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Structures of Diethynyl Sulfide and Bis(phenylethynyl) Sulfide

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Rotational transitions for four isotopomers of diethynyl sulfide, $S(CCH)_2$, were observed by using a pulsed nozzle Fourier transform microwave spectrometer. Vibration−rotation interaction constants obtained from ab initio calculated force fields were used to convert the ground-state rotational constants to equilibrium values. The latter were used to derive structural parameters, several of which are not in good agreement with those obtained from high level ab initio calculations. The structure has planar C_{2v} symmetry with the following parameters: $d(\mathrm{S{-}C}) = 1.708(20)$ Å, $d(\mathrm{C{\equiv}C}) = 1.211(10)$ Å, $d(\mathrm{C{-}H}) = 1.061(10)$ Å, $\angle(\mathrm{C{-}S{-}C}) = 100.5(5)°$, $\angle(\mathrm{S{-}C{\equiv}C})_{\text{outside angle}} = 174.4(15)°$, $\angle(\mathrm{C{\equiv}C{-}H})_{\text{inside angle}} = 177.0(25)°$. The structure of bis(phenylethynyl) sulfide, $S(C{\equiv}CC_6H_5)_2$, was determined by X-ray crystallography. The unit cell contains two inequivalent molecules. The structural parameters are (average of both species; uncertainties represent 1σ) $d(\mathrm{S{-}C}) = 1.695(4)$ Å, $d(\mathrm{C{\equiv}C}) = 1.198(2)$ Å, $d(\mathrm{C{-}C_{phenyl}}) = 1.440(4)$ Å, $\angle(\mathrm{C{-}S{-}C}) = 101.4(9)°$, $\angle(\mathrm{S{-}C{\equiv}C}) = 176.4(19)°$, and $\angle(\mathrm{C{\equiv}C{-}C_{phenyl}}) = 178.2(8)°$. The phenyl groups are twisted out of the C−S−C plane from 20 to 85° such that each phenyl ring is oriented nearly 90° to its intramolecular mate. The structural parameters are compared with several other sulfides and with hydrocarbons containing acetylenic linkages. The nonlinearity about the acetylenic bond follows a pattern seen in other similar species, although it is more pronounced in $S(CCH)_2$ than in hydrocarbons. These data constitute the first experimental structural studies on uncomplexed diethynyl sulfides.

Introduction

There has been a growing interest in C_xS_y and $C_xS_yH_z$ species due to their implication in interstellar chemistry and material science applications. Regarding the C_xS system, CS, C_2S, C_3S, and possibly C_5S have been identified in the interstellar medium,[1−4] stimulating many subsequent observations and modeling of their abundance and genesis.[5−7] The materials science interest arises from the change in properties of carbon clusters upon introduction of a heteroatom. There are data indicating that organic films of approximate C_3S composition exhibit unusual electrical properties.[8] Several recent papers summarize much of the experimental and theoretical work on this system.[9−13]

The carbon rich C_xS species are highly unsaturated, and hydrogen atom addition to them leads to the HC_xS system. These species are also prospects for identification in the hydrogen-rich interstellar medium (ISM)[14,15] similar to the linear cyanopolyenes, $HC_{2n}CN$ ($n = 1−5$), which have already been observed in the ISM.[16] This has led to a number of recent experimental and theoretical studies of various HC_xS species,[13,17−21] including high-resolution spectra studies of the HC_2S, HC_3S, and HC_4S radicals.[14,15,22,23]

Addition of two hydrogen atoms (H_2C_xS) gives rise to more conventional valence bond forms obeying the octet rule, including two simple unsaturated species, $HSC{\equiv}CH$ and $S(C{\equiv}CH)_2$, containing the ethynyl (acetylene) group. Surprisingly, these are not well-characterized species. The monoethynyl sulfide has only been observed by IR spectroscopy in low-temperature matrices after formation by photolysis.[24−26] The diethynyl sulfide is a useful synthetic reagent but quite reactive and usually generated and reacted in situ.[27−29] It has not been characterized by liquid- or gas-phase structural techniques except for proton NMR. Ab initio studies of the structure and electronic properties of both species have been reported.[30−36]

There are several reports of the characterization and reactions of a similar prototype diacetylenic species, bis(phenylethynyl) sulfide, $S(C{\equiv}CC_6H_5)_2$.[37a−c] A study of its detailed structure has not been undertaken, although some parameters are available for its reaction product with dicobaltoctacarbonyl containing a $SC{\equiv}CC_6H_5$ group.[37b]

