The Structure of Phenylsulfanylacetylene, PhSCCH, as Determined in the Gas Phase by Electron Diffraction, in the Crystalline Phase at 150 K by X-Ray Diffraction and by *Ab Initio* Computations

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The structure of phenylsulfanylacetylene, PhSCCH, has been determined at 150 K by X-ray crystallography and in the gas phase by electron diffraction. The results indicate that although the dihedral angle between the planes of the benzene ring and the sulfanylacetylene group is *ca.* 10° in the solid phase, in the gas phase there is effectively free rotation about the C(ring)–S bond. Salient structural parameters are (*a*) for the solid phase, *r*[S(1)–C(2)] 168.3(2), *r*[S(1)–C(5)] 177.8(2), *r*[C(2)–C(3)] 119.2(3) and $r(\mathrm{C{-}C})_{\mathrm{ring}}$ (mean) 138.8(1) pm; C(2)S(1)C(5) 102.7(1)° and C(6)C(5)S(1)C(2) 9.6(2)°; and (*b*) gas phase (r_a), *r*[S(1)–C(2)] 169.6(5), *r*[S(1)–C(5)] 177.3(4), *r*[C(2)–C(3)] 119.5(6) and $r(\mathrm{C{-}C})_{\mathrm{ring}}$ (mean) 139.9(1) pm; C(2)S(1)C(5) 103.8(6)°. These values agree well with those obtained in an *ab initio* (HF/6-31G* and MP2/6-31G* level) study of the molecular geometry.

Phenylsulfanylacetylene, PhSCCH (**1**), known since 1956,[1] has recently been identified as a useful reagent in organic synthesis and a number of new syntheses have been proposed.[2,3] However, no complete structural study has been undertaken for this or any other compound containing the sulfanylacetylene unit. An early microwave study of methylsulfanylacetylene, MeSCCH, has been published but the number of refined structural parameters was very limited.[4] We have carried out a structural study of PhSCCH in the solid phase by low-temperature single-crystal X-ray diffraction and, for comparison, in the gas phase by electron diffraction.

In the initial refinements of the gas phase structure, both a planar and twisted conformation of the SCCH group were found to fit the electron-diffraction data. This was interesting since recently Schaefer and Sebastian[5] have reported theoretical evidence for a non-planar global energy minimum and a four-fold internal rotational-energy barrier for the parent thiophenol, PhSH. Therefore, to address both the question of the global minimum structure of **1** and the nature of the potential surface associated with rotation of the SCCH group about the C_6H_5–S bond, we have performed *ab initio* calculations at a reasonable level of theory (MP2/6-31G*//6-31G*).

Experimental

Synthesis.—Phenylsulfanylacetylene was prepared by flash-vacuum pyrolysis of 2,2-dimethyl-5-(phenylsulfanylmethylene)-1,3-dioxane-4,6-dione as described previously.[2] The purity of the compound was checked by reference to the ^1H and ^{13}C NMR spectra of a solution in $CDCl_3$.[2]

X-Ray Structure Determination of PhSCCH.—A colourless cylinder (0.8 × 0.5 × 0.5 mm) suitable for X-ray analysis was obtained by slow cooling of a liquid sample sealed in a Pyrex-glass capillary.

Crystal data. C_8H_6S, $M = 134.2$, monoclinic, space group $P2_1/c$, $a = 574.4(1)$, $b = 752.7(3)$, $c = 1601.0(4)$ pm, $\beta = 94.30(3)°$, $U = 690.2 \times 10^6$ pm^3 [from accurate 2θ values for 26 reflections with $2\theta = 30$–$32°$, $\lambda = 71.073$ pm], $Z = 4$, $D_c = 1.291$ g cm^{-3}, $T = 150$ K, $\mu = 0.348$ mm^{-1}, $F(000) = 280$.

Data collection and processing. Stoë Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device,[6a] Mo-Kα radiation, ω-2θ scans using on-line profile-fitting,[6b] 1919 data collected ($2\theta_{\max}$ 60°, h −8 to 8, k 0–10, l 0–22), of which 1572 with $F \geqslant 4\sigma(F)$ were used in all calculations. Three standard reflections were collected every 60 min; the maximum drift correction was 2%.

Electron-diffraction (*ED*) *Measurements.*—Electron-scattering intensities were recorded on Kodak Electron Image plates using the Edinburgh gas-diffraction apparatus operating at *ca.* 44.5 kV (electron wavelength *ca.* 5.7 pm).[7] Nozzle-to-plate distances were *ca.* 95 and 260 mm, yielding data in the s range 20–300 nm^{-1}; three usable plates were obtained at each distance. The sample and nozzle were held at *ca.* 408 and 433 K, respectively, during the exposure periods; a black solid remained in the sample tube indicating some decomposition.

