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Solution Phase Photolysis of 1,2-Dithiane Alone and with Single-Walled Carbon Nanotubes

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S *Supporting Information*

ABSTRACT: Photolysis of 1,2-dithiane (**1**) in acetonitrile with single walled carbon nanotubes (SWCNTs) was earlier reported to form thiol-functionalized SWCNTs via the butane-1,4-dithiyl diradical (**2**). The present study shows that **2** instead undergoes a facile rearrangement to thiophane-2-thiol (**6**). This photoreaction is clean, rapid, and irreversible under 313 nm irradiation. The secondary photolysis of **6** with SWCNTs at a shorter wavelength (254 nm) leads to 2-thiophanyl radicals **8**, which derivatize SWCNTs by covalent attachment. Pyrolysis of the resulting "sulfurized SWCNTs" affords a mixture of organosulfur compounds, including thiophene formed by dehydrogenation. An unknown additional mechanism causes high TGA weight loss and a large incorporation of sulfur.
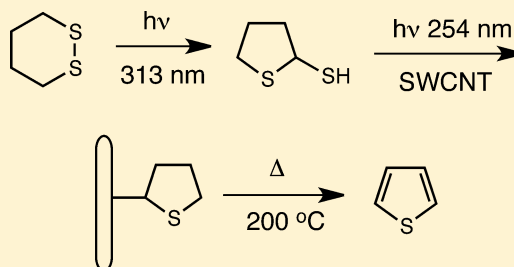
INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) have been functionalized by a variety of methods,[1−6] many of which involve free radicals.[7−18] In 2006 and 2007, Nakamura and co-workers[19,20] published an unusual functionalization approach based upon biradicals. Irradiation of cyclic disulfides, e.g., **1** generated dithiyl biradicals **2**, which were claimed to attack SWCNTs and produce thiol-functionalized SWCNTs **4**, as illustrated in Figure 1.
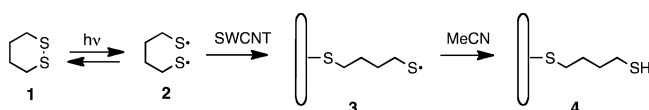
Figure 1. Reported mechanism for the photochemical functionalization of SWNCTs with 1,2-dithiane.

Although thiol groups would be useful for attaching small molecules to SWCNTs,[21,22] and indeed several sulfur-derivatized carbon nanotubes have been reported,[22−27] certain aspects of Nakamura's work are open to question. For example, biradicals are generally very short-lived[28] and hence are not likely to engage in bimolecular reactions, especially with a suspended solid. Second, theoretical calculations predict a SWCNT-sulfur bond energy of less than 10 kcal/mol so structures **3** and **4** should be thermodynamically unstable. The last step, hydrogen atom transfer from the acetonitrile (MeCN) solvent to thiyl radical **3**, should be unfavorable. Alkanethiyl radicals can abstract H[•] from reactive allylic and benzylic CH bonds[29,30] but MeCN is a poor H[•] donor[31] and the electrophilic RS[•] should react slowly with the electron-poor MeCN. Finally, we have worked with a number of cyclic disulfides and in agreement with the literature,[32,33] we found

that the larger rings polymerized spontaneously.[34] It was therefore surprising that the earlier study[19,20] included functionalization of SWCNTs with the seven- and eight-membered analogs of **1**. In view of these concerns, we have reinvestigated the photolysis of **1** alone and in the presence of SWCNTs.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed in a fume hood. The starting materials for the synthesis of disulfides were purchased from Sigma-Aldrich whereas sodium deoxycholate was from Fisher Scientific. SWCNTs (batch no. 195.2, average diameter, 0.87 nm) were prepared at Rice University by the HiPco process from carbon monoxide and $Fe(CO)_5$ catalyst. The tubes were used without purification and their absorption and fluorescence spectra were analyzed on a NS1 Nanospectralyzer made by Applied NanoFluorescence, yielding the diameter distribution shown in Figure S4, Supporting Information. Acetonitrile (HPLC grade) was degassed with N_2 and used for photochemical and UV−vis absorption studies. The UV−vis absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectropho-tometer. ^1H and ^{13}C NMR spectra were obtained on a Bruker instrument (400 or 500 MHz) using $CDCl_3$ as solvent. Photolyses were performed at 254 nm in a homemade photoreactor with four 15 W germicidal lamps, and at 313 nm using a 500 W high pressure mercury lamp with a chromate solution filter. 1,2-Dithiane (10 mg/10 mL) was irradiated in acetonitrile and the products were monitored by GC (Hewlett-

