Reactive Intermediates

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A Formal Carbon–Sulfur Triple Bond: H–C≡S–O–H**

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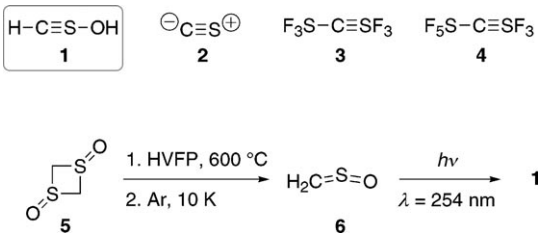
Multiple bonding of heavier main-group elements continues to fascinate chemists, and unusual structures often challenge widely accepted rules of chemical bonding.[1] Compounds containing a carbon–sulfur triple bond are particularly rare. Apart from well-known, highly reactive CS (**2**, Scheme 1),[2] only two other compounds have been reported to date that



Scheme 1. Structures with formal carbon–sulfur triple bonds and the experimental route for the preparation of **1** from **5**.

suggest the existence of carbon–sulfur triple bonds, namely $F_3S–C{\equiv}SF_3$ (**3**) and $F_5S–C{\equiv}SF_3$ (**4**).[3] The argument in favor of a carbon–sulfur triple bond in these compounds has not been left without criticism,[4] despite the very short C–S distances (1.42–1.43 Å for **3** and 1.39–1.40 Å for **4**) and the large S-C-S angles (155–171°). As a consequence, the C≡S bonds in **3** and **4** have been termed "nonclassical".[3] Here we report on a novel structure with a formal triple bond, H–C≡S–O–H (**1**); we analyze and compare the bonding situation in **1** on the basis of experimental spectroscopic as well as quantum chemical data.

In our continuing studies of the new class of hydroxycarbenes[5] we envisaged preparing hydroxy mercaptocarbene[6] (HS–C–OH, cf. potential energy surface (PES) Figure 2) through the generation and photochemical rearrangement of thioformaldehyde *S*-oxide ($H_2C{=}S{=}O$ (**6**), Scheme 1), generated thermally by high-vacuum flash pyrolysis (HVFP) from its dimer **5**. Although structure **6** has been characterized spectroscopically,[7,8] we report the UV spectrum of this parent compound for the first time (see the Supporting Information). The absorption maximum at 243 nm is well reproduced computationally (240 nm at TD-B3LYP/6-311+G(3df,3pd)) and can be assigned to a π–π* transition. The analogous absorption in the related 1,3-dipole $H_2C{=}S{=}S$ can be observed at 356 nm.[9]

The photochemical route to the carbene proved unsuccessful but we unexpectedly generated **1** instead. Photolysis of **6** in an argon matrix with a broad-band light source ($\lambda > 300$ nm) only led to unspecific decomposition to CO, COS, and ethylene.[7,8] As the choice of the excitation wavelength turned out to be critical, we repeated the matrix photolysis of **6** and its deuterated isotopologue [D_2]**6** monochromatic light sources and were thus able to induce specific rearrangement to **1** at $\lambda = 254$ nm, which is close to the actual UV absorption maximum.

The excellent agreement of the experimental and high-level-computed [CCSD(T)/cc-pVTZ] IR spectrum are taken as firm evidence for the successful preparation of **1** (Figure 1 a). Equally good agreement was found for the dideuterated [D_2]**1**, prepared via [D_2]**6** from perdeuterated [D_4]**5** (Figure 1 b). The maximum UV absorption of **1** lies, according to time-dependent DFT computations at TD-B3LYP/6-311+G(3df,3pd), at $\lambda_{max} = 202$ nm, which is, however, below the range of common UV spectrometers. A second UV absorption computed to be at $\lambda = 361$ nm has very low intensity and could not be measured. However, the observed back-reaction of **1** to **6** upon irradiation with light at $\lambda = 366$ nm indirectly supports the existence of an absorption close to this wavelength (Figure 1).