Given the interest in small carbon−hydrogen−sulfur species and prompted by our previous structural studies of unsaturated prototype species such as $CH_2(C{\equiv}CH)_2$[38] and XCH═CHX (X = C_2H,[39] CN[40]), we decided to investigate the structure of $S(C{\equiv}CH)_2$ by high-resolution spectroscopy and to compare it with an X-ray structure determination of $S(C{\equiv}CC_6H_5)_2$. This paper reports the results of this study including high level ab

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TABLE 1: Observed Frequencies of Rotational Transitions for the Normal and Three Isotopic Species of Diethynyl Sulfide

	$S(C{\equiv}CH)_2$		$^{34}S(C{\equiv}CH)_2$		$S(C{\equiv}CH)(C{\equiv}CD)$		$S(^{13}C{\equiv}CH)(C{\equiv}CH)$	
$J'_{KaKc} - J''_{KaKc}$	υ, MHz	$\Delta\upsilon$,[a] kHz	υ, MHz	$\Delta\upsilon$,[a] kHz	υ, MHz	$\Delta\upsilon$,[a] kHz	υ, MHz	$\Delta\upsilon$,[a] kHz
1_{10} 1_{01}	8118.942	−8	7817.746	−27	7794.587	−20	8126.244	99
2_{11} 2_{02}	8688.225	43	8403.147	25	8331.410	20	8686.222	−24
3_{12} 3_{03}	9593.576	68	9337.375	61	9184.383	58	9576.280	9
4_{13} 4_{04}	10892.558	−43	10682.738	−36	10406.998	−34		
1_{11} 0_{00}	12284.036	−121	11955.919	−48	11759.560	−50	12260.872	−169
2_{12} 1_{01}	16449.425	61	16094.185	24	15724.639	25	16396.021	84

[a] $\Delta\upsilon = \upsilon_{obsd} - \upsilon_{calcd}$ with υ_{calcd} obtained with the rotational constants in Table 2.

initio calculations of $S(C{\equiv}CH)_2$. The ab initio structure is compared with the experimental equilibrium structure derived by making corrections for vibration−rotation effects to the spectroscopic data.

Diethynyl Sulfide

Synthesis. Diethynyl sulfide (**1**) was prepared following a literature procedure with some modifications.[27,29] A solution of bis(trimethylsilylethynyl) sulfide (0.554 g, 2.45 mmol) in ethylene glycol (6.5 g) was treated with tetrabutylammonium fluoride trihydrate (1.54 g, 4.88 mmol). An additional 3.5 g of ethylene glycol was added to the rapidly stirring solution, which turned dark with the formation of some solid. After a minimum of 30 min of stirring, small amounts of the solvent and **1** were distilled at room temperature on a high vacuum line into a 1-L bulb for microwave spectroscopic analysis. The sample bulb typically contained about 0.5 mmol of **1** which we estimate has a vapor pressure of between 1 and 5 torr at room temperature. This provided enough material for several hours of microwave spectroscopy. The sample transfer from the reaction pot could be repeated 3−4 times before signals became too weak for efficient work. The gas-phase concentration of **1** in the sample bulb after filling it with 1−2 atm of a buffer gas was low, likely 0.06−0.6%, reducing the signals below optimal levels. However, this was sufficient to observe transitions of the normal isotopic species with S/N of about 20/1−30/1 after about 500 gas pulses and to identify the ^{34}S isotopomer in natural abundance after more averaging. An enriched d_1 isotopomer was prepared by using deuterated ethylene glycol (∼90% deuterium) for the solvent. This gave a sample with weak, nearly equal intensity transitions for the normal isotopomer and the d_1 species. This sample was depleted before a search could be attempted for transitions of the d_2 species. Several samples were prepared with variations in the procedure (quantities, solvent, purification) in an effort to observe the ^{13}C isotopomers in natural abundance, but no improvements in signal intensity were obtained probably because a low vapor pressure for the material proves limiting. The reactive, potentially hazardous nature of **1** dissuaded us from further purifying and concentrating it or scaling up the synthesis. Enriched ^{13}C syntheses were not feasible.

Spectrometer. The rotational transitions were observed with Fourier transform microwave spectrometers operating between 5.5 and 17.0 GHz.[41a,b] The spectrometers used software and hardware modifications developed at the University of Kiel enabling automatic scanning over several hundred megahertz.[41c] Pulsed gas nozzles were employed. One spectrometer used a modified Bosch fuel injector. The second employed a General Valve Series 9 valve with a 0.8-mm-diameter orifice. A few drops of the sample (a mixture of diethynyl sulfide and solvent, usually ethylene glycol) were transferred on a vacuum line from the reaction pot to a 1-L bulb (vide supra). A buffer gas was added (necessary for cooling and to prevent aggregation) and the gaseous mixture was expanded through the nozzles. The gas expansions used “first run” neon−helium mixtures (∼10% He, 90% Ne) at 1−2 atm as the buffer gas. The expansions were directed perpendicular to the microwave cavity axis, resulting in line widths of about 30 kHz fwhm, sans Doppler doubling. Center frequencies were accurate to about 4 kHz.