Packard 5890) with DB-WAX (0.53 mm ×30 m) and HP-5 (0.25 mm ×30 m) columns. GC/MS data were collected on an Agilent 6890N using a 0.25 mm × 30 m 35% diphenyl-65% dimethylpolysiloxane column with an average velocity of 31 cm/s. The low temperature photolysis of **6** was carried out in a nonsilvered Dewar flask. During irradiation of **1** with SWCNTs in acetonitrile (4−5 mg/mL), argon gas was bubbled through the solution, but cessation of the gas purge resulted in immediate precipitation. The reacted SWCNTs were washed with THF and hexane and then characterized by Raman spectroscopy using a Renishaw 1000 micro-Raman system with a 785 nm laser source. The elemental composition was obtained by XPS/ESCA, using a physical electronics (PHI QUANTERA) system, with a base pressure of 5×10^{-9} Torr, a monochromatic Al X-ray source with 140 eV pass energy, a 45° takeoff angle and a 100−200 μm beam diameter. TGA data (cf. Figure S6, Supporting Information) were obtained with a SDT 2960 TA Instrument under argon by heating the sample to 700 at 10 °C/min.

Pyrolysis/GC/MS. The pyrolysis GC/MS (pyr/GC/MS) experiment on SWCNTs photolyzed with **1** was performed at the Thermal Analysis Laboratory of Western Kentucky University. The samples were analyzed on a CDS 5200 pyrolyzer and a GC/MS consisting of a Varian 3800 GC and Varian 2200 Ion Trap MS with a mass range of 40−650 amu. A ~2 mg sample was placed in the pyrolyzer and heated to 300 °C at 20 °C/min and then maintained for 6 min in a helium atmosphere. The Tenax TA resin, which was used to trap volatile compounds, was held at about 50 °C, then the contents were desorbed at 300 °C and the GC trace was obtained. In the GC/MS system, the carrier gas was helium and the capillary column was DB-5MS+DG: 30 m × 0.25 mm × 0.5 μm. An 1177 injector was used in splitless mode at 275 °C and the transfer line was maintained at 300 °C. The GC oven conditions were as follows: initial temperature of 40 °C for 10 min, ramped to 275 at 5 °C/min, and held at 275 °C for 10 min.

Theoretical Methods. The reaction path for the photolysis of **1** was studied by employing the M06−2X/6-311+G(3df,2p) method.[35,36] The C−S and S−S bond dissociation energies of **1** were evaluated at the CCSD(T)/cc-pV(T+d)Z[37−41] and G3 levels of theory.[42] The coupled cluster calculations were performed with CFOUR[43,44] and the G3 ones with Gaussian 2009.[45] The reactivity of SWCNTs was studied by means of first principle periodic and non periodic density functional theory calculations. Although M06-L is less accurate than M06-2X, we used the former functional in the periodic calculations because M06-2X uses exact exchange integrals and thus the calculations become unmanageably complex when molecular size increases. The periodic calculations were conducted using four and two unit cells for the (5,5) and (10,0) SWCNTs, respectively. The unit cells were sampled employing 200 K points along the periodic direction. For the cluster model calculations, we used the M06-L/6-31G* and M06-2X/6-31G* methods. The $C_{80}H_{20}$ model was constructed to mimic an infinite (5,5) tube. The difference between the periodic and nonperiodic M06-L/6-31G* calculations was dubbed the "cluster effect" and was used to correct the M06-2X/6-31G* results. The reason for using the M06-L functional is that this method provides an accurate description of nonbonded interactions.[35]

■ RESULTS AND DISCUSSION

Irradiation of **1** at 313 nm in CD₃CN leads rapidly and exclusively to the known thiophane-2-thiol **6**[46] (Figure 2), which we characterized completely by ¹H and ¹³C NMR.
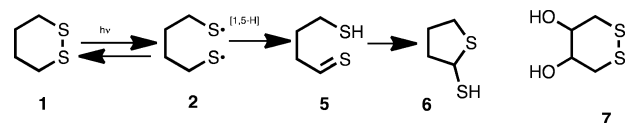

Figure 2. Photorearrangement of 1,2-dithiane.