To pin down the energetics for **1** and related structures we computed these at the CCSD(T)/cc-pVTZ + ZPVE level (ΔH_0, Figure 2; all optimized structures can be found in the Supporting Information). It is remarkable that **1** can be accessed instead of the significantly lower-lying hydroxy mercaptocarbene isomer, which lies energetically between **1** and **6** but cannot be identified in our matrix IR spectra. The barrier for the [1,3]H-shift back-reaction of **1** to starting material **6** is 22.2 kcal mol^{-1}. The most stable molecular combination of this stoichiometry is $H_2 + OCS$, which lies about 36 kcal mol^{-1} below **6**.

The optimized structure of **1** displays C_s symmetry with a total of four conformers, based on the *cis/trans* orientation of the O atom relative to the HCS and of the H atom relative to the CSO moiety; we label these as *cc*-**1**, *ct*-**1**, *tc*-**1**, and *tt*-**1**. Remarkably, the *cc*-**1** isomer depicted in Figure 2 is the most stable although isomers *ct*-**1** and *tc*-**1** are within 2 kcal mol^{-1}.

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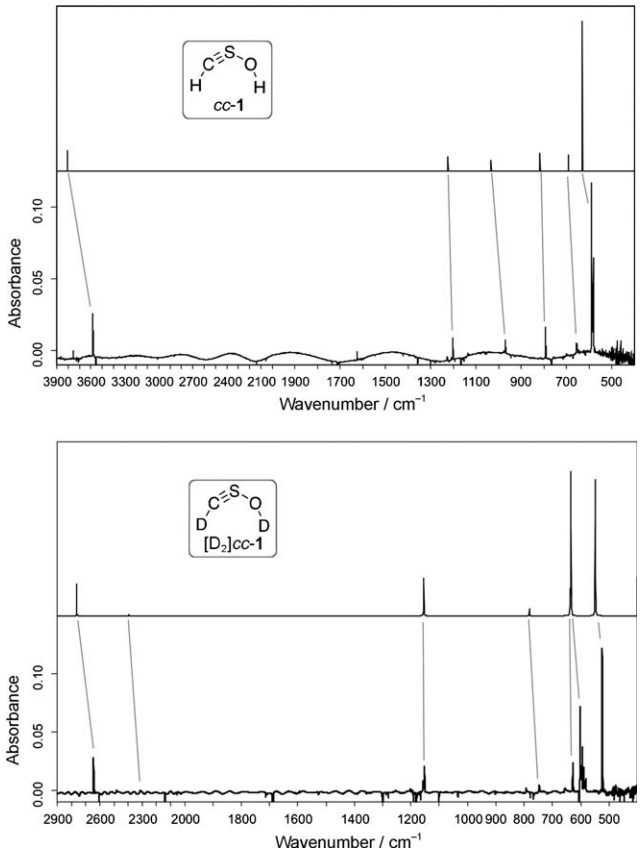


Figure 1. Experimental (bottom) Ar (10 K) difference spectra and CCSD(T)/cc-pVTZ (unscaled) computed IR spectra of *cc*-**1** (top) and [D_2]*cc*-**1** (bottom) from photoconversion into **6** ([D_2]**6**) with $\lambda = 366$ nm.

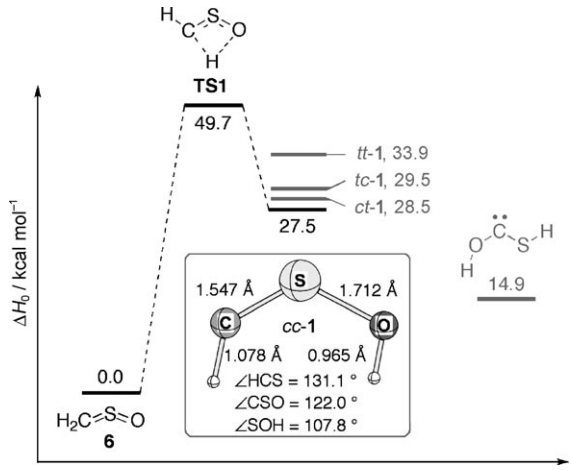
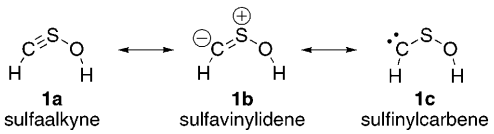


