.* **1997**, *69*, 1299.
- [3] P. Hassanzadeh, L. Andrews, *J. Phys. Chem.* **1992**, *96*, 6579.
- [4] G. D. Brabson, Z. Mielke, L. Andrews, *J. Phys. Chem.* **1991**, *95*, 79.
- [5] B. Meyer, T. V. Oommen, T. Stroyer, *J. Mol. Spectrosc.* **1972**, *42*, 335.
- [6] J. R. Lyons, *J. Sulfur Chem.* **2008**, *29*, 269.
- [7] J. I. Moses, M. Y. Zolotov, B. Fegley, *Icarus* **2002**, *156*, 76.
- [8] J. R. Spencer, K. L. Jessup, M. A. McGrath, G. E. Ballester, R. Yelle, *Science* **2000**, *288*, 1208.
- [9] J. S. Lewis, F. A. Kreimendahl, *Icarus* **1980**, *42*, 330.
- [10] J. Nakayama, *J. Sulfur Chem.* **2009**, *30*, 393.
- [11] M. K. Denk, *Eur. J. Inorg. Chem.* **2009**, 1358.
- [12] L. Rene-Boisneuf, J. C. Scaiano, *Chem. Mater.* **2008**, *20*, 6638.
- [13] R. Steudel, in: *Chemistry of the Non-Metals*, W. de Gruyter, Pub., New York, **1977**, 204.
- [14] H. L. Casal, J. C. Scaiano, *J. Photochem.* **1985**, *30*, 253.
- [15] F. N. Tebbe, E. Wasserman, W. G. Peet, A. Vatvars, A. C. Hayman, *J. Am. Chem. Soc.* **1982**, *104*, 4971.
- [16] A. Ishii, M. Nakabayashi, J. Nakayama, *J. Am. Chem. Soc.* **1999**, *121*, 7959.
- [17] A. Mahendran, A. Vuong, D. Aebischer, Y. Gong, R. Bittman, G. Arthur, A. Kawamura, A. Greer *J. Org. Chem.* **2010**, *75*, 5549.
- [18] E. M. Brzostowska, M. Paulynice, R. Bentley, A. Greer, *Chem. Res. Toxicol.* **2007**, *20*, 1046.
- [19] E. M. Brzostowska, A. Greer, *J. Am. Chem. Soc.* **2003**, *125*, 396.
- [20] A. Greer *J. Am. Chem. Soc.* **2001**, *123*, 10379.
- [21] P. M. F. J. Costa, U. K. Gautam, Y. Bando, D. Golberg *Carbon* **2010**, *49*, 342.
- [22] K. Kobayashi, K. Suenaga, T. Saito, H. Shinohara, S. Iijima, *Adv. Mater.* **2010**, *22*, 3156.
- [23] Y. Wang, Y. Huang, B. Yang, R. Liu, *Carbon* **2008**, *46*, 276.
- [24] D. Nishide, H. Dohi, T. Wakabayashi, E. Nishibori, S. Aoyagi, M. Ishida, S. Kikuchi, R. Kitaura, T. Sugai, M. Sakata, *Chem. Phys. Lett.* **2006**, *428*, 356.
- [25] W.-L. Yim, J. K. J. Johnson, *J. Phys. Chem. C* **2009**, *113*, 17636.
- [26] A. Maranzana, G. Serra, A. Giordana, G. Tonachini, G. Barco, M. Causa *J. Phys. Chem. A* **2005**, *109*, 10929.
- [27] Z. Chen, K. J. Ziegler, J. Shaver, R. H. Hauge, R. E. Smalley, *J. Phys. Chem. B* **2006**, *110*, 11624.
- [28] T. Kar, B. Akdim, X. Duan, R. Pachter, *Chem. Phys. Lett.* **2004**, *392*, 176.
- [29] S. Osuna, K. N. Houk, *Chem. Eur. J.* **2009**, *15*, 13219.
- [30] D. Sabirov, S. Khursan, R. Bulgakov, *Russ. Chem. Bull.* **2008**, *57*, 2520.
- [31] D. Ogrin, J. Chattopadhyay, A. K. Sadana, W. E. Billups, A. R. Barron, *J. Am. Chem. Soc.* **2006**, *128*, 11322.