Although this specific case has not been reported previously, the same photorearrangement was first observed in an elegant study of the analogous **7**.[47] The reaction surely proceeds via biradical **2**,[33,34,46−50] but surprisingly, the SS and CS bond dissociation energies are calculated to be similar. At the G3 level of theory, the values are 56.86 and 56.85 kcal/mol, respectively, whereas at the CCSD(T)/cc-pV(T+d)Z level, the CS bond is only 0.8 kcal/mol stronger than the SS one. Rupture of a disulfide CS bond is known at short wavelengths and when the forming alkyl radical is more stable,[51−53] but we found no evidence for this process in **1**.

We attempted to estimate the lifetime of **2** by irradiating **1** in neat 1,4-cyclohexadiene (1,4-CHD), which should rapidly transfer hydrogen atoms to **2**.[54,55] At 313 nm, **1** in 1,4-CHD still led predominantly to **6** but there was also a GC peak due to 1,4-butanedithiol (1,4-BDT). The relative areas on a HP-5 column after 40 min irradiation were 6.1% **1**, 70.6% **6**, 10.5% 1,4-butanedithiol, and 9.3% unknown at 18.68 min. Using hydrogen transfer from 1,4-CHD to **2** in a competition kinetics treatment, we can calculate the rearrangement rate of **2** as ~10^{10} s⁻¹. This number is obtained, ignoring the 9.3% unknown product, simply as the ratio of **6** to 1,4-BDT times the pseudo-first-order rate constant for hydrogen transfer. The latter is assumed to equal the value for cyclohexanethiyl radicals and 9,10-dihydroanthracene[30] times the concentration of neat 1,4-CHD (10.6 M). The unimolecular rearrangement rate of **2** is too fast for it to react with SWCNTs. The fast rate also argues against an alternate mechanism for **1** to **6** via a 1,2-hydrogen shift (see below). Cumene, a poorer H• donor than 1,4-CHD, was used previously to trap a dithiyl diradical but the chain was far larger than in **2**.[50]

Disulfide **1** absorbs light at considerably longer wavelength (λ_{max} = 290 nm) than larger ring and acyclic disulfides,[56,57] whereas **6** should hardly absorb at 313 nm.[58] These properties allowed the nearly quantitative conversion of **1** to **6**, as shown in Figure S5, Supporting Information. The same rearrangement occurred at 254 nm, but we noticed that the appearance rate of **6** slowed down with time. In an earlier related study,[59] this decrease was explained as reversibility of the **1** to **6** rearrangement. To test for photoreversibility, a solution of **1** in MeCN was irradiated at 313 nm for 40 min, which converted 99.7% of it to **6**. This solution was then irradiated at 254 nm and monitored by GC. As seen in Table 1, the percent of **6** decreased steadily while **1** increased. A new peak that built up at short retention time was identified as thiophane (**10**). It is known that the S−C−S group absorbs light at a longer wavelength (~240 nm)[58] than expected for such a non-conjugated system, which explains why **6** was photoreactive at 254 nm. The ratio of **10** to **1** increases at long times because 254 nm light converts **1** to **6**. Thus the initial ratio should be in the region of 0.3.

Table 1. GC Analysis of 1 and 6 Irradiated in MeCN[a]

time, wavelength	area % 1	area % 6	area % 10
40 min, 313 nm	0.7	99.3	
10 min, 254 nm	13.7	76.1	4.5
40 min, 254 nm	20.4	51.2	11.7
60 min, 254 nm	21.8	46.5	19.4

[a]A solution of **1** was irradiated at 313 nm for 40 min; then, the same solution was irradiated at 254 nm for cumulative times of 10, 40, and 69 min. The GC retention times on HP-5 were **1**, 13.9 min; **6**, 14.1 min; and **10**, 8.2 min. Unknown early peaks accounted for <4% of the total area whereas unknown late peaks were <15%.

