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REACTION OF HYDROXYLAMINE WITH BENZENESULFONYL CHLORIDE. X-RAY CRYSTAL STRUCTURE OF PILOTY'S ACID AND OTHER BENZENESULFONYLHYDROXYLAMINES.

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The X-ray crystal structures of the four stable phenylhydroxylamines ($PhSO_2NHOH$, $(PhSO_2)_2NOH$, $PhSO_2NHOSO_2Ph$, $(PhSO_2)_2NOSO_2Ph$), and of $PhSO_3^-{}^+H_3NHNSO_2Ph$ are presented. The last of these is a by-product obtained during the isolation of $PhSO_2NHOH$ (Piloty's Acid). The formation of and the bonding in these molecules are discussed.

Piloty's acid, $PhSO_2NHOH$, **1**, was first prepared nearly one hundred years ago by the reaction of benzenesulfonyl chloride ($PhSO_2Cl$) with one equivalent of hydroxylamine hydrochloride in basic medium.[1] Perusal of the literature revealed that although the original synthesis has been repeated a number of times, no new synthetic approach has been described.[2] The many reported melting points of **1** lie between 120 and 129 °C[3], but in our hands, the melting point was never greater than 109-10 °C regardless of the solvent used for recrystallization.[4] This discrepancy led us to determine the structure of our material by X-ray crystallography, which confirmed that it was indeed Piloty's acid.

During the recrystallization of **1**, a hitherto unreported white solid was isolated and shown to be $PhSO_3^-{}^+H_3NNHSO_2Ph$ (**5**) by X-ray crystallography and elemental analysis. Another component of the mother liquor, PhSH, can be accounted for by the reduction of $PhSO_2Cl$ by $HONH_2$;[5,6] however, we found no precedent for the formation of **5**.

As in the case of **1**, widely discrepant melting points have been reported for $(PhSO_2)_2NOH$, (**2**).[7] The melting point problem for **1** and **2**, coupled with the great difficulty in distinguishing the N-S from the O-S linkage spectroscopically, led us to undertake X-ray structure determinations of the entire set of phenylsulphonylhydroxylamines (cf. Figures 1 - 4 and Table 1).

Formation and Identification of 1 - 5

Prior to this work, the structure of **1** was deduced from the elemental composition,[1] IR (NH and OH bands), ^{13}C NMR (monosubstituted phenyl ring),[8] and the chemistry of **1**.[9,10,11,12] The labile nature of $TsONH_2$[13] coupled with the observation that sulphonyl chlorides react with $HONH_2$ at nitrogen[14] lent credibility to the structural assignment. The X-ray structure determination of **1** (see below) confirmed the identity of this compound as $PhSO_2NHOH$. Since mixtures containing up to 25% **5** melted below 110 °C, contamination of Piloty's acid with **5** is not responsible for the higher melting points previously reported.

The fact that **5** is a new compound[15] led us to identify it by X-ray crystallography, elemental analysis, and mixed melting points with an authentic sample (cf. Figure 5). The elemental analysis was critical in deducing its structure because X-ray crystallography alone did not readily distinguish N from O. This salt analyzed as

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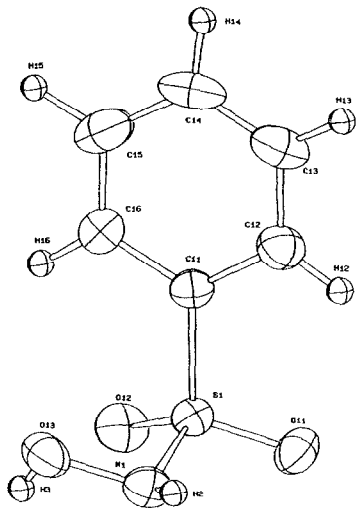


Figure 1: ORTEP drawing of the S-enantiomer of **1**.

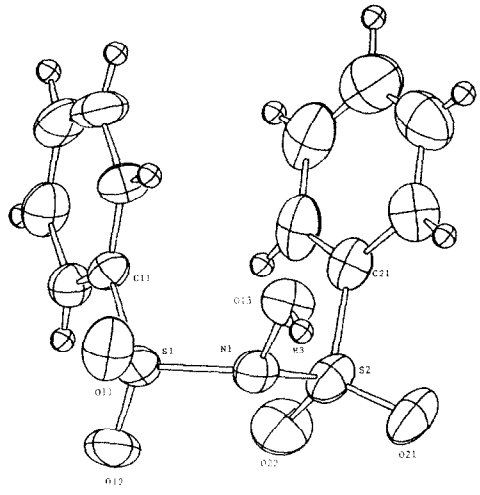


Figure 2: ORTEP drawing of **2**.