Figure 2. Potential energy surface (ΔH_0 in kcal mol^{-1}) of **1** and related species at CCSD(T)/cc-pVTZ + ZPVE. Other structures of interest are shown in gray.

The chemically "intuitive" all-*trans* structure *tt*-**1** lies 6.4 kcal mol^{-1} above *cc*-**1** (Figure 2, vide infra).

The key question is: what is the nature of the carbon–sulfur bond in **1**? Which of the formal resonance structures corresponding to a sulfaalkyne (**1a**), a sulfavinylidene (**1b**), or a sulfinylcarbene (**1c**)[4] best describes **1** (Scheme 2)?



Scheme 2. Resonance structures of **1**.

First of all, the C–S distance in *cc*-**1** of 1.547 Å [CCSD(T)/cc-pVTZ] is about the same as that of **2** (1.545 Å; expt. r_e = 1.535 Å),[2] but slightly shorter than the C=S bonds in CS_2 (1.560; expt. $r_e = 1.553$ Å)[10] and thioformaldehyde (1.618; expt. $r_e = 1.611$ Å).[11] Pyykkö et al. suggest triple-bond covalent radii for C = 0.60 Å and S = 0.95 Å,[12] giving a theoretical bond length for a carbon–sulfur triple bond of 1.55 Å, which is exactly the value we compute for *cc*-**1**.

A second way to judge the nature of the CS bond in **1** is the CS stretching vibration and comparisons with related systems. This is, however, difficult for larger molecules, as vibrations in polyatomic molecules couple to varying degrees. The IR absorption corresponding to the CS vibration for *cc*-**1** is at 1201.3 cm^{-1} (1223.0 cm^{-1} at CCSD(T)/cc-pVTZ), for **2** at 1272 cm^{-1}[2] (gas phase, theor.: 1280 cm^{-1}), for CS_2 at 1097 cm^{-1} (neat, theor. 1119 cm^{-1}; the average value of the asymmetric and symmetric stretch at 1559 and 670 cm^{-1}, respectively, was taken), and for $H_2C=S$ at 1055 cm^{-1} (1073 cm^{-1} expt. in Ar[13]). The good agreement between the unscaled computed frequencies and those from experiment lends confidence to the quality of the structures and properties computed at this level. The corresponding vibration in **3** mixes so strongly with other vibrations that a unique value for comparison cannot be given with confidence. Hence, the evaluation of the vibrational band origins shows again that the bonding situation in **1** should be comparable to that in **2**; the CS bond in **1** is likely to be stronger than the double bonds in CS_2 or H_2C=S.

Figure 3 presents an MO analysis of *cc*-**1** and **2** in form of a correlation diagram utilizing the three highest-lying MP2/cc-pVTZ C–C bonding natural orbitals;[14] for an MO analysis of related (experimentally unknown) $F_3S \equiv CH$ see reference [15]. Two π bonds in **2** are transformed into the corresponding in-plane A′ HOMO and out-of-plane A″ HOMO-1; these MOs display antibonding interactions with the C–O bonding MO and the oxygen lone pair in *cc*-**1**, respectively. The coefficients of the Σ-bonding MO (HOMO-2) in **2** significantly change upon bending to the A′ HOMO-2 in *cc*-**1**. The MOs of *cc*-**1** show clear evidence for the tendency of the heavier elements to avoid strong multiple bonding and the preference for the formation of lone pairs.[1] This is apparent from the shape and orientation of the remaining sulfur lone pair when going from the Σ MO of **2** to the HOMO-2 of A′ symmetry in **1**. This helps understand the nonlinearity of the title compound and the preference for the all-*cis* conformation.