When this experiment was repeated in cyclohexane, 60 min irradiation at 313 nm gave only a 43% conversion of **1** to **6** (Table 2). There were also a number of minor products (∼10%

Table 2. GC Analysis of 1 and 6 Irradiated in Cyclohexane[a]

time, wavelength	area % 1	area % 6	area % 9
30 min, 313 nm	59.6	29.2	
60 min, 313 nm	46.8	43.4	0
60 min, 313 nm; 60 min, 254 nm	51.3	31.0	2.4

[a]Times are cumulative.

of total GC peak area) that were not identifiable. The rearrangement is considerably slower and is not as clean in cyclohexane as in MeCN. Irradiation of the **1** + **6** mixture at 254 nm for 1 h increased the percentage of **1** and also led to **10**, just as in MeCN. Although there were several minor products of longer retention time, 1,4-BDT was not seen.

The above results show that 254 nm irradiation of **6** causes C−S bond homolysis to afford **10** and **1**. Thiophane **10** is easily understood as loss of the SH group followed by hydrogen abstraction from MeCN but formation of **1** requires a 1,2-H shift from **9** to **2**. We have carried out theoretical calculations on the relevant species, leading to the energies (kcal/mol) shown in Scheme 1. On the basis of the loss of •SH from **6**, we

Scheme 1. Possible Mechanistic Paths and Calculated Enthalpies (kcal/mol) for the Conversion of 1 to 6
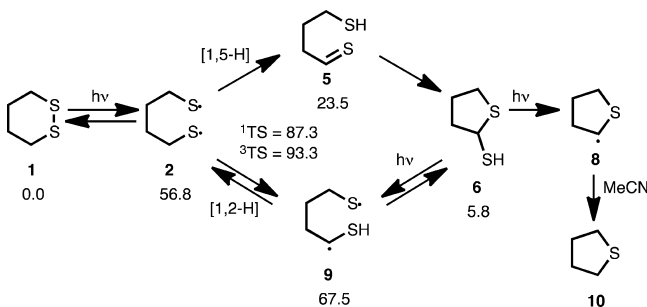
would expect the excited state of **6** also to yield **9** by cleavage of the ring C−S bond; subsequently, the 10.7 kcal/mol exothermic 1,2-H shift would afford **2**. However, the calculated barrier for the 1,2-shift from triplet **9** to **2** is 25.8 kcal/mol. If this scheme is correct and the barrier to 1,2-H shift is substantial, the production of **1** should decrease at lower temperatures while thiophane remains constant. To test this idea, we generated **6** from **1** at 313 nm; we then irradiated **6** at 254 nm below −60 °C. EtCN was chosen as solvent because it

freezes at a lower temperature (−93 °C) than MeCN (−48 °C). As seen in Table 3, the ratio of **10** to **1** was about 0.3, the

Table 3. GC Analysis of 6 Irradiated in EtCN at 254 nm[a]

time, wavelength	area % 6	area % 1	area % 10	10:1 ratio
0 min	99.1	0.8	0.1	0.13
30 min, 254 nm	96.4	2.9	0.7	0.24
45 min, 254 nm	94.0	4.6	1.4	0.30
60 min, 254 nm	88.7	8.9	2.4	0.27

[a]Analyzed on HP-5. Irradiation was carried out below −60 °C. **6** was generated in >99% conversion by 313 nm irradiation of **1**.

same as in MeCN at room temperature. Thus there is no sizable barrier for the 1,2-H shift of **9** to **2**. One might consider an ionic mechanism[60] for the **6** to **1** photorearrangement, but the same reaction was found in cyclohexane at 25 °C as in MeCN. Most likely, the exothermic 1,2-H shift reaction proceeds via quantum mechanical tunneling, which is known in a carbon-centered biradical.[61]

The mechanism of the **1** to **6** conversion is also of interest and has already been considered for analog **7**. Thus Barron et al.[47] envisioned two pathways, one proceeding via a 1,5-hydrogen shift **2** to **5** and the other via a 1,2-hydrogen shift **2** to **9**, possibly assisted by solvent. In the first case, **5** closes ionically to **6**, consistent with Gais's failure to detect the reverse reaction.[46] In the second mechanism, biradical **9** closes to **6**, a very exothermic process that should encounter no activation barrier. Because the 1,5-H shift (**2** → **5**) is exothermic by 33.3 kcal/mol and the closure of **5** is exothermic by 17.7 kcal/mol, the first mechanism is very favorable. The barrier for the 1,5-H shift was not calculated, but such processes are common in radical chemistry, particularly in diradicals.[62,63] Because we never observed **5** by NMR during the **1** to **6** reaction, it is likely that the **5** to **6** barrier is small.