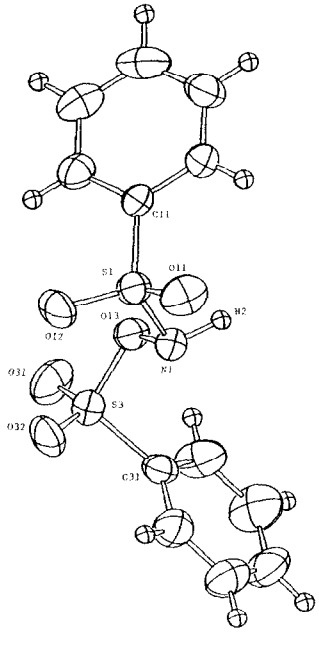


Figure 3: ORTEP drawing of the R-enantiomer of **3**.

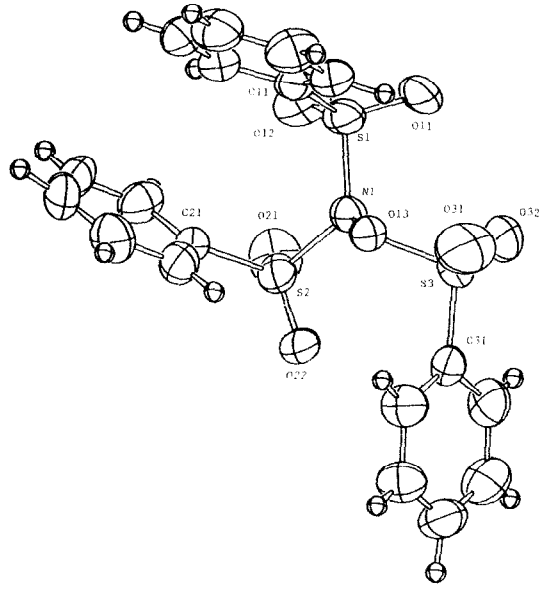
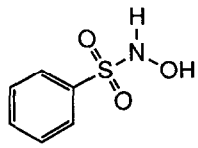
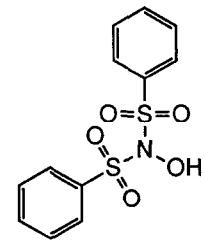


Figure 4: ORTEP drawing of **4**.

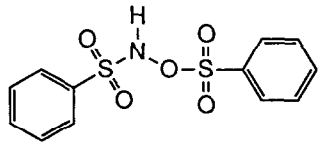
Table 1: Names and Registry Numbers of the Phenylsulfonylhydroxylamine Series[a]



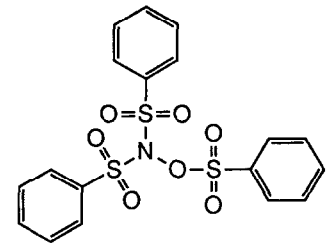
(1) [599-71-3]
N-(hydroxy)benzenesulfonamide
N-(phenylsulfonyl)hydroxylamine



(2) [5700-23-2]
N-(hydroxy)-N-(phenylsulfonyl)benzenesulfonamide
N,N-bis(phenylsulfonyl)hydroxylamine



(3) [24230-24-8]
N,O-bis(phenylsulfonyl)hydroxylamine[b]
N-[(phenylsulfonyl)oxy]benzenesulfonamide



(4) [73968-58-8]
N-(phenylsulfonyl)-O-[(phenylsulfonyl)oxy]benzenesulfonamide
N,N,O-tris(phenylsulfonyl)hydroxylamine

[a]CAS name listed first. [b]This CAS name is not consistent with the others.