The scattering patterns of benzene were also recorded for the purpose of calibration; these were analysed in exactly the same way as those of the phenylsulfanylacetylene so as to minimise systematic errors in the wavelengths and camera distances. Nozzle-to-plate distances, weighting functions used to set up the off-diagonal weight matrix, correlation parameters, final scale factors, and electron wavelengths for the measurements are collected together in Table 1.

The electron-scattering patterns were converted into digital form using a computer-controlled Joyce–Loebl MDM6 microdensitometer with a scanning program described elsewhere.[8] The programs used for data reduction[8] and least-squares refinement[9] have been described previously; standard complex scattering factors were employed.[10]

Theoretical Calculations.—*Ab initio* computations employed standard procedures and basis sets[11] using the GAUSSIAN92 program.[12] The theoretical relative energies are given in the notation 'level of the energy calculation//geometry employed'. The calculations were performed on IBM-RS/6000 workstations of the *Rechenzentrum der Universität Zürich.*

Table 1 Nozzle-to-plate distances, weighting functions, correlation parameters, scale factors and electron wavelengths used in the electron-diffraction study

Nozzle-to-plate distance/mm	Weighting function/nm^{-1}					Correlation parameter	Scale factor k[a]	Electron wavelength/pm[b]
	Δs	s_{min}	sw_1	sw_2	s_{max}			
259.62	2	20	40	140	164	0.486	0.813(15)	5.687
95.01	4	100	120	256	300	0.373	0.685(29)	5.693

[a] Figures in parentheses are the estimated standard deviations. [b] Determined by reference to the scattering pattern of benzene vapour.

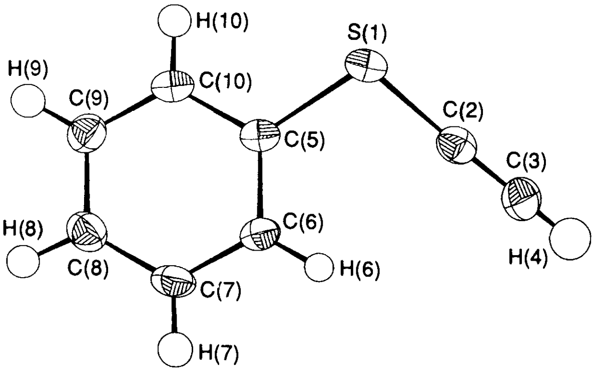

Fig. 1 Thermal ellipsoid plot of a single molecule of PhSCCH, showing the atom numbering scheme adopted

Results

X-Ray Structure Solution and Refinement.—The structure was solved by direct methods using SHELXS-86[13] and refined using SHELX-76.[14] Approximate positions of all non-hydrogen atoms were found in the first Fourier map; all hydrogen atoms were found by difference synthesis and refined isotropically. No absorption correction was made. At final convergence R = 0.040, R' = 0.054, S = 1.05 for 106 parameters and the final ΔF synthesis showed no peak outside the range $(-0.40$ to $0.50) \times 10^{-6}$ e pm^{-3}. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,489\,F^2$ gave satisfactory agreement analyses and in the final cycle $(\Delta/\sigma)_{max} = 0.06$. Tables of bond lengths and angles, fractional coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.† Plots of the structure, including the atom numbering scheme, are shown in Fig. 1.

ED Structural Analysis: Molecular Model.—The parameters used to generate the atomic coordinates of PhSCCH are listed in Table 2. The Ph ring was assumed to possess C_{2v} symmetry, and its structure was defined by four distance and two angle parameters: an average C–H distance (p_4), the average C–C distance (p_5), the difference between C(7)–C(8) and the mean of C(5)–C(6) and C(6)–C(7) (p_6), the difference between C(5)–C(6) and C(6)–C(7) (p_7), the *ipso* angle C(10)C(5)C(6) (p_8), and the angle C(5)C(6)C(7) (p_9). The C–H bond axes were assumed to bisect their respective CCC angles.

The sulfanylacetylene group was defined initially by six parameters: an average and a difference of the S–C bond distances (p_1 and p_2, respectively), the C≡C bond length (p_3), the angles C(2)C(1)C(5) (p_{10}) and S(1)C(2)C(3) (p_{11}), and the dihedral angle C(6)C(5)S(1)C(2) (p_{12}) defining the position of the SCCH group out of the plane ($p_{12} = 0°$) of the ring. The distance r[C(4)–H(4)] was assumed to be 2 pm shorter than the ring r(C–H) distance. In the later refinements, however, a model describing free rotation of the SCCH group was adopted. The rotation was represented by a set of five fixed conformations of the SCCH group over the range $0° < \varphi < 90°$ of the rotation angle φ (φ = C(6)C(5)S(1)C(2) = 0° defined as the SCCH group in the plane of the Ph ring). Thus, the continuous torsion-sensitive distance distribution was approximated by calculating all the torsion-dependent distances [the non-bonding distances C(2) ··· C(6,7,9,10), C(2) ··· H(6,7,9,10), C(3) ··· C(6,7,9,10), C(3) ··· H(6,7,9,10), H(4) ··· C(6,7,9,10) and H(4) ··· H(6,7,9,10)] at angle increments of $\Delta\varphi = 18°$. Each of the distinct non-bonded distances was then given a weight of 0.2.