The **2** to **9** 1,2-H shift is endothermic by 10.7 kcal/mol and must surmount a calculated barrier of at least 30.5 kcal/mol (87.3 − 56.8). Although 1,2-H shifts are common in carbocation chemistry, they are seldom observed in radicals,[64] except at high temperatures for alkoxy radicals or in aqueous solution.[65−69] As mentioned above, the lifetime of **2** is short and the rearrangement is very efficient,[47] indicating that the conversion of **2** to **6** is fast. It is difficult to reconcile this fast rate with the calculated high barrier of the 1,2-shift mechanism. Thus we favor **5** rather than **9** as the intermediate in the **1**→**6** reaction. The **1**,**6** system is an interesting case where the forward and reverse photoreactions proceed via different intermediates.

The last step of the Nakamura mechanism is hydrogen transfer from MeCN to an alkanethiyl radical. However, we calculated that this process for **2** is endothermic by $\Delta H = +12.6$ kcal/mol at 298 K. To test the efficiency of such a reaction experimentally, we irradiated di-*n*-hexyl disulfide simultaneously in separate tubes in MeCN and in cyclohexane using tetradecane as an internal GC standard. The GC peak area ratios clearly showed a steady decrease of the disulfide in both solvents, but far more *n*-hexanethiol was produced in cyclohexane (cf. Table 4). An unknown byproduct at 8.10 min that formed in MeCN was not large enough to account for the greater disappearance of disulfide than *n*-hexanethiol produced. However, TLC of the 85 min reaction revealed a spot at the origin that was not investigated further. In cyclohexane, the 8.1 min peak was larger than in MeCN but

Table 4. Irradiation of Di-*n*-hexyl Disulfide at 254 nm

solvent	time, min	di-*n*-hexyl disulfide[a]	*n*-hexanethiol[a]
c-C$_6$H$_{12}$	0	7.06	0
c-C$_6$H$_{12}$	10	6.97	0.231
c-C$_6$H$_{12}$	40	5.38	0.660
MeCN	0	0.408	0
MeCN	10	0.310	0.007
MeCN	40	0.232	0
MeCN	85	0.180	0.028

[a]GC Area ratio of compound to *n*-tetradecane internal GC standard.

of similar size to hexanethiol; perhaps it is derived from the solvent or from C−S cleavage.[51−53] Although the photolysis of di-*n*-dihexyl disulfide could be explored further, the key point is that MeCN is a poor hydrogen atom donor to alkanethiyl radicals, thus casting doubt on the **3→4** reaction in Figure 1.

If the observations of Nakamura et al. were correct, attack of **2** on SWCNTs would have to compete with its very fast unimolecular rearrangement to **6**. However, the authors made no mention of **6**, despite its powerful and obnoxious odor. We repeated their irradiation of **1** at 25 °C in a MeCN suspension of SWCNTs at two wavelengths. After 1 h of 313 nm exposure, the SWCNTs were isolated, washed, and analyzed by XPS and Raman spectroscopy using multiple spots of the sample. The sulfur content was only 0.1% and the Raman spectrum showed a D:G height ratio of 0.10 versus 0.09 for starting SWCNTs. Despite the fact that **1** opens to biradical **2** at 313 nm, there was no attack of **2** on SWCNTs. These experimental results are supported by theoretical calculations which indicate that a covalent bond between **2** and a (5,5) or (10,0) SWCNT cannot persist.[18]

With 254 nm irradiation, as used by Nakamura et al., we found by XPS that the sulfur:carbon ratio was now 0.26 versus the published value of 0.13. TGA analysis revealed a weight loss of ∼40% from 180 to 280 °C, with a final (680 °C) value of ∼50%. The product, to which we shall refer as sulfurized SWCNTs, could not be suspended in aqueous sodium doecylbenzene sulfonate nor *N*-methylpyrolidone. In contrast, pristine SWCNTs are readily suspended in these media. The sulfurized SWCNTs are also less easily suspended in MeCN than are pristine SWCNTs. The C 1s XPS peak at 284.4 eV was ∼50% broader in the irradiated sample than it was in the starting SWCNTs. These results show that the SWCNTs definitely became modified in some way, but it is not clear exactly how this occurs, as discussed below.