The analysis of the natural populations (NPA) and natural orbitals (NBOs) also yields the charges and the bond orders of molecules.[14] As this analysis is method sensitive, we performed it at the MP2(fc)/cc-pVTZ and B3LYP/6-311 + G(3df,2pd) levels of theory (with the structures also optimized at these levels, see the Supporting Information) for **1**–**3**

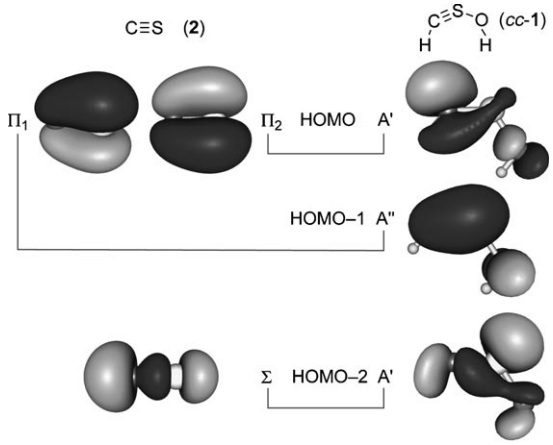


Figure 3. Correlation diagram for the natural molecular orbitals for *cc*-**1** and **2**; MOs from MP2/cc-pVTZ computations (depicted in order of their relative energies); contour value = 0.05 a.u.

for comparison; the results are rather similar. Irrespective of the level of theory, the NBO analysis ascribes CS triple bonds to all three systems, although the Wiberg bond indices (cf. Table 1) assign less than a full triple CS bond owing to strong polarization (vide infra). On this basis, the CS bond character of **1** and **2** also is quite comparable.

Table 1: Bond length, force constant, reciprocal compliance constant comparison, and Wiberg bond indices for the specified C–S bonds at B3LYP/6-311 + G(3df,2pd).

Species	r_{CS} [Å]	C–S force constant [N cm^{-1}]	C–S reciprocal compliance constant [N cm^{-1}]	Wiberg bond index
H_3C-SH	1.842	3.17	2.76	1.0
$H_2C=S$	1.606	6.86	6.72	2.1
C≡S (**2**)	1.532	8.86	8.86	2.7
HC≡SOH (*cc*-**1**)	1.531	8.21	6.45	2.3

Structures **1**–**3** show significant charge build-up on the atoms, as expected from their very different electronegativities. The sulfur atoms are all positively polarized (NPA charges), albeit much more so in **1** ($+0.9e$) and particularly in **3** ($+2.1e$) as compared to **2** ($+0.2e$).

Finally, we performed an analysis of the so-called compliance force constants, which can be obtained from the inverted force constant matrix.[16] The matrix inversion removes the dependence of the numerical value of the force constants[17] on the choice of internal coordinates. This approach arguably[18] offers a unique description of bond strength and subsequently bond orders, and it has been used to analyze multiple bonding, for instance, between C and Si.[19] We computed the compliance force constants for *cc*-**1**, **2**, $H_2C=S$, and H_3C-SH (Table 1); for convenience, the reciprocal numerical values of the compliance constants are given (often referred to as relaxed force constants). As found for the analysis of the formal triple bonding between C and Si in HCSiH,[19] the relaxed force constants for the central bond in *cc*-**1** is comparable to a double bond (as, for instance, in thioformaldehyde), and is considerably smaller than for **2**.