Spectrum. An ab initio calculation (CCD/6-31G**) predicted a sparse *b*-dipole spectra based on rotational constants of about 10 200, 2640, and 2100 MHz. The four strongest transitions were observed after a few days of searching near the predicted regions. These were the 0_{00}–1_{11}, 1_{01}–2_{12}, 1_{01}–1_{10}, and 2_{02}–2_{11} transitions. These transitions were confirmed by their splitting patterns in an electric field. For the normal species, the next three members of the Q-branch series were also observed. The highest *J* member of this series ($J = 5$) was of diminished intensity due to rotational cooling so that it was only reproducible with freshly prepared samples, as were two higher *J*, R-branch transitions.[42]

The two strongest R-branch transitions and the first four members of the Q-branch series could be observed in natural abundance for the ^{34}S species and for the enriched d_1 species (HCCSCCD). Their positions were predicted to about 5 MHz or less based on the expected isotope shifts for the initial structural model. The 0_{00}–1_{11} transitions were confirmed by Stark splittings. The lines for the d_1 species were broadened due to unresolved deuterium quadrupole splitting. Unfortunately the low intensity of these transitions precluded observation of additional weaker ones. The species with $^{13}C_{\text{next to S}}$ was observed after considerable signal averaging (5000−10000 gas pulses). Each of these transitions were observed at least 4 times when the corresponding transitions of the normal species were their strongest. The assignment of the $^{13}C_{\text{next to S}}$ species is based on the isotope shift predicted from the 3-isotopomer fit (see below) and an inertial defect closely similar to the normal species. The species with $^{13}C_{\text{next to H}}$ was more problematical. Prospects for the 0_{00}–1_{11}, 1_{01}–1_{10}, and 2_{02}–2_{11} were observed[43] and reproduced several times with fresh samples “on good days” but the additional weaker transitions were not forthcoming and so this assignment is not considered confirmed. These transitions appeared to be split (perhaps a ^{13}C spin rotation effect), reducing their intensity. After numerous sample preparations, the assignment effort for this species was suspended.[44]

Table 1 lists the observed transitions for the four isotopic species. Because of the small number of transitions it was not appropriate to determine any centrifugal distortion terms in the fitting. Hence the calculated spectra are from a rigid rotor Hamiltonian fit and show some deviation due to distortion effects contributing from 0.1 to 3 MHz to the energy levels. Neglect of these effects is expected to affect the rotational constants listed in Table 2 by about 0.1−0.4 MHz. This was estimated by incorporating calculated distortion constants into some fits. The quartic distortion constants were obtained from an ab initio force-field calculation (see below) and ranged between 0.001 and 0.181 MHz.

TABLE 2: Experimental Rotational Constants and Planar Inertial Moments for Four Isotopic Species of $S(C{\equiv}CH)_2$

	normal	^{34}S	D_1	^{13}C
A, MHz	10 201.554(52)	9886.870(30)	9777.108(29)	10 193.593(92)
B, MHz	2623.865(43)	2623.865(25)	2493.347(24)	2600.462(104)
C, MHz	2082.604(29)	2069.097(17)	1982.502(16)	2067.448(448)
P_{aa},[a] amu Å^2	192.8681	192.8717	202.9604	194.6049
P_{bb}, amu Å^2	49.7987	51.3793	51.9594	49.8410
P_{cc}, amu Å^2	−0.2594	−0.2631	−0.2694	−0.2628
$\Delta_{\mathrm{i.d.}}$,[b] amu Å^2	0.5188	0.5262	0.5388	0.5256

[a] $P_{aa} = 0.5\ (I_b + I_c - I_a) = \Sigma m_i a_i^2$, and similarly for P_{bb}, P_{cc}. $I_aA = 505\ 379.01$ MHz Amu Å^2. [b] $\Delta_{\mathrm{i.d.}} = I_c - I_b - I_a$ (inertial defect).