Because 254 nm irradiation of **1** caused sulfur incorporation but 313 nm did not, we are dealing with either a wavelength effect or a photoreaction of **6** rather than **1**. To distinguish these possibilities, we irradiated **1** at 313 nm until it was almost entirely converted to **6**. Then SWCNTs were added and irradiation was continued at 254 nm. Because the reisolated SWCNTs showed a S:C ratio of 7.1% by XPS, sulfur compounds were incorporated into SWCNTs and **6** is at least partly responsible for Nakamura's reaction.

To characterize these sulfurized SWCNTs further, a pyrolysis/GC/MS (pyr/GC/MS) experiment was performed. This technique is much more powerful than TGA/MS, which provides a sometimes uninterpretable spectrum of a mixture. SWCNTs were irradiated with **1** at 254 nm in MeCN for 6 h, the solid was filtered off using a Teflon membrane, and the sample was washed repeatedly with hexanes and then EtOH to remove unreacted **1** and **6**. The dried sample was heated to 300

°C and the evolved organics were trapped in Tenax TA absorbent. The products were then desorbed at 300 °C and separated by GC into four major plus several minor peaks (cf. Figure 3), whose mass spectra were recorded. Peak 1 was
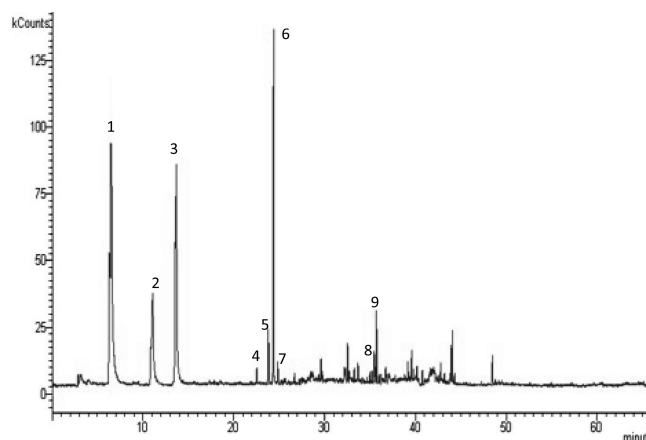

Figure 3. Pyr-GC trace of volatiles from sulfurized SWCNTs desorbed from Tenax at 300 °C.

assigned as thiophene (**12**), on the basis of its retention time, molecular ion at *m/z* = 84 and its (*m* + 2)/*m* ratio of 5.4%, which is close to the value for one sulfur. Its mass spectrum matched thiophene in the NIST database with 62.9% probability, and the spectrum agreed reasonably well with that of authentic thiophene determined at Rice. Peak 2 matched 2,5-dihydrothiophene in the NIST database (74% probability), though it could also be 2,3-dihydrothiophene. Not surprisingly, these isomers give very similar EI mass spectra.[70,71] Its GC retention time fell between those of thiophene and thiophane, consistent with the proposed structure. Peak 3 was assigned to thiophane (**10**) based in part on its GC retention time. The molecular ion and base peak were at *m/z* = 88 and its (*m* + 2)/*m* ratio of 6.4% was somewhat above the value for one sulfur atom. The fragmentation pattern was similar to that observed for authentic thiophane on a HP-GC/MS. The (*m* + 2)/*m* ratio of peak 4 suggests two sulfurs and its molecular weight appears to be 102. However, no reasonable structure comes to mind. Peak 5 is clearly residual **1**, judging from its retention time and its molecular ion and base peak at *m/z* = 120. Its (*m* + 2)/*m* corresponds to two sulfurs, and its fragmentation pattern matches that of authentic 1,2-dithiane. Peak 6 is assigned to **6** for the same reasons as peak 5, except that the *m/z* = 87 fragment was much weaker in the pyr/GC/MS than in the EI/MS of the authentic compound. Peak 7 appears to be a dehydrogenation product of **6** or **1**, but the exact structure cannot be deduced from the MS alone. Peaks 8 and 9 are isomers that the NIST database assigned as bithiophenes (probability match 51% and 62%, respectively). Thus the structure of all four major products (peaks 1, 2, 3, 6) is secure but many of the minor ones are unknown. The generation of thiophene from sulfurized SWCNTs was initially surprising, but the structure was confirmed by heating a sample of sulfurized SWCNTs to 300 °C in a sand bath and analyzing the distillate by ^{1}H NMR. Thiophene was present but 1,4-BDT was not, further arguing against attachment of **2** to SWCNTs.