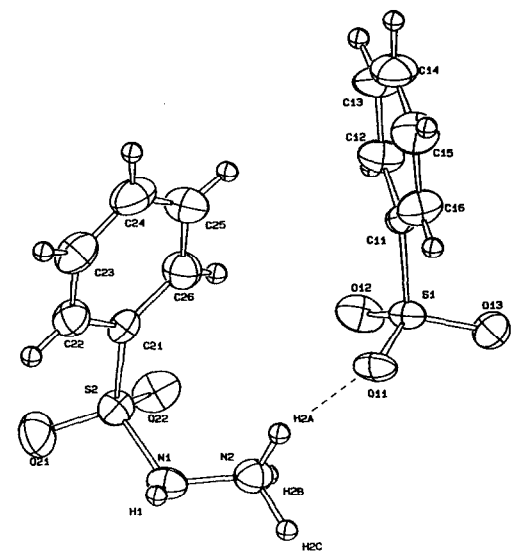


Figure 5: ORTEP drawing showing the asymmetric unit of **5** with the R-enantiomer of the hydrazinium group. The dashed line indicates the N2-H2A··O11 H-bond.

$C_{12}H_{14}N_2O_5S_2$ and showed free υ(NH) and broad, hydrogen bonded υ(OH) and/or υ(NH) in the IR spectrum. The ^{13}C NMR spectrum, which matched that of the authentic sample, contained eight resonances readily assigned, on the basis of their relative intensities and of DEPT measurements, to two distinguishable phenyl rings. Although the origin of **5** is uncertain, we established that it does not arise from hydrazine present as an impurity in our hydroxylamine. Reduction of **1** to $PhSO_2NH_2$ by $HONH_2$,[5] followed by the reaction of $PhSO_2NH_2$ with the transient species $PhSO_2ONH_2$ to give $PhSO_2NHNH_2$ is one explanation, while condensation of $PhSO_2NH_2$ with **1** to afford $PhSO_2NHNHSO_2Ph$ is another. Hydrolysis of the symmetrical disulfonylhydrazine could liberate $PhSO_2NHNH_2$ which reacts with $PhSO_3H$ derived from hydrolysis of $PhSO_2Cl$. Since **5** was only a minor product, its origin was not studied experimentally.

Although not recognized as such, *N,N-bis*-(arylsulphonyl)hydroxylamines were first prepared by the reaction of arenesulphinic acids with nitrous acid.[16] More recently, this reaction has been developed into an efficient synthesis of substituted analogs of $(ArSO_2)_2NOH$.[17] Though Piloty claimed to have prepared **2** by the addition of $ArSO_2Cl$ to an equivalent of $ArSO_2NHOH$ in the presence of base,[1] this reaction actually gives *N,O-bis*-(arylsulphonyl)hydroxylamines.[9,11,18] The two isomeric *bis*-(phenylsulphonyl)hydroxyl-amines, *N,N-bis*- (**2**) and *N,O-bis*-(**3**), of composition $C_{12}H_{11}NO_5S_2$, were previously differentiated by melting point and by the broad υ(OH) IR band in the 3200-3400 cm^{-1} region, possible only in **2**, and the υ(NH) IR band in the 3100-3200 cm^{-1} region, possible only in **3**. Our ^{13}C NMR spectrum of **2** revealed only four resonances, indicating that the two phenyl groups are equivalent, while the spectrum of **3** contained eight resonances, indicating that the two phenyl groups are not equivalent. Relative intensities and DEPT measurements supported this conclusion. X-ray structure determination confirmed the previous structure assignment of $(PhSO_2)_2NOH$ to **2** and $(PhSO_2)NHO(SO_2Ph)$ to **3**.

It is of interest to note that *N*-substitution to yield **1** occurs when hydroxylamine reacts with one equivalent of $PhSO_2Cl$, but that subsequent reaction with a second equivalent proceeds with *O*-substitution rather than further *N*-substitution, leading to **3** rather than to **2**. In the supernucleophile[19] $HONH_2$, the nitrogen atom is the more nucleophilic center towards sulphonyl chlorides,[14] but the nucleophilicity of nitrogen is sufficiently reduced by substitution of a single $PhSO_2$ group to render the hydroxyl oxygen the more nucleophilic center in **1** as evidenced by the formation of **3**. The preparation of **2** from benzenesuphinic acid follows an entirely different course,[20] but again, the nature of the bis-isomer formed is determined by the electron-withdrawing capacity of the $PhSO_2$ group. The initial rate-limiting reaction of $PhSO_2H$ or $PhSO_2^-$ (both are reactive) with $H_2NO_2^+$ (or NO^+) yields the nitrosulphinate intermediate $PhSO_2NO$ (see below), which then reacts rapidly with a second mole of $PhSO_2^-$ to give $(PhSO_2)_2NO^-$, protonation of which provides **2**. Since $PhSO_2NO$ acts in the second step as an electrophile, the $PhSO_2$ substituent ensures that its reaction with the nucleophile $PhSO_2^-$ yields $(PhSO_2)_2NO^-$ rather than $[(PhSO_2)NO(SO_2Ph)]^-$, thus leading to **2** rather than to **3**