Refinement of the Structure.—The radial-distribution curve for PhSCCH shows eight peaks at *ca.* 140, 170, 240, 280, 340, 400, 455 and 500 pm, together with two distinct shoulders at *ca.* 115 and 215 pm. The peaks at $r < 200$ pm correspond to scattering from bonded pairs; the C–H and C≡C pairs contribute to the shoulder at *ca.* 115 pm, the peak at *ca.* 140 pm consists of the ring C–C bond distances and the peak at *ca.* 170 pm corresponds to the two S–C bonded distances. The two-bond C ··· H (ring) non-bonded pairs contribute mainly to the shoulder at *ca.* 215 pm and the two-bond C ··· C (ring) non-bonded pairs are identified with the peak at *ca.* 240 pm. The peak at *ca.* 280 pm consists of scattering from S(1) ··· C(6), C(5) ··· C(8) and S(1) ··· C(3) non-bonded pairs, augmented by contributions from the C(2) ··· C(5) and S(1) ··· H(6) non-bonded pairs. Three-bond C ··· H (ring) non-bonded pairs are identified with the peak at *ca.* 340 pm and the S(1) ··· C(7) and S(1) ··· C(8) non-bonded pairs are the major contributors to the peaks at *ca.* 400 and 455 pm, respectively.

Initial refinements of the molecular structure employing a static model, *i.e.* with p_{12} as the C(6)C(5)S(1)C(2) dihedral angle, yielded parameters similar to those reported in Table 2, with $p_{12} = 47.0(38)°$. However, the low potential energy barrier to rotation calculated *ab initio* (*ca.* 1.6 kJ mol^{-1} at the MP2/6-31G*//6-31G* level, see below), together with the large values of amplitudes of vibration indicated for the C(2) ··· C(6,7,9,10) and C(3) ··· C(6,7,9,10) non-bonded pairs (typically > 20 pm), were indicative of a structure in which the barrier to rotation of the SCCH moiety about the S–C(ring) bond is low. Subsequent refinements therefore employed a model incorporating free rotation of the sulfanylacetylene moiety. The low symmetry of the molecule coupled to the relatively poor quality of the data precluded the possibility of refinements of a dynamic model incorporating a function such as $V = V_0(1 - \cos 4\varphi)$ to describe the nature of the barrier.

Of the 11 independent parameters defining the molecular geometry, six yielded to simultaneous refinement in the final analysis. The bond-difference and angle parameters defining the ring geometry were fixed at values commensurate with those found in both the X-ray and theoretical structures and in the structures of similar aromatic compounds.[15] The angle S(1)C(2)C(3), p_{11}, was fixed at 4° from linearity (measured away from the Ph ring) on the evidence of both the X-ray and *ab initio* geometries; the R_G value improved by 0.3% on introducing this distortion. In addition, it was possible to refine nine amplitudes of vibration. Ratios used in constraints of some of these amplitudes, together with the values of amplitudes

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† For details of the CCDC deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1.

Table 2 Molecular parameters (r_a) as determined by electron diffraction assuming free rotation of the S(1)C(2)C(3)H(4) group about the S–C(ring) bond