We can rationalize the wavelength effect if 2-thiophanyl radicals **8** produced by 254 nm photolysis of **6** attack the sidewalls of SWCNTs. Heating these sulfurized SWCNTs

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releases **8**, which leads to products **10–13** by the reasonable sequence of radical reactions proposed in Scheme 2.

Scheme 2. Suggested Mechanism for the Formation of Products 10–13 from Sulfurized SWCNTs
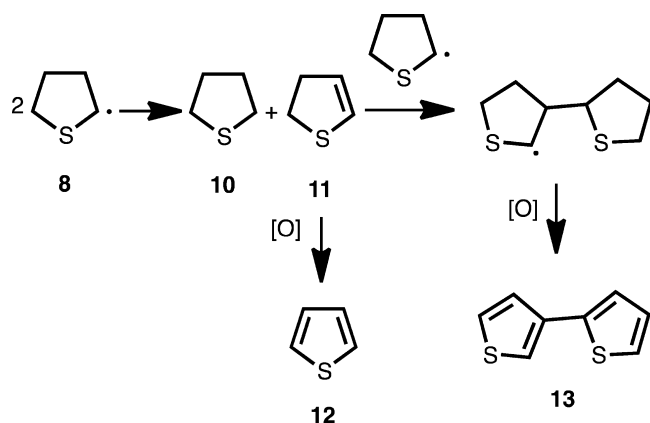
The SWCNT to carbon bond is calculated to be much stronger than the one to sulfur (see below) and indeed the TGA of sulfurized SWCNTs is similar to that of other alkyl-functionalized SWCNTs.[8,15,72] The dehydrogenation reactions in Scheme 2 are in line with the known SWCNT-induced dehydrogenation of hydrocarbons.[73] However, as we shall see below, this mechanism is far from complete.

Energetics of Covalent and Noncovalent Attachment. According to our theoretical calculations, covalent thiophanyl radical functionalization of the HiPco SWCNTs used here is energetically possible. At the M06-2X/6-31G* level of theory, the SWCNT-thiophanyl bond dissociation energy (BDE) is 22.3 kcal/mol but the M06-L/6-31G* BDE is smaller by 7.6 kcal/mol. Using the latter value and the BDE computed with M06-L/6-31G* and employing the infinite model, we obtain our best estimate for the (5,5) SWCNT-thiophanyl BDE of 21.6 kcal/mol.

The attachment of free radicals to SWCNTs is strongly influenced by entropy. Thus it is important to evaluate the free energy change and check whether the bond-forming reaction is exergonic. Employing the $C_{80}H_{20}$ cluster model, we determined that $\Delta G^{\circ}_{298} = -6.5$ kcal/mol.

(5,5) SWCNT have a diameter of 0.69 nm, but reactivity diminishes when the diameter is increased. For a (10,0) SWCNT (0.794 nm diameter) we found that the BDE is 9.1 kcal/mol, which is significantly smaller than the 21.6 kcal/mol for (5,5) SWCNTs. The low BDE is due to both the smaller curvature of the (10,0) SWCNT and the fact that (5,5) SWCNTs have metallic characteristics whereas the (10,0) is semiconducting. Thus, for the attachment of one free radical, the metallic tube will be more reactive because it can donate electrons more easily, as we observed previously.[17,18] Although the BDE of a thiophanyl to (10,0) SWCNT bond is only 9.1 kcal/mol, it can be significantly increased if two free radicals are attached para on the same hexagon.

We consider only para addition because steric hindrance makes ortho attachment impossible. If two thiophanyl radicals are attached para, the BDE increases greatly from 9.1 to 26.7 kcal/mol. The same effect is observed for the (5,5) SWCNT but it is weaker. Thus when two thiophanyl radicals are attached para on one ring, the BDE per functional group is 29.0 kcal/mol. It is tempting to think that the BDE may be further

increased if more free radicals are attached, forming a longer sequence of para additions. However, the size of the thiophanyl radical renders such polyfunctionalization unfavorable. The "para effect" has two important consequences: (a) it increases the BDE of the thiohanyl radicals b) the reactivity gap between metallic and semiconducting nanotubes is reduced. It is interesting to compare the BDE of the thiophanyl radical with those determined for alkyl radicals. At the M06-2X level of theory, the BDE's of the methyl, ethyl, isopropyl, and *tert*-butyl radicals and a (5,5) SWCNT are 30.0, 28.4, 25.2, and 18.9 kcal/mol, respectively. Our computed value for the thiophanyl radical (21.6 kcal/mol) therefore lies, as expected, between those of isopropyl and *tert*-butyl radicals.