Oxidation of **2** with PbO_2 provides **4**, of composition $C_{18}H_{15}NO_7S_3$, but distinctly different from the known $(PhSO_2)_3NO$.[21] Previous structural assignment was made by analogy with the *N,N,O*-tris(4-X-phenylsulphonyl)-hydroxylamines (X = F or MeO) whose NMR spectra show two distinct resonances for the X substituents, ^{19}F or ^1H, respectively. Our ^{13}C NMR spectrum of **4** contained eight peaks, four of which were approximately twice the intensity of the other four, indicating the presence of two equivalent phenyl rings and a third, nonequivalent, phenyl ring. DEPT measurements supported this conclusion. Again, X-ray structure determination (see below) confirmed the structure as $(PhSO_2)_2NOSO_2Ph$.

The mechanism originally proposed[17] to account for the formation of **4** (and nitrate) by oxidation of **2** is shown in Scheme 1. When this mechanism was first set forth, compounds of the type $ArSO_2NO$ were unknown

Scheme 1: Oxidation of **2** by PbO_2

$$(PhSO_2)_2NOH \;(\mathbf{2}) \longrightarrow (PhSO_2)_2NO^{\cdot} \longrightarrow PhSO_2^{\cdot} + PhSO_2NO$$

$$PhSO_2NO \longrightarrow PhSO_2^{\cdot} + NO$$

$$(PhSO_2)_2NO^{\cdot} + PhSO_2^{\cdot} \longrightarrow (PhSO_2)_2NOSO_2Ph\;(\mathbf{4})$$

and our attempts[22] to produce $PhSO_2NO$ by oxidation of **1** were largely unsuccessful. Such compounds have subsequently been isolated from the reaction of sulphinic acids, $ArSO_2H$, with N_2O_4.[23] In the toluene analog TsNO, reaction with weak acids such as methanol afforded Ts_2NOH. Thermal decomposition gave NO and the known Ts_2NOTs[17] while borohydride reduction gave TsNHOH. The fact that PbO_2 oxidation of **1** yielded[22] **4** may therefore indicate the intermediate formation of $PhSO_2NO$ followed by its rapid decomposition. $PhSO_2NO$ has also been invoked,[20] from kinetic studies, as an intermediate in the formation of **2** by the reaction of $PhSO_2H$ with nitrous acid. Further support for the free-radical character of the oxidation of $(ArSO_2)_2NOH$ to $(ArSO_2)_2NOSO_2Ar$ was found in the observation[8] that apparently analytically pure samples of $(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$ (X = H, CH_3, F, Cl) prepared by oxidation of $(p\text{-}XC_6H_4SO_2)_2NOH$ gave e.s.r. spectra in solution, readily assigned to $(p\text{-}XC_6H_4SO_2)_2NO$, whereas similar samples prepared by reaction of $(p\text{-}XC_6H_4SO_2)_2NOH$ with $p\text{-}XC_6H_4SO_2Cl$ did not.

Crystal Structures

The consistent atom numbering scheme employed here was derived by considering **1** as the basic unit for the series. Atom labels of the moieties substituted at N1 and O13 begin with the number '2' and '3', respectively. The bond distances (1.345(5) - 1.394(5)Å) and inner bond angles (118.0(3) - 121.8(2)°) for the phenyl rings agree well with those reported in the literature. Despite the fact that the observed hydrogen bonds (H-bonds) would be considered weak by Novak's standards,[24] they play a major role in the molecular packing of **1**, **2**, and **3** (cf. Table 2).