TABLE 3: Empirical Equilibrium Rotational Constants (MHz) for $S(CCH)_2$ and Isotopomers

	A_e	B_e	C_e	$A_o - A_e$	$B_o - B_e$	$C_o - C_e$
Force Field I SCF/DZP						
normal	10 143.06	2628.78	2087.13	58.49	−4.92	−4.53
^{34}S	9 830.87	2628.69	2073.51	56.00	−4.83	−4.41
D_1	9 719.96	2497.80	1986.60	57.15	−4.46	−4.10
^{13}C	10 135.70	2605.31	2071.94	57.89	−4.85	−4.49

Dipole Moment. Stark splitting measurements were made on the 0_{00}–1_{11} and 1_{01}–1_{10} transitions of the normal isotopic species at several electric field values. The experimental setup and calibration procedure has been described previously.[45] The shifts of the components ranged from 0.038 to 0.213 MHz for the first transition and from 0.339 to 1.325 MHz for the second. Using the second-order perturbation coefficients calculated with the rotational constants in Table 2, a dipole moment of 0.75(2) D was obtained.

Ab Initio Analysis. The ab initio calculations mentioned above, which were used to guide the initial experiments, were subsequently improved by high-level treatments. This was undertaken to provide a "state of the art" ab initio structure for comparison with an experimental equilibrium structure. The latter is obtained by calculating the vibration−rotation interaction constants from an ab initio force field and using them to modify the observed ground-state constants to give so-called experimental (or empirical) equilibrium values. Before discussing these results, this section will outline the methodology employed in the ab initio analysis.

The calculations reported in this section were performed with a local version of the ACES II programs.[46] Structure optimizations used the coupled cluster approximation with single and double excitations, CCSD,[47] and CCSD augmented with a correction for triple excitation effects, CCSD(T).[48] Basis sets used in the geometry optimizations were the cc-pwCVTZ set for sulfur[49] and the cc-pCVTZ for carbon and hydrogen.[50] The structure from the latter calculation is given in Table 4 as the ab initio equilibrium structure.

To determine the empirical equilibrium rotational constants, the ground-state rotational constants were corrected for the zero-point vibrational effects by using the relationship

$$A_0 = A_e - \Sigma\alpha_i^A/2$$

where A_0 is the ground-state rotational constant (Table 2), A_e is the equilibrium value, and α_i^A are the vibration−rotation interaction constants. The summation is over the $3N - 6$ vibrational modes and there is an analogous equation for the B and C rotational constants. The α's are functions of the harmonic and anharmonic force constants. Recent work[38,39,51−55] has shown that these terms, related to the force field of course, can be evaluated relatively accurately at somewhat low levels of theory (often SCF level) and considerably improve structure determinations compared to using just the ground-state moments.

TABLE 4: Structural Parameters for $S(C{\equiv}CH)_2$

	experimental		ab initio	
	r_o[a]	r_e[b]	r_e[c]	r_e[d]
Bond Lengths, Å				
S−C	1.7230	1.7209	1.6947	1.7105
C≡C	1.2066	1.2102	1.2109	1.2114
C−H	1.0573	1.0596	1.0633	1.0630
Bond Angles, deg				
C−S−C	100.24	100.21	100.83	100.55
S−C≡C$_{\mathrm{outer}}$[e]	173.30	173.56	175.31	174.20
C≡C−H$_{\mathrm{inner}}$[e]	174.80	174.99	179.10	178.11
Dihedral Angles, deg				
S−C≡C−H	180.00	180.00	180.00	180.00
C−S−C≡C	180.00	180.00	180.00	180.00

[a] Fit of I_a, I_b ground-state moments for four isotopic species. [b] Fit of the I_a, I_b moments corrected for vibration−rotation interaction effects. [c] CCSD(T); basis sets were cc-pwCVTZ for sulfur and cc-pCVTZ for carbon and hydrogen. [d] CCD/6-31G** using Gaussian 98W.[63] [e] The "outer" implies the C≡C bonds bend away from each other. The "inner" implies that the C−H bonds bend toward each other. See dihedral angles in next rows and Figure 1.

In this work, we have followed a procedure that was used in two recent studies to calculate α values.[38,39] The quadratic and cubic force fields were determined at the SCF level by a procedure based on numerical differentiation of analytically computed second deriviatives.[55−57] These were then employed to calculate the α's by using equations from the literature.[58] The force field (hereafter force field I-FFI) was calculated at the SCF level using the DZP basis to obtain the corresponding quadratic and cubic force constants along with the equilibrium structure. These α's and equilibrium rotational constants are listed in Table 3. The equilibrium structures obtained from these rotational constants are given in Table 4.