Parameter[a]	Distance (pm) or angle (°)[b]	Amplitude of vibration/pm[b]
(*a*) Independent		
p_1 r(S–C) (mean)	173.4(2)	
p_2 r(S–C) (difference)	7.7(8)	
p_3 r[C(2)–C(3)]	119.5(6)	
p_4 $r(\text{C–H})_{\text{ring}}$	110.7(8)	
p_5 $r(\text{C–C})_{\text{ring}}$ (mean)	139.9(1)	
p_6 $r[\text{C}(7)\text{–C}(8)] - \frac{1}{2}\{r[\text{C}(5)\text{–C}(6)] + r[\text{C}(6)\text{–C}(7)]\}$	1.03(f)	
p_7 $r[\text{C}(5)\text{–C}(6)] - r[\text{C}(6)\text{–C}(7)]$	−0.5(f)	
p_8 C(6)C(5)C(10)	121.0(f)	
p_9 C(5)C(6)C(7)	119.5(f)	
p_{10} C(2)S(1)C(5)	103.8(6)	
p_{11} S(1)C(2)C(3)	176.0(f)	
(*b*) Dependent[c]		
r_1 r[C(5)–C(6)]	139.3(1)	4.5(3)
r_2 r[C(6)–C(7)]	139.8(1)	
r_3 r[C(7)–C(8)]	140.6(1)	
r_4 r[C(5)–S(1)]	177.3(4)	4.1 (tied to u_5)
r_5 r[S(1)–C(2)]	169.6(5)	4.3(6)
r_6 r[C(2)–C(3)]	119.5(6)	3.9(10)
r_7 r[C(3)–H(4)]	108.7(8)	7.4(f)
r_8 r[C(6)–H(6)]	110.7(8)	7.7(f)
r_9 r[C(5)···C(7)]	241.1(2)	6.5(3)
r_{10} r[C(6)···C(8)]	243.3(2)	
r_{11} r[C(6)···C(10)]	242.5(2)	
r_{12} r[C(7)···C(9)]	242.5(2)	
r_{13} r[S(1)···C(6)]	274.1(3)	9.2(8)
r_{14} r[S(1)···C(3)]	288.9(7)	6.1(10)
r_{15} r[C(2)···C(5)]	273.0(11)	9.5(f)
r_{16} r[C(5)···H(6)]	217.2(7)	10.4(7)
r_{17} r[C(6)···H(7)]	217.2(7)	
r_{18} r[C(7)···H(8)]	218.6(7)	
r_{19} r[C(7)···H(6)]	217.7(7)	
r_{20} r[C(8)···H(7)]	217.9(7)	
r_{21} r[C(2)···H(4)]	228.2(10)	8.0(f)
r_{22} r[C(5)···C(8)]	279.6(2)	7.1 (tied to u_9)
r_{23} r[C(6)···C(9)]	279.9(2)	
r_{24} r[S(1)···C(7)]	404.3(3)	10.2(5)
r_{25} r[C(2)···C(6)][d]	290.4(16)	12.9(f)
r_{26} r[C(2)···C(10)][d]	404.0(9)	8.7(f)
r_{27} r[C(3)···C(5)]	377.1(14)	11.7(f)
r_{28} r[C(5)···H(7)]	341.5(8)	10.7 (tied to u_{16})
r_{29} r[C(6)···H(8)]	343.7(8)	
r_{30} r[C(6)···H(10)]	342.7(8)	
r_{31} r[C(7)···H(9)]	343.0(8)	
r_{32} r[C(8)···H(6)]	343.8(8)	
r_{33} r[S(1)···H(6)]	288.4(3)	13.2(f)
r_{34} r[S(1)···H(4)]	397.6(11)	8.4(f)
r_{35} r[S(1)···C(8)]	456.8(4)	8.6(8)
r_{36} r[C(2)···C(7)][d]	428.9(17)	13.4(f)
r_{37} r[C(2)···C(9)][d]	512.7(12)	9.8(f)
r_{38} r[C(3)···C(6)][d]	360.2(22)	18.3(f)
r_{39} r[C(3)···C(10)][d]	513.0(13)	13.7(f)
r_{40} r[C(5)···H(8)]	390.3(9)	9.4(f)
r_{41} r[C(6)···H(9)]	390.6(9)	9.5(f)
r_{42} r[S(1)···H(7)]	491.3(7)	10.9(f)
r_{43} r[S(1)···H(8)]	567.5(9)	9.5(f)

[a] For definitions of parameters, see the text. [b] Figures in parentheses are the estimated standard deviations; f = fixed. [c] Other non-bonded distances were included in the refinement (a total of 171) but are not shown here. [d] Torsion-dependent distance; amplitudes were calculated by molecular-mechanics methods.

for the rotation-sensitive distances, were calculated using the molecular-mechanics program MM3.[16]

The success of the final refinement, for which $R_G = 0.099$ ($R_D = 0.065$), may be assessed on the basis of the difference between the experimental and calculated radial-distribution curves (see Fig. 2); Fig. 3 offers a similar comparison between the experimental and calculated molecular-scattering curves. The relatively high value of R_G may be ascribed to background noise which was rather marked due, presumably, to scattering from small amounts of volatile decomposition products. Part of the least-squares correlation matrix is shown in Table 3† and the structural details and vibrational amplitudes of the optimum refinement are listed in Table 2.

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† The full form of this matrix has been deposited under the Supplementary Publications Scheme. For details of the scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1. [Supp. Publ. No. 57012 (2 pp.)].

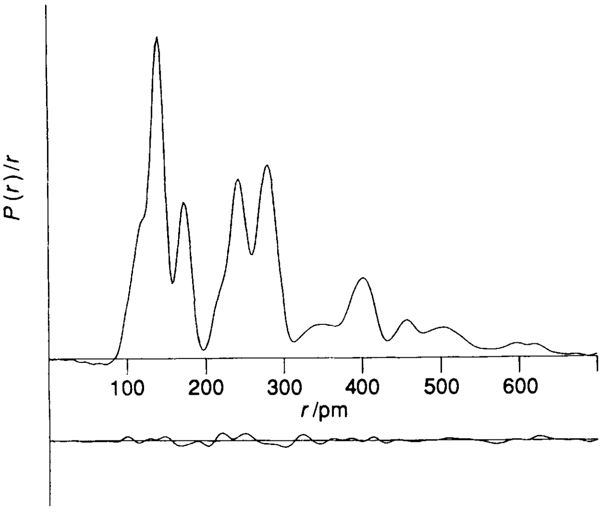

Fig. 2 Observed and final weighted difference radial-distribution curves for PhSCCH. Before Fourier inversion, the data were multiplied by $s \exp[(-0.000\,02\, s^2)/(Z_S - f_S)(Z_C - f_C)]$.