The molecular packing of **1** contains a complex H-bonding network which involves both enantiomers, where N1 is the chiral center. Structure refinement for each enantiomer converged to the same R value. Molecules of **1** stack up the B-axis in columns composed of one enantiomer. Each molecule in this stack is H-bonded (N1-H2··O12) to the molecules above and below it on the B-axis (cf. Figure 6 and 7). Across the C-axis, rows of the B-axis stacks are composed of the same enantiomer, however, the orientation of the stacks alternates between head to tail and tail to head. In each B-axis stack, each atom of one molecule is separated by the length of the B-axis of the unit cell from that same atom in the molecule to which it is H-bonded. Along the C-axis, the B-axis stacks are offset by half of the length of the B-axis of the unit cell. H-bonds exist between the B-axis stacks which give rise to 16 membered H-bonded rings (cf. Figure 7).

Table 2: Hydrogen Bond Data

C[a]	A[b]	D[c]	Operation[d]			Translation a b c	Length (Å)
(1)	O_{11}	O_{13}	1/2 - X,	1/2 + Y,	1/2 + Z	0 1 0	2.907(6)
	O_{12}	N_1	+ X,	+ Y,	+ Z	0 1 0	3.068(7)
(2)	O_{11}	O_{13}	- X,	- Y,	- Z	1 0 1	2.729(3)
(3)	O_{12}	N_1	1/2 + X,	1/2 - Y,	+ Z	0 1 0	2.988(4)
(4)			>>> Contains no hydrogen bonds <<<<				
(5)	O_{11}	N_2	>>> D & A in same asymmetric unit <<<				2.795(5)
	O_{11}	N_2	- X,	- Y,	- Z	1 1 1	2.717(5)
	O_{12}	N_2	+ X,	+ Y,	+ Z	-1 0 0	2.814(5)
	O_{13}	N_2	- X,	- Y,	- Z	0 1 1	2.783(5)

[a]C = Compound. [b]A = Proton acceptor. [c]D = Proton Donor. [d]The position of the donor atom can be generated from its coordinates by performing the operation listed and then translating the number of cell translations on the given axis.

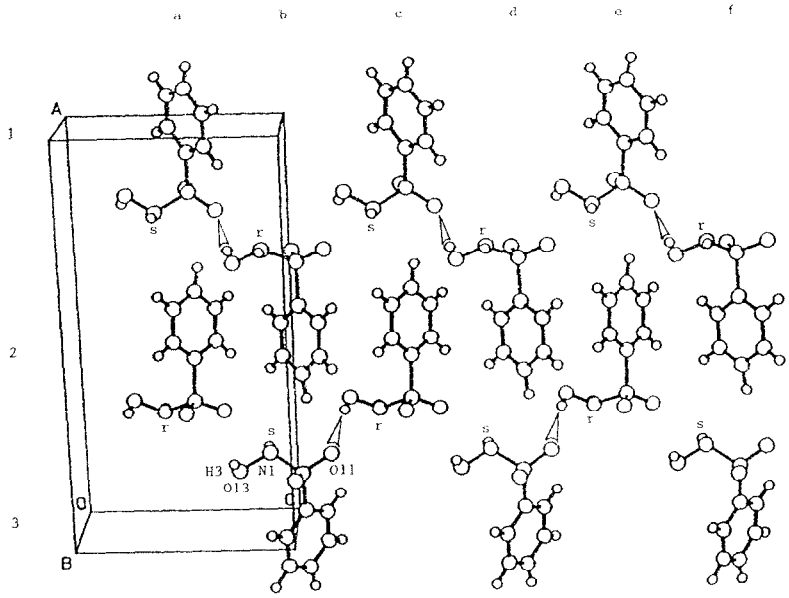


Figure 6: Ball and stick drawing showing the crystal packing of the molecules of **1** which contain atoms within the axis limits of $0 \le A \le 1$, $0 \le B \le 1$, and $0 \le C \le 3$. The r and s next to each N1 atom indicates that atom's chirality. The wedges indicate the perspective of the O13-H3···O11 H-bond. The molecules in columns b, d, and f reside about the plane of the page, while those in columns a, c, and e reside beneath the page.