We have prepared and characterized hydroxysulfaalkyne **1**, a novel compound with a formal triple bond, through a photochemical [1,3]H-shift from parent thioformaldehyde *S*-oxide (**6**). As such, the photoreactivity of **6** is very different from thiosulfine reported earlier.[9] The successful preparation of **1** is evident from essentially perfect agreement of experimentally measured and high-level-computed infrared spectra (at CCSD(T)/cc-pVTZ). The bonding analysis on the basis of bond lengths, vibrational frequencies, molecular orbital overlap, natural overlap populations, and compliance constants emphasizes the limits of Lewis-type structural depictions that require clear-cut bond orders. Referring to the three expected bonding situations in Scheme 2, we can exclude the carbene resonance structure **1c**. The collective evidence of the bonding analyses above defines the "true" structure of **1** as a composite of **1a** and **1b**. That is, one may view **1** as structure with a rather strong CS double bond or a weak CS triple bond.

Experimental Section

1,3-Dithietan-1,3-dioxide (**5**) was prepared according a procedure reported by Block et al.[8] The precursor bis(chloromethyl) sulfoxide was prepared based on the procedure described by Venier et al. using thionyl chloride and diazomethane.[20] [D_4]-1,3-Dithietan-1,3-dioxide was obtained by carrying out the following procedure twice: dissolving the parent compound in a large excess of slightly alkaline D_2O, keeping the solution for 2 h at 70 °C, and evaporating the solvent under reduced pressure at 0 °C.

Matrix isolation experiments: The cryostat used for the matrix isolation studies was an APD Cryogenics HC-2 closed-cycle refrigerator system fitted with CsI windows for IR and BaF_2 windows for UV/Vis measurements. IR spectra were recorded with a Bruker IFS 55 FTIR spectrometer (4500–300 cm^{-1}, resolution 0.7 cm^{-1}), UV/Vis spectra with a JASCO V-670 spectrophotometer. For the combination of high-vacuum flash pyrolysis with matrix isolation a small home-built water-cooled oven directly connected to the vacuum shroud of the cryostat was used. The pyrolysis zone consisted of a completely empty quartz tube (inner diameter 8 mm, length of heating zone 50 mm) resistively heated by a coax heating wire. The temperature was controlled by a Ni/CrNi thermocouple. The precursors were evaporated from a heated storage bulb (ca. 65–75 °C) into the quartz pyrolysis tube. Immediately after leaving the tube, at a distance of ca. 50 mm, the pyrolysis products were co-condensed with a large excess of argon on the surface of the 10 K matrix window. For irradiations either a mercury low-pressure spiral lamp (Gräntzel) with an interference filter (254 nm) or a vycor long-pass filter $\lambda > 210$ nm, or a mercury high-pressure lamp (HBO 200, Osram) with a monochromator (Bausch&Lomb) was used. Irradiation time for an almost complete conversion of **6** to **1** (254 nm) was 15–30 min, irradiation time for the back-reaction (monochromator, 366 nm) **1** to **6** was 5 min.

Computations: The electronic structure computations employed the correlation-consistent triple-ζ atomic orbital basis set cc-pVTZ.[21] All geometries were optimized with single-reference all-electron (AE) coupled-cluster theory, incorporating all single and double excitations, and with perturbative inclusion of connected triple excitations [AE-CCSD(T)]. All structures were characterized as minima or transition structures by computing harmonic vibrational frequencies. For these computations we employed the ACES2-MAB program.[22] Density functional theory (DFT) computations at the B3LYP[23] level utilizing a large 6-311 + G(3df,2pd) were employed to

compute structure **4** for comparison. This level was also employed for determining the UV maximum of *cc*-**1** (TD-B3LYP); all DFT computations utilized the Gaussian03 program suite.[24]

Compliance constants: We utilized a procedure by Winnewisser et al.[25] for the conversion of the cartesian force constants, obtained from DFT computations, to internal force constants. The transformation of the cartesian to internal coordinates was accomplished with with the General Vibrational Analysis System.[26] The compliance matrix was generated by computing the inverse of the force constant matrix in internal coordinates with MATLAB7. Alternatively, we utilized the program "compliance";[27] the results were the same.

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