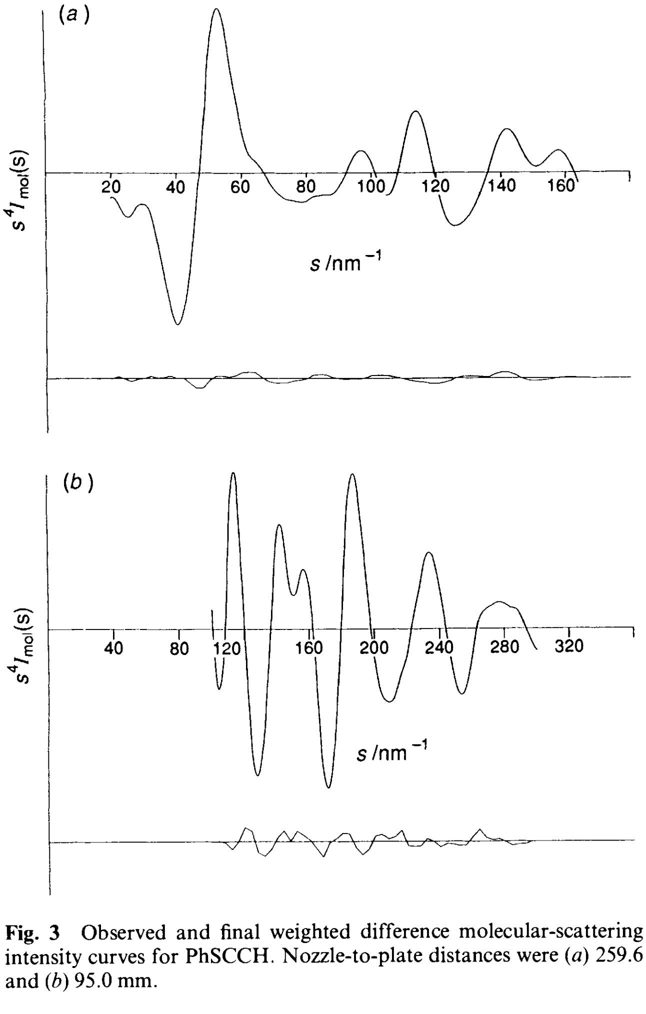

Fig. 3 Observed and final weighted difference molecular-scattering intensity curves for PhSCCH. Nozzle-to-plate distances were (*a*) 259.6 and (*b*) 95.0 mm.

Table 3 Significant values (*i.e.* > 50%) of the least-squares correlation matrix (× 100) for the electron-diffraction study[a]

u_5	u_6	u_{13}	u_{14}	k_1	k_2	
−67						p_2
		−51				p_3
	56			−56		p_4
		−58				p_5
					78	u_1
					65	u_9
			73	51		u_{13}

[a] k_1 and k_2 are scale factors.

Ab Initio *Calculations*.—In the initial electron-diffraction refinements of the structure of PhSCCH, both planar and twisted conformations [C(6)C(5)S(1)C(2) = *ca.* 0 and 47°, respectively] for the SCCH group were found to fit the ED data almost equally well. To address the question of the magnitude of the rotational energy barrier about the S–C(ring) bond, we have optimised geometries at the HF/6-31G* level for various C(6)C(5)S(1)C(2) angles over the range 0–90°, followed by single-point energy calculations at the correlated MP2/6-31G* level (frozen core approximation). The results are shown in Table 4. At a similar level, the internal rotation in conjugated molecules is described reasonably well.[17]