Structure Analysis. Ethynyl sulfide is expected to have planar C_{2v} symmetry**.** For a planar molecule, only two of the three equilibrium moments of inertia are independent since $I_a + I_b = I_c$. The ground-state moments of inertia do not quite obey this relationship because of vibration−rotation contributions. The so-called inertial defect ($\Delta_{\mathrm{i.d.}} \equiv I_c - I_b - I_a$) calculated from these moments is close to 0.52 amu Å^2 for the four isotopomers. This is a large but not unusual value for a planar molecule of this size with low-frequency vibrations. By use of the empirical equilibrium rotational constants from FFI, the inertial defect is reduced to 0.067 amu Å^2. This value is typical for moments with residual contributions from centrifugal distortion effects and electrons as well as errors in the force field.[39] The small value essentially confirms the expected planarity of the species. A 3:1 alternation of intensity for odd/even rotational transitions should also provide evidence of a C_2 axis, which exchanges a pair of equivalent H atoms. The 0_{00}–1_{11} and 1_{01}–1_{10} pair was weak, strong consistent with this. In contrast, and conflicting, the 2_{02}–2_{11} was usually more intense than the 1_{01}–1_{10}. Since there is no reason to doubt there is a C_2

axis based on the dipole moment and inertial analysis, these inconsistent results are attributed to the well-known problem of obtaining meaningful intensities in FTMW spectrometers. This arises from difficulties in consistently maintaining a $\pi/2$ condition in polarizing the transitions and problems with the spectrometer components responding linearly when transitions are well separated. The molecular beam may also be colder than we usually expect (1−2 K), contributing somewhat to these results.

Given a planar moiety, the first three isotopic species that were assigned (normal, ^{34}S, d_1) provided six independent moments of inertia to determine the structural parameters. This is just sufficient since ethynyl sulfide has six parameters conveniently chosen as three bond distances and three bond angles. A typical procedure for determining these quantities is to employ a nonlinear least-squares fitting program such as the STRFIT (or STRFITQ) program used by many spectroscopists.[59] This program gives a mathematically satisfactory fit with a low residual (essentially zero) for $\Delta I_{\mathrm{rms.}}$[60] However, the structural parameters have a large statistical uncertainty, since the equations contain a near linear dependence and several parameters can vary markedly without affecting $\Delta I_{\mathrm{rms.}}$ The structural parameters obtained were close to the values labeled R_0 in column 2 of Table 4. In essence, there is a correlation between the positions of the two carbon atoms that can vary in a systematic manner, altering the structural parameters while still giving a small ΔI_{rms}. This correlation can be reduced, minimizing the structural uncertainties by obtaining additional isotopic shift data involving the carbon atoms. Using this derived structure, the spectra of two ^{13}C singly substituted species were predicted and transitions for the $^{13}C_{\text{next to S}}$ species were observed close to the expected frequencies, as discussed above. When these moments were added to the fit, the linear dependence was removed and the fitting program gave low uncertainties.

Table 4 lists the structural parameters obtained from the various procedures. The second column labeled r_0 has the quantities obtained from fitting eight ground-state moments of inertia (I_a, I_b) for the four isotopomers. This so-called "effective structure" contains uncertainties arising from the uncompensated vibrational effects; for example, the parameters vary over a range of 0.01 Å and 1.2° (bonds and angles, respectively) if instead the I_a, I_c; I_b, I_c; or I_a, I_b, I_c set is fitted due to the large value of the inertial defect. The third column lists the experimental equilibrium (or empirical) r_e structures obtained from fitting the eight corrected ground-state constants (I_a, I_b) by using FFI. If other sets of moments are chosen, the variation is about 0.004 Å and 0.3° since the inertial defect is smaller. Column 4 contains the equilibrium parameters obtained from the high level ab initio calculation, while column 5 is a lower level calculation. There is reasonably close agreement for three of the r_e structural parameters, while r(S−C), ∠C≡C−H, and ∠S−C≡C vary about 0.02 Å and 2−4°, considerably larger than expected based on our previous experience with systems such as HC≡C−CH═CH−C≡CH[38] and NC−CH═CH−CN.[39] The reasons for this larger range are unclear but probably arise from a combination of factors: the larger uncertainty in the experimental I's and deficiencies in the ab initio force field calculations. Consequently our best estimate of the equilibrium structure is an average of columns 3 and 4 with uncertainties sufficient to encompass them; viz., r(S−C) = 1.708(20) Å, r(C≡C) = 1.211(10) Å, r(C−H) = 1.061(10) Å, ∠C−S−C = 100.5(10)°, ∠S−C≡C$_{\text{(outside angle)}}$ = 174.4(15)°, ∠C≡C−H$_{\text{(inside angle)}}$ = 177.0(25)°. This structure is illustrated in Figure 1.

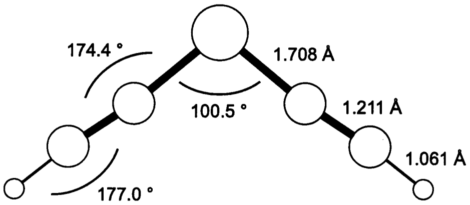

Figure 1. Structural parameters in diethynyl sulfide.