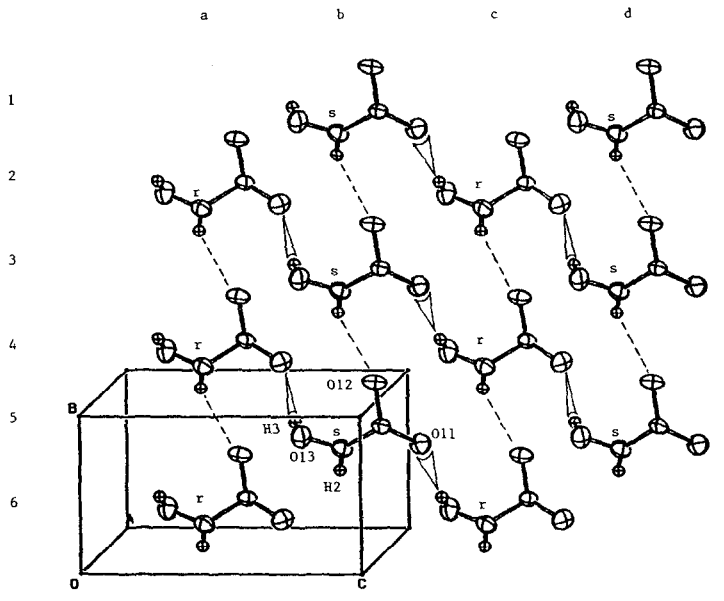


Figure 7: ORTEP drawing showing the crystal packing of the molecules of **1** which contain atoms within the axis limits of $0 \leq A \leq 1/2$, $0 \leq B \leq 3$, and $0 \leq C \leq 2$ omitting the phenyl rings in order to view the H-bond network. The r and s next to each N1 atom indicates that atom's chirality. The wedges indicate the perspective of the O13-H3··O11 H-bond. The dashed lines indicate the perspective of the N1-H2··O12 H-bond. The molecules in columns b and d reside about the plane of the page, while those in columns a and c reside beneath the page. The phenyl rings for molecules in columns b and d would be projected above the page, while those in columns a and c below the page. Note that the atoms in position b5 correspond to the molecule in position b3 of Figure 6. Similarly, a6 = a2, c6 = c2, and d5 = d3.

The H-bonding in **1** is more complex than that observed for **2** or **3** because **1** has two hydrogens available for H-bonding while **2** and **3** have only one. Since **4** has no hydrogens on N or O, it is not surprising that no close intermolecular contacts were observed. H-bond (O13-H3··O11) formation in **2** results in a centrosymmetric dimer containing a 10-member ring (cf. Figure 8). Similar to **1**, **3** is also chiral and both enantiomers are present in the molecular packing. H-Bond (N1-H2··O12) formation in **3** results in chains of alternating enantiomers (cf. Figure 9).

The S-N bond length of **1** is about 0.5Å longer than that of $PhSO_2NH_2$ which lacks the hydroxyl group on nitrogen.[25,26] The longer S-N bond in **1** is due to a decrease in nitrogen lone pair donation to the 3d orbital of sulfur ($d\pi$-$p\pi$ bonding) caused by the electronegative character of the hydroxyl group. Similarly, the enhanced acidity of **1** over that of $PhSO_2NH_2$ was attributed to the electronegative character of the hydroxyl group.[27]

The N1-S1 and N1-S2 bond length increases with increasing substitution about N1 (cf. Table 3), as was observed for the methyl analogs of **1** and **4**.[28,29] Since the nitrogen lone pair of **2** must be shared by two $d\pi$-$p\pi$ bonds, there is less double bond character in the N-S bonds of **2** than of **1**. The N-S bond of **3** is longer than that of **1** but shorter than that of **2**, showing that substitution of SO_2Ph at nitrogen affects the N-S bond more than a similar substitution at oxygen. The OSO_2Ph in **3** has a greater -I inductive effect, which is bond lengthening, than the OH substituent in **1**. Similarly, the N-S bonds of **4** are longer than those of **2**.