Both the planar (**1a**) and perpendicular [C(6)C(5)S(1)C(2) = 90°] (**1b**) conformations of PhSCCH were fully optimised in C_s symmetry. At the HF/6-31G*//6-31G* level, **1b** is calculated to be more stable than **1a** by *ca.* 2 kJ mol^{-1}.† However, inclusion of electron correlation at the MP2/6-31G*//6-31G* level reverses these relative stabilities; **1a** is then more stable than **1b** by *ca.* 1 kJ mol^{-1} (see Table 4). Clearly, the shape of the potential-energy surface (PES) changes when the effects of electron correlation are included. To study this further, structures with conformations intermediate between **1a** and **1b** were optimised with the C(6)C(5)S(1)C(2) dihedral angle fixed at 30 and 60°. The HF/6-31G*//6-31G* energies of these two conformations lie between those of **1a** and **1b**, suggesting a two-fold rotational barrier, with the perpendicular conformation as the minimum. However, the MP2/6-31G*//6-31G* energies of the 30 and 60° conformations lie below those of **1a** and **1b**, consistent with a non-planar conformation and, hence, a four-fold barrier (see Table 4). At this level of theory, the barrier to rotation about the Ph–S bond is predicted to be *ca.* 1.6 kJ mol^{-1}, the difference between the most stable structure [C(6)C(5)S(1)C(2) = 30°] and the least stable [C(6)C(5)S(1)C(2) = 90°]. Whilst this value may change somewhat at higher levels of theory, it is rather less than RT under the ED experimental conditions (T = 433 K, RT = 3.6 kJ mol^{-1}) and the rotation may be reasonably modelled as being essentially unhindered.

Additional information concerning the equilibrium structure of PhSCCH (*i.e.* the minimum on the PES surface) was provided by a full MP2/6-31G* optimisation under C_1 symmetry. The geometrical parameters are included in Table 4.

Discussion

The present measurements on phenylsulfanylacetylene provide the first structural information for this compound. The analyses of both the electron-diffraction and the single-crystal X-ray patterns endorse the spectroscopic evidence[2] that the molecule consists of a benzene ring substituted with an sulfanylacetylene (SCCH) group. In the gas-phase structure, the SCCH moiety is effectively free to rotate about the Ph–S bond, whereas in the solid-phase structure, the dihedral angle between the planes of this group and of the benzene ring is *ca.* 10°. Values of the principal bond distances and angles derived from the three methods employed in this work are compared in Table 5.

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† At the HF/3-21G level, the perpendicular conformation is calculated to lie at a potential-energy minimum and the planar conformation is a transition state; the imaginary frequency of the latter, however, is only 6 cm^{-1}.

Table 4 Bond lengths (pm) and angles (°) calculated by *ab initio* methods

	Dihedral angle C(6)C(5)S(1)C(2)				
Distance or angle	0[a]	30[b]	60[b]	90[a]	37.5[c]
S(1)–C(2)	169.8	170.1	170.5	170.7	169.3
S(1)–C(5)	179.0	179.1	179.2	179.3	178.8
C(2)–C(3)	118.9	118.9	118.9	118.9	122.4
C(5)–C(6)	138.5	138.7	138.9	138.8	139.8
C(5)–C(10)	139.0	138.8	138.6	138.8	139.9
C(6)–C(7)	138.7	138.5	138.3	138.5	139.5
C(7)–C(8)	138.3	138.6	138.8	138.6	139.7
C(8)–C(9)	138.6	138.5	138.3	138.6	139.6
C(9)–C(10)	138.3	138.5	138.8	138.5	139.6
C(3)–H(4)	105.7	105.7	105.7	105.7	106.7
$(C\text{–}H)_{ring}$ (mean)	107.5	107.5	107.5	107.5	108.7
C(5)S(1)C(2)	103.9	103.2	102.1	101.8	101.1
C(10)C(5)C(6)	120.1	120.1	120.2	120.1	120.4
C(5)C(10)C(9)	119.9	119.9	119.8	119.9	119.7
C(5)C(6)C(7)	119.5	119.6	119.7	119.9	119.4
S(1)C(2)C(3)	176.0	176.3	176.6	177.0	174.0
E_{rel}(HF)[d]/kJ mol^{-1}	0.0	−0.8	−1.7	−2.0	—
E_{rel}(MP2)[e]/kJ mol^{-1}	0.0	−0.8	−0.4	0.8	—

[a] Geometry optimised in C_s symmetry at the HF/6-31G* level. [b] Geometry partially optimised (dihedral angle constrained) at the HF/6-31G* level. [c] Geometry fully optimised at the MP2/6-31G* level. [d] HF/6-31G*//HF/6-31G* energy relative to the planar conformation. [e] MP2/6-31G*//HF/6-31G* energy relative to the planar conformation.

Table 5 Comparison of the principal structural parameters obtained from the X-ray, electron-diffraction (ED) and *ab initio* analyses[a]

Parameter	X-ray	ED[b]	*Ab initio*[c]
S(1)–C(2)	168.3(2)	169.6(5)	169.3
S(1)–C(5)	177.8(2)	177.3(4)	178.8
C(2)–C(3)	119.2(3)	119.5(6)	122.4
C–C (ring mean)	138.8(1)	139.9(1)	139.7
C(5)S(1)C(2)	102.7(1)	103.8(6)	101.1
C(10)C(5)C(6)	123.7(1)	121.0(f)	120.4
S(1)C(2)C(3)	177.5(2)	176.0(f)	174.0
C(6)C(5)S(1)C(2)	9.6(2)	—[d]	37.5

[a] Figures in parentheses are the estimated standard deviations. [b] Distances are r_a; f = fixed. [c] MP2/6-31G* optimised. [d] Free rotation.