Bis(phenylethynyl) Sulfide

Synthesis. Bis(phenylethynyl) sulfide (**2**) was prepared by the literature procedure and purified by column chromatography on silica gel eluting with hexanes.[37a,b]

X-ray Structure Determination. The single-crystal X-ray structure of bis(phenylethynyl) sulfide was determined on a Bruker SMART system. The compound crystallized in the P-1 (triclinic space group) with $Z = 4$ and therefore contains two inequivalent molecules in the asymmetric unit which are illustrated in Figure 2.[61] Key distances and angles are listed in Table 6. The experimental values for the S−C≡C bonds in this compound are 1.695(4) Å. This is significantly elongated relative to the corresponding distances for CS−C≡C in the Cambridge Structural Database (CSD).[62] (Ordered organic structures of ethynyl sulfides with an additional carbon substituent were searched yielding 19 compounds and 66 unique types of bonds in the April 2002 version of the database. See Figure 3.) Since most of the ethynyl sulfide structures in the CSD have an alkyl substituent, this can likely be ascribed to a decreased contribution from the dipolar resonance structure in the diethynyl sulfides: $C{\equiv}CS^{+}{=}C{=}C^{-}$. The S−C≡C bond angle is an average of 176.4(19)° and is within the typical values in the CSD for organic structures that include cyclics. The ethynyl units bend away from one another but to varying degree consistent with the flexibility of the acetylenic units and a contribution from crystal packing forces. The average C≡C−C$_{\text{phenyl}}$ bond angle measures 178.2(8)° and three of the four unique bonds bend toward one another. The phenyl groups are twisted out of the C−S−C plane from 20 to 85° such that each ring is oriented nearly 90° to its intramolecular mate.

Discussion

In both title compounds it is clear that the S−C≡C linkages are nonlinear as if the carbons distant from the sulfur are repelling each other. The C≡C−H linkages in **1** and three of the four C≡C−C$_{\text{phenyl}}$ angles in **2** are also nonlinear, as if the H or C$_{\text{phenyl}}$ are weakly attracting. There is now considerable precedence for some distortion from 180° about the X−C≡C and C≡C−H linkages as noted in our recent work.[38,39] The nonlinearity in S−C≡C appears to be a few degrees larger than previous cases where the ethynyl group is attached to a carbon atom. A similar large (repulsive) deviation from linearity of 5° is seen in $S(CN)_2$ for the SCN linkage.[64] These subtle changes are not readily rationalized as arising from electronic effects such as dipole−dipole or through space orbital interactions without considerable additional analysis and interpretation of the quantum calculations.

A noteworthy parameter in both compounds is r(C−S), which falls between a typical C−S single bond (1.815 Å in $S(CH_3)_2$)[65] and a C═S double bond (1.611 Å in $H_2C{=}S$).[66] This is often attributed to a manifestation of the differences in size between sp, sp^2, and sp^3 carbon. Some interaction of the sulfur with the ethynyl groups where donation from sulfur occurs has also been proposed.[36] As noted in the previous section, there is some

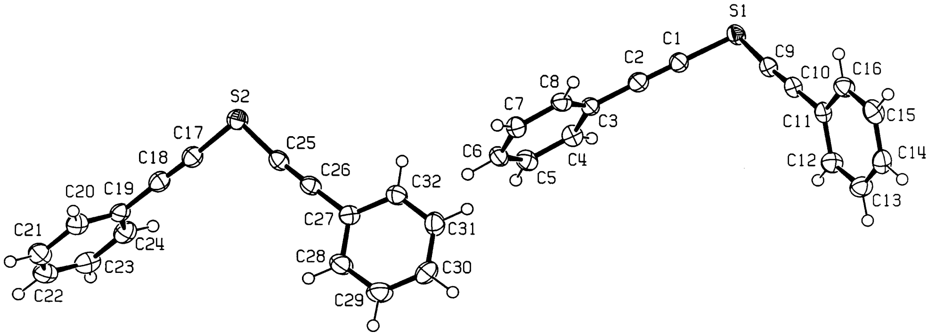

Figure 2. Atom numbering and orientation of two bis(phenylethynyl) sulfide species in the crystal.