In addition to covalent bonding, we also investigated whether the noncovalent encapsulation of **1**, **6**, and thiophene is possible for our tubes. As seen in Table 5, the encapsulation energies of

Table 5. Encapsulation Energies (kcal/mol) for 1 and 6, at the M06-L/6-31G* Level of Theory

SWCNT	1 parallel to tube axis	1 perpendicular to tube axis	6
(11,0)	20.3	15.2	25.1
(12,0)	26.1	25.5	27.0
(13,0)	22.5	19.1	20.3

1 and **6** are quite large and suggest that if the ends of the SWCNTs are open, these compounds could be found inside the tubes. Regarding external adsorption, we found that **1** and **6** interact weakly with one SWCNT via CH–π interactions. For **1** and **6** the adsorption energies are 4.3 and 6.4 kcal/mol, respectively, which is roughly 1 kcal/mol per H that interacts with the nanotube. Larger interaction energies are expected for groove and interstitial sites but they will still be smaller than those determined for internal adsorption.

Sulfurized SWCNTs. Covalent functionalization of SWCNT is supported by the requirement of 254 nm light to effect reaction, by the TGA/GC/MS analysis of the thermolysis products, and by the calculated thiophanyl-SWCNT bond dissociation energy. However, a UV absorption spectrum of sulfurized SWCNTs suspended in aqueous sodium deoxy-cholate appeared essentially identical to that of pristine SWCNTs. This result, coupled with our observed small Raman D:G enhancement, suggests that only a minor part of the reaction involves covalent bond formation.[74,75] One might explain away the Raman result but we are still left with the unperturbed UV spectrum, a large TGA weight loss, and a high sulfur content as evidence for an additional sulfurization mechanism. Raman D:G ratios show little enhancement if functional groups are present in localized regions[76] or only at defect sites;[74,77] in fact, Raman spectroscopy does not reliably assess the degree of SWCNT functionalization.[78] We considered encapsulation as the additional mechanism, which is predicted to be feasible by our theoretical calculations. However, our raw nanotubes are not likely to have open ends, which instead are plugged by iron catalyst.

We believed initially that the pyr/GC/MS products were merely adsorbed onto the SWCNT surface,[79,80] but this notion is unlikely because **11–13** are not photoproducts of **6** in MeCN. Moreover, our calculations show only small adsorption energies. By way of experimental support, stirring a MeCN solution of 1,4-BDT, **1**, or **6** with SWCNTs at 25 °C for at least 4 h showed no incorporation of sulfur by XPS in the reisolated SWCNTs. It is difficult to imagine how UV irradiation would

facilitate adsorption of small organics. Another possible explanation for our results is attachment of a polymer to SWCNTs, especially because **1** is known to polymerize thermally or under the influence of catalysts.[32] However, **1** does not give polymer upon 254 nm irradiation, and DSC analysis of sulfurized SWCNTs showed no endotherm at 44 °C, as expected for melting of the polymer.[32] If a polymer is involved, it does not contain a SWCNT-sulfur bond for the reasons indicated above.

CONCLUSIONS

The photolysis of **1** with SWCNTs does not lead to SWCNT—sulfur bonds, which are too weak to exist at ordinary temperatures. Instead, irradiation of **1** produces **6** by a very rapid 1,5-hydrogen shift of dithiyl biradical **2**. Short wavelength irradiation of **6** leads to carbon-centered 2-thiophanyl radicals **8**, which are partly responsible for SWCNT functionalization. Heating the resulting sulfurized SWCNTs produces a set of products **10**—**13** arising from typical radical reactions of **8** and dehydrogenation of the initial products. This mechanism is also likely for irradiation of **1** with diamond films.[81] Another, unknown mechanism for formation of sulfurized SWCNTs gives a high sulfur content and a large TGA weight loss. Further characterization of sulfurized SWCNTs in a different laboratory will be required to better elucidate this mechanism.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S1—S6 showing NMR spectra of **6**, SWCNT diameter distribution, UV monitoring of the **1** → **6** photoreaction, and the TGA trace of sulfurized SWCNTs. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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