The structural parameters derived by the full *ab initio* optimisation at the MP2/6-31G* level (Table 4) are in good agreement with those refined from the diffraction data. The computed C–C equilibrium bond lengths for the benzene ring are essentially equal, 139.5–139.9 pm. As in acetylene itself [r(C≡C) = 121.8 pm (MP2(full)/6-31G* level), 120.3 pm (experimental)],[11] the C–C triple bond length is overestimated at the MP2/6-31G* level, 122.4 pm *vs.* 119.5(6) pm obtained experimentally (gas-phase electron diffraction, GED). The S(1)C(2)C(3) bond angle is computed to show a slight deviation from linearity (6° away from the benzene ring) and this is also observed in the experimental refinements. The C(6)C(5)S(1)C(2) torsion angle optimised to a value of 37.5°, close to the value of the analogous CCSH torsion angle computed for thiophenol by Schaefer and Sebastian (*ca.* 38°).[5] The small value of the C(6)C(5)S(1)C(2) torsion angle in the solid-phase structure is presumably a result of intermolecular forces and the low intramolecular potential-energy barrier to rotation.

The packing of the phenylsulfanylacetylene molecules in the crystal is shown in Fig. 4(*a*). The molecules are ordered in a 'head-to-tail' chain arrangement such that the sulfur atom of one molecule lies below the benzene ring of another, close to the pseudo six-fold axis; the intermolecular S(1) • • • C(5–10) distances span the range 383.0(2)–395.8(1) pm. There would thus appear to be an intermolecular sulfur • • • benzene ring interaction as represented in Fig. 4(*b*). The S–C(ring) bond in each molecule lies *ca.* 3° out of the plane of its respective benzene ring.

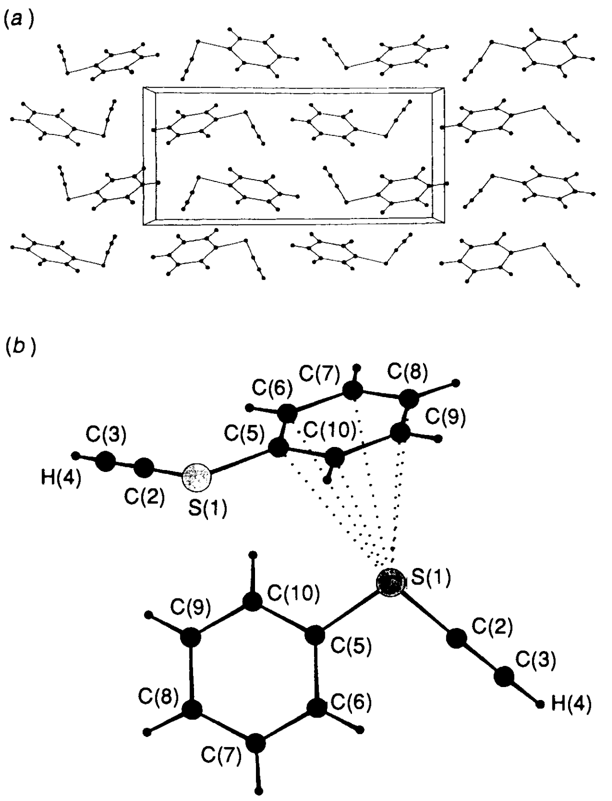

Fig. 4 (*a*) The molecular packing in the crystal. (*b*) The sulfur atoms in one molecule lie below the plane of the benzene ring of another; the intermolecular S • • • C distances lie within the range *ca.* 383–396 pm.

Table 6 shows structural parameters for some sulfides. Although care must be exercised in comparing results from different techniques, it would appear that the S–C(aromatic) bond length and the CSC angle for PhSCCH are typical of the values found for other Ph–S–X systems. As has been illustrated elsewhere,[23] the S–C bond length shows a very marked variation dependent upon the environments of the carbon and sulfur atoms. The difference r[S–C(sp^3)] − r[S–C(sp^2)] is 2.5–6.6 pm and the difference r[S–C(sp^2)] − r[S–C(sp)] is 5.3–10.7 pm. Such large differences are substantially greater than those typically observed for the analogous r(C–C) and r(Si–C) series. In particular, the r[S–C(sp)] bond lengths are very short, at < 170 pm (*cf.* SF$_5$C≡CH, r_z(S–C) = 173.6(6) pm);[24] at 169.5(5) pm (GED) in PhSCCH, the r[S–C(sp)] bond length is in good agreement with the value (168.0 pm) derived from the somewhat limited microwave study of MeSCCH.[4]

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Table 6 Structural parameters (distances in pm, angles in °) for some sulfides[a]