TABLE 5: Comparison of Structural Parameters[a]

	$\mathrm{C{\equiv}C}$	$\mathrm{CC{-}S}$	$\mathrm{S{-}CH_3}$	∠CSC	ref
$\mathrm{S{-}(C{\equiv}CH)_2}$	1.211(10)	1.708(20)		100.5(10)	this work
$\mathrm{CH_3S{-}C{\equiv}CH}$	1.205(7)	1.685(5)	1.813(2)	99.9(2)	67
$\mathrm{CH_3S{-}C{\equiv}C{-}S{-}CH_3}$	1.211	1.671(2)	1.806(2)	86.5(50)	68
$\mathrm{S{-}(CH{=}CH)_2}$		1.758(4)		101.8(21)	69
$\mathrm{S{-}(CN)_2}$		1.700		97.9	64
$\mathrm{S{-}(CH_3)_2}$			1.815		65
$\mathrm{H_2C{=}S}$			1.611		66
$\mathrm{S{-}(C{\equiv}C{-}C_6H_5)_2}$	1.198(2)	1.695(4)		101.4(9)	this work
crystal data survey [b]	1.202(6)	1.678(6)		102.0(1.3)	62

[a] Bond distances in angstroms, angles in degrees. [b] 19 organic compounds were retrieved from the Cambridge Structural Database containing 66 unique $\mathrm{S{-}C{\equiv}C}$ linkages. The mean value and one standard deviation are listed.

TABLE 6: Selected Structural Parameters for Bis(phenylethynyl)[a] **Sulfide**[b]

$\mathrm{S_1{-}C_1}$	1.696(2)	$\mathrm{C_1{-}C_2}$	1.197(2)	$\mathrm{C_2{-}C_3}$	1.440(2)
$\mathrm{S_1{-}C_9}$	1.698(2)	$\mathrm{C_9{-}C_{10}}$	1.196(2)	$\mathrm{C_{10}{-}C_{11}}$	1.443(2)
$\mathrm{S_2{-}C_{17}}$	1.690(2)	$\mathrm{C_{17}{-}C_{18}}$	1.201(2)	$\mathrm{C_{18}{-}C_{19}}$	1.441(2)
$\mathrm{S_2{-}C_{25}}$	1.697(2)	$\mathrm{C_{25}{-}C_{26}}$	1.198(2)	$\mathrm{C_{26}{-}C_{27}}$	1.435(2)
$\mathrm{C_1{-}S_1{-}C_9}$	100.8(1)	$\mathrm{C_{17}{-}S_2{-}C_{17}}$	102.1(1)		
$\mathrm{S_1{-}C_1{-}C_2}$	178.5(2)	$\mathrm{S_2{-}C_{17}{-}C_{18}}$	177.2(2)		
$\mathrm{S_1{-}C_9{-}C_{10}}$	175.7(2)	$\mathrm{S_2{-}C_{25}{-}C_{26}}$	174.1(2)		
$\mathrm{C_1{-}C_2{-}C_3}$	177.4(2)	$\mathrm{C_{17}{-}C_{18}{-}C_{19}}$	177.9(2)		
$\mathrm{C_9{-}C_{10}{-}C_{11}}$	179.0(2)	$\mathrm{C_{25}{-}C_{26}{-}C_{27}}$	178.6(2)		
ring 1—ring 2[c]	88.47(8)				
ring 3—ring 4	88.41(9)				

[a] See Figure 2 for atom numbers. [b] Bond distances in angstroms, angles in degrees. [c] Angle between the mean planes of the phenyl rings. Ring 1 contains $\mathrm{C_3{-}C_8}$; ring 2, $\mathrm{C_{11}{-}C_{16}}$; ring 3, $\mathrm{C_{19}{-}C_{24}}$; ring 4, $\mathrm{C_{27}{-}C_{32}}$. See Figure 2.

increase in this length in bis(phenylethynyl) sulfide compared to ethynyl sulfides in the CSD. This increase (roughly 0.01−0.03 Å) is also manifest in diethynyl sulfide, even considering the large uncertainties, compared to most of the crystallographic values. The large majority of these latter data have a single $\mathrm{SC{\equiv}C}$ moiety and many are appended to ring systems so that the comparison may not be closely electronically equivalent.

For comparison, an experimental R_o structure has been determined for the closely related $\mathrm{HC{\equiv}CSCH_3}$.[67] This is listed in Table 5 along with electron diffraction structures for $\mathrm{CH_3SC{\equiv}CSCH_3}$[68] and $\mathrm{S(CH{=}CH_2)_2}$[69] and a near-experimental R_e structure for $\mathrm{S(CN)_2}$.[64] There also are several ab initio calculations for $\mathrm{HC{\equiv}C{-}SCH_3}$ and $\mathrm{HC{\equiv}C{-}SH}$ with $r(\mathrm{C{\equiv}C})$ between 1.170 and 1.223 Å and $r(\mathrm{C{-}S})$ between 1.697 and 1.720 Å.[30−36,70]

In our previous structural studies of the unsaturated prototype species $\mathrm{CH_2(C{\equiv}CH)_2}$[38] and $\mathrm{XCH{=}CHX}$ ($\mathrm{X} = \mathrm{C_2H}$[39] or CN[40]), the agreement between the empirical equilibrium structure and the highest level ab initio structures was very good (conservatively better than 0.005 Å and 0.5°). The agreement is less satisfying for diethynyl sulfide, for three of its six parameters in this case (roughly 0.02 Å). This deterioration is presumably due to a larger uncertainty in the experimental I's and deficiencies in the ab initio force field calculations arising from basis set inadequacies for the third row element (S). This matter needs further investigation before it is completely resolved.