- [32] S. Park, D. Srivastava, K. Cho, *Nano Lett.* **2003**, *3*, 1273.
- [33] T. Y. Astakhova, G. A. Vinogradov, O. D. Gurin, M. Menon, *Russ. Chem. Bull.* **2002**, *51*, 764.
- [34] Y.-F. Zhang, Z.-F. Liu, *J. Phys. Chem. B* **2004**, *108*, 11435.
- [35] S.-P. Chan, G. Chen, X. G. Gong, Z.-F. Liu, *Phys. Rev. Lett.* **2003**, *90*, 086403.
- [36] T. Lin, W.-D. Zhang, J. Huang, C. J. He, *J. Phys. Chem. B* **2005**, *109*, 13755.
- [37] C. D. Doyle, J.-D. R. Rocha, R. B. Weisman, J. M. Tour, *J. Am. Chem. Soc.* **2008**, *130*, 6795.
- [38] D. N. Harpp, R. A. Smith, *J. Am. Chem. Soc.* **1982**, *104*, 6045.
- [39] E. H. Fort, P. M. Donovan, L. T. Scott, *J. Am. Chem. Soc.* **2009**, *131*, 16006.
- [40] E. Del Canto, K. Flavin, D. Movia, C. Navois, C. Bittencourt, S. Giordani, *Chem. Mater.* **2011**, *23*, 67.
- [41] P. A. Denis, *J. Phys. Chem. C* **2009**, *113*, 5612.
- [42] P. A. Denis, *Int. J. Quantum Chem.* **2009**, *109*, 772.
- [43] P. A. Denis, R. Faccio, *Chem. Phys. Lett.* **2008**, *460*, 486.
- [44] J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. S. Shon, T. R. Lee, D. T. Colbert, R. E. Smalley, *Science* **1998**, *280*, 1253.
- [45] M. S. Dresselhaus, G. Dresselhaus, R. Saito, *Solid State Commun.* **1992**, *84*, 201.
- [46] A. C. Dillon, *Chem. Rev.* **2010**, *110*, 6856.
- [47] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox Gaussian, Inc.: Wallingford, CT, **2009**.
- [48] F. Jensen, *Introduction to Computational Chemistry*, 2nd edn, Wiley, Chichester, UK, **2007**, 177–203.
- [49] C. J. Cramer, *Essentials of Computational Chemistry*, 2nd edn, Wiley, Chichester, U.K., **2004**, 249–300.
- [50] Y. Zhao, D. G. Truhlar, *J. Chem. Theory Comput.* **2008**, *4*, 1849.
- [51] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
- [52] J. P. Perdew, *Phys. Rev. B Condens. Matter* **1986**, *33*, 8822.
- [53] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
- [54] J. C. Slater, in: *The Self-Consistent Field for Molecular and Solids, Quantum Theory of Molecular and Solids*, Vol. 4, McGraw-Hill, New York, **1974**.
- [55] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200.
- [56] T. Matsubara, F. Maseras, N. Koga, K. Morokuma, *J. Phys. Chem.* **1996**, *100*, 2573.
- [57] M. Svensson, S. Humbel, R. D. J. Froese, T. Matsubara, S. Sieber, K. Morokuma, *J. Phys. Chem.* **1996**, *100*, 19357.
- [58] M. C. McCarthy, S. Thorwirth, C. A. Gottlieb, P. Thaddeus, *J. Am. Chem. Soc.* **2004**, *126*, 4096.
- [59] J. E. Rice, R. D. Amos, N. C. Handy, T. J. Lee, H. F. Schaefer, *J. Chem. Phys.* **1986**, *85*, 963.
- [60] S. Millefiori, A. Alparone, *J. Phys. Chem. A* **2001**, *105*, 9489.
- [61] J. D. Goddard, X. Chen, G. J. Orlova, *J. Phys. Chem. A* **1999**, *103*, 4078.
- [62] W. Koch, J. Natterer, C. J. Heinemann, *Chem. Phys.* **1995**, *102*, 6159.
- [63] J. S. Francisco, J. R. Lyons, I. H. Williams, *J. Chem. Phys.* **2005**, *123*, 054302.