Compound	S–C(aro)[b]	S–C(other)	CSC	CCSC[c]	Method[d]
PhSMe	174.9(4)	180.3(4)	105.6(7)	45.3(28)	GED[e]
PhS(CH$_2$)$_2$SO$_2$Me	177.4(2)	181.0(2)	104.0(1)	23.9(2)	XRD[f]
PhSCH=CH$_2$	174.9(5)[g]	174.9(5)[g]	109.2(18)	42.9(87)	GED[h]
(PhS)$_2$C=C(SPh)$_2$	177.0(3)	176.5(2)	103.2(1)	44.5(2)	XRD[i]
	176.7(3)	176.7(3)	103.6(1)	37.1(2)	
PhSC≡CH	177.8(2)	168.3(2)	102.7(1)	9.6(2)	XRD[j]
	177.3(4)	169.6(5)	103.8(6)	—[k]	GED[j]
MeSC≡CH	—	181.5	101.0	—	MW[l]
		168.0			
MeSC≡CSMe	—	180.6(2)	102.7(2)	—	GED[m]
		167.1(2)			

[a] Figures in parentheses are the estimated standard deviations. [b] aro = aromatic. [c] Dihedral angle between the benzene ring and the substituent S–C bond. [d] GED = gas-phase electron diffraction, XRD = X-ray diffraction of a single crystal, MW = microwave spectroscopy. [e] Ref. 18. [f] Ref. 19. [g] r(S–C) assumed to be equal. [h] Ref. 20. [i] Ref. 21. [j] This work. [k] Free rotation of the substituent about the S–C(aro) bond. [l] Ref. 4. [m] Ref. 22.

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References

1 W. E. Parham and P. L. Stright, *J. Am. Chem. Soc.*, 1956, **78**, 4783.

2 G. A. Hunter and H. McNab, *Synthesis*, 1993, 1067.

3 P. A. Magriotis and J. T. Brown, *Org. Synth.*, 1993, **72**, 252.

4 D. d. Engelsen, *J. Mol. Spectrosc.*, 1967, **22**, 426.

5 T. Schaefer and R. Sebastian, *J. Mol. Struct.*, 1993, **284**, 171.

6 (*a*) J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105; (*b*) W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

7 C. M. Huntley, G. S. Laurenson and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1980, 954.

8 S. Cradock, J. Koprowski and D. W. H. Rankin, *J. Mol. Struct.*, 1981, **77**, 113.

9 A. S. F. Boyd, G. S. Laurenson and D. W. H. Rankin, *J. Mol. Struct.*, 1981, **71**, 217.

10 A. W. Ross, M. Fink and R. Hilderbrandt, *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, Boston and London, 1992, vol. C, p. 245.

11 See W. Hehre, P. v. R. Schleyer, L. Radom and J. A. Pople, Ab Initio *Molecular Orbital Theory*, Wiley, New York, 1986.

12 GAUSSIAN92: M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, H. B. Schlegal, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, R. Martin, D. J. Fox, D. J. DeFrees, J. Baker, J. J. P. Stewart and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1992.

13 G. M. Sheldrick, SHELXS-86, program for crystal-structure solution, University of Göttingen, Germany, 1986.

14 G. M. Sheldrick, SHELX-76, program for crystal-structure refinement, University of Cambridge, UK, 1976.

15 See, *e.g.* A. Domenicano, in *Stereochemical Applications of Gas-Phase Electron Diffraction*, eds. I. Hargittai and M. Hargittai, VCH, New York, 1988, part B, ch. 7.

16 P. Aped and N. L. Allinger, *J. Am. Chem. Soc.*, 1992, **114**, 1.

17 M. Head-Gordon and J. A. Pople, *J. Phys. Chem.*, 1993, **97**, 1147.

18 N. M. Zaripov, *J. Struct. Chem.* (*Engl. Trans.*), 1976, **17**, 640.

19 F. Mo, B. C. Hauback and S. Winther, *Acta Crystallogr., Sect. B*, 1984, **40**, 288.

20 N. M. Zaripov and T. G. Mannafov, *J. Struct. Chem.* (*Engl. Trans.*), 1975, **16**, 768.

21 R. C. Collins and R. E. Davies, *Acta Crystallogr., Sect. B*, 1978, **34**, 285.

22 B. Beagley, V. Ulbrecht, S. Katsumata, D. R. Lloyd, J. A. Connor and G. A. Hudson, *J. Chem. Soc., Faraday Trans. 2*, 1977, **73**, 1278.

23 I. Hargittai, *The Structure of Volatile Sulphur Compounds*, Riedel, Dordrecht and Akadémiai Kiadó, Budapest, 1985.

24 P. Zylka, D. Christen, H. Oberhammer, G. L. Gard and R. J. Terjeson, *J. Mol. Struct.*, 1991, **249**, 285.

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