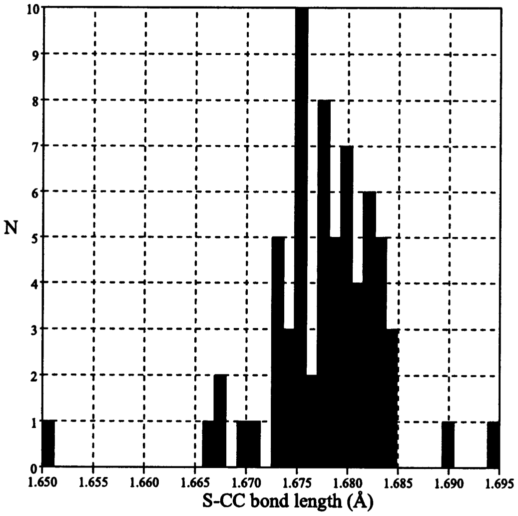

Figure 3. Histogram of S—C bond distances for selected ethynylsulfide species from the CSD.

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(42) For the normal isotopic species, the following three transitions were not seen consistently enough or sufficiently intense to consider them rigorously confirmed: 5_{05}–5_{14}, 12 651.353 MHz; 2_{12}–3_{03}, 6942.775 MHz; 3_{13}–4_{04}, 12 202.248 MHz.

(43) In the search for the $^{13}C_{\text{near the H}}$ species, three possible transitions were observed (in MHz): 1_{01}–1_{10}, 8025.460; 2_{02}–2_{11}, 8572.372; 0_{00}–1_{11}, 12 087.170.

(44) The three transitions in ref 43 give plausible rotational constants (MHz) of $A = 10\,056.31$, $B = 2551.61$, $C = 2030.85$, and $\Delta_{\text{i.d}} = 0.53$ amu Å^2. These compare well with the predicted values from the R_0 fit in Table 4, column 2 of 10 056.31, 2551.72, and 2031.03 (with an inertial defect estimate of 0.520 amu Å^2).

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(60) $\Delta I = I_x(\text{obsd}) - I_x(\text{calcd})$ where $I_x(\text{obsd})$ is one of the ground state or equilibrium moments of inertia and $I_x(\text{calcd})$ is the value for the structure obtained from the least-squares fitting analysis. Fitting programs use equations either for the moments of inertia or the rotational constants; these give virtually identical results ($I_aA = 505\,379.05$ amu Å^2, etc.). The STRFIT/STRFITQ program uses I's.

(61) Colorless crystals of bis(phenylethynyl) sulfide were obtained by cooling a solution of 3 mg in 1 mL of ethanol with 0.1 mL of water to −10 °C for 16 h. Crystal data for bis(phenylethynyl) sulfide: colorless plates, $0.38 \times 0.34 \times 0.08$ mm (cut from a larger mass), triclinic, space group *P*-1, $a = 8.830(2)$ Å, $b = 11.296(3)$ Å, $c = 12.947(3)$ Å, $\alpha = 91.747(4)°$, $\beta = 103.129(4)°$, $\gamma = 105.872(4)°$, $V = 1203.8(5)$ Å^3, $\lambda = 0.710\,73$ Å, $Z = 4$, $D_c = 1.293$ mg m^{-3}; μ(Mo Kα) = 0.240 mm^{-1}; ω scans, $2\theta_{\max} = 54.39°$; $T = 153(2)$ K.; 11 013 reflns collected, 5253 independent ($R_{\text{int}} = 0.0251$) included in the refinement. Data were processed and corrected for absorption (SADABS, $T_{\max}/T_{\min} = 0.977/0.929$), and full matrix least-squares refinement based on F^2 was carried out (SHELXTL, v. 5.10); $R1 = 0.0470$, $wR2 = 0.0974$ for all data; conventional $R1 = 0.0370$ computed for 5253 data ($I > 2\sigma(I)$) with 0 restraints and 387 parameters. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms located on a difference Fourier map and allowed to refine isotropically. Crystallographic data (excluding structure factors) for bis(phenylethynyl) sulfide have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (deposition number CCDC 190812).

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