- [64] Z. Azizi, B. O. Roos, V. Veryazov, *Phys. Chem. Chem. Phys.* **2006**, *8*, 2727.
- [65] G. A. Oyedepo, A. K. Wilson, *J. Phys. Chem. A* **2010**, *114*, 8806.
- [66] B. Flemmig, P. T. Wolczanski, R. Hoffmann, *J. Am. Chem. Soc.* **2005**, *127*, 1278.
- [67] J. Ivancic, G. J. Atchity, K. Ruedenberg, *J. Chem. Phys.* **1997**, *107*, 4307.
- [68] V.-A. Glezakou, S. T. Elbert, S. S. Xantheas, K. Ruedenberg, *J. Phys. Chem. A* **2010**, *114*, 8923.
- [69] M. D. Halls, H. B. Schlegel, *J. Phys. Chem. B* **2002**, *106*, 1921.
- [70] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.
- [71] T. Yumura, *Phys. Chem. Chem. Phys.* **2011**, *13*, 337.
- [72] M. K. Denk, *Eur. J. Inorg. Chem.* **2009**, 1358.
- [73] A. H. Otto, R. Steudel, *Eur. J. Inorg. Chem.* **1999**, 2057.
- [74] R. O. Jones, P. Ballone, *J. Chem. Phys.* **2004**, *121*, 7535.
- [75] R. O. Jones, P. Ballone, *J. Chem. Phys.* **2003**, *118*, 9257.
- [76] S. Hunsicker, R. O. Jones, G. Ganteför, *J. Chem. Phys.* **1995**, *102*, 5917.

- [77] R. O. Jones, *J. Chem. Phys.* **1986**, *84*, 318.
- [78] X. Lei, C. E. Doubleday, M. B. Zimmt, N. J. Turro, *J. Am. Chem. Soc.* **1986**, *108*, 2444.
- [79] A. A. Eliseev, M. V. Chernysheva, N. I. Verbitskii, E. A. Kiseleva, A. V. Lukashin, Y. D. Tretyakov, N. A. Kiselev, O. M. Zhigalina, R. M. Zakalyukin, A. L. Vasiliev, A. V. Krestinin, J. L. Hutchison, B. Freitag, *Chem. Mater.* **2009**, *21*, 5001.
- [80] H. M. Lawler, D. Areshkin, J. W. Mintmire, C. T. White, *Phys. Rev. B Condens. Matter* **2005**, *72*, 233403.
- [81] Y. Steudel, R. Steudel, M. W. Wong, *Chem. Eur. J.* **2002**, *8*, 217.
- [82] P. A. Denis, F. Iribarne, *Int. J. Quantum Chem.* **2010**, *110*, 1764.
- [83] K. N. Houk, *Helv. Chim. Acta* **2010**, *93*, 1241.
- [84] D. Heymann, S. M. Bachilo, R. B. Weisman, T. Marriott, F. Cataldo, *Fullerenes Nanotubes Carbon Nanostruct.* **2002**, *10*, 37.
- [85] D. S. Sabirov, S. L. Khursan, R. G. Bulgakov, *J. Molec. Graph. Model.* **2008**, *27*, 124.
- [86] D. Heymann, *Fullerenes Nanotubes Carbon Nanostruct.* **2004**, *12*, 715.
- [87] Y. Sugihara, K. Abe, J. Nakayama, *Heteroatom Chem.* **1999**, *10*, 638.
- [88] N. Yomoji, S. Takahashi, S.-I. Chida, S. Ogawa, R. Sato, *J. Chem. Soc. Perkin Trans.* **1993**, *1*, 1995.
- [89] T. Kimura, M. Hanzawa, K. Tsujimura, T. Takahashi, Y. Kawai, E. Horn, T. Fujii, S. Ogawa, R. Sato, *Bull. Chem. Soc. Jpn* **2002**, *75*, 817.
- [90] A. Bil, Z. Latajka, C. A. Morrison, *J. Phys. Chem. A* **2009**, *113*, 9891.
- [91] R. Criegee, *Angew. Chem. Int. Ed Engl.* **1975**, *87*, 745.