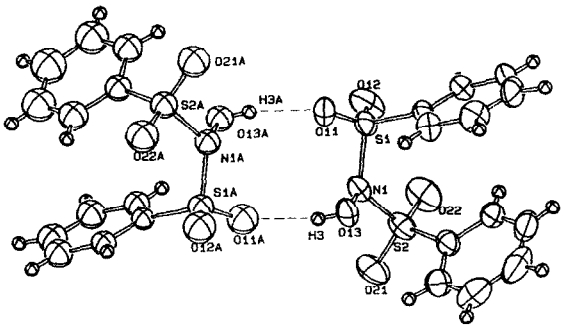


Figure 8: ORTEP drawing of the centrosymmetric H-bonded dimer of **2**. The dashed lines indicate the O13-H3··O11 H-bond.

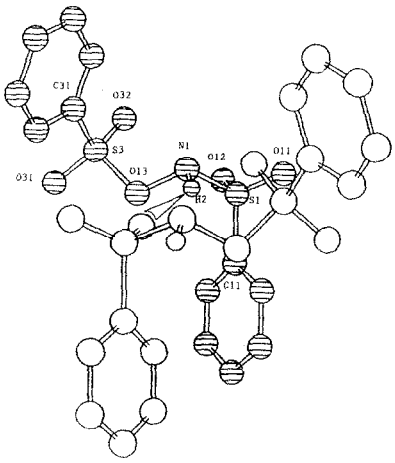


Figure 9: Ball and stick drawing showing the crystal packing of **3**. The outlined molecule is an S-enantiomer and resides about the plane of the page. The shaded molecule is an R-enantiomer and resides beneath the plane of the page. The wedge indicates the perspective of the N1-H2··O12 H-bond.

Table 3: Bond Lengths and Angles of the N-O Moiety

C[a]	X[b]	N1-O13 (Å)	SX-N1 (Å)	S3-O13 (Å)	∠ SX-N1-O13 (°)	∠ S3-O13-N1 (°)
(1)	1	1.415(6)	1.646(5)		109.6(4)	
(2)	1	1.410(3)	1.712(2)		111.0(1)	
	2		1.715(2)		108.1(1)	
(3)	1	1.433(4)	1.689(4)	1.620(3)	108.6(2)	112.2(2)
(4)	1	1.419(3)	1.735(2)	1.661(2)	107.8(1)	115.7(1)
	2		1.747(2)		110.7(1)	
(5)	2	1.427(5)[c]	1.659(4)		115.2(3)[d]	

[a]C = Compound. [b]Atom label for S. [c]N1-N2. [d]∠ S2-N1-N2.

Since no geometrical changes are required by dπ-pπ bonding,[30] the observed pseudo-tetrahedral geometries about N1, O13, and the S atoms are reasonable. The lack of variation in the S=O bond lengths of sulphonamides has been well documented[31] (cf. Table 4). In compounds **1** - **4**, the S=O bond length of the N1-S=O moiety not perturbed by a H-bond ranges from 1.414(2)Å to 1.425(2)Å, in agreement with the values previously reported.[31] However the length of a H-bonded S=O is greater due to decreasing donation of the oxygen lone pairs to the 3d orbital of sulfur when these lone pairs are required for the H-bonding.

Table 4: Bond Lengths and Angles of the A-SO_2-C Moiety

C[a]	A[b]	X[c]	Y[d]	SX=OXY (Å)	∠ OX1-SX-OX2 (°)	∠ A-SX-OXY (°)	SX-CX1 (Å)	∠ CX1-S1-OXY (°)
(1)	N	1	1	1.435(4)[e]	119.4(3)	106.9(3)	1.755(4)	108.2(2)
	N	1	2	1.425(3)		103.9(2)		108.9(2)
(2)	N	1	1	1.438(2)[e]	120.4(1)	102.8(1)	1.745(2)	108.2(1)
	N	1	2	1.414(2)		105.7(1)		110.1(1)
	N	2	1	1.425(2)	120.7(1)	103.6(1)	1.749(3)	109.8(1)
	N	2	2	1.417(2)		105.0(1)		110.8(1)
(3)	N	1	1	1.418(4)	121.7(2)	103.2(2)	1.748(4)	109.9(2)
	N	1	2	1.425(3)[e]		105.6(2)		108.5(2)
	O	3	1	1.415(4)	120.9(2)	101.2(2)	1.746(5)	109.3(2)
	O	3	2	1.417(3)		109.3(2)		109.1(2)
(4)	N	1	1	1.420(2)	121.7(1)	103.5(1)	1.757(3)	108.0(1)
	N	1	2	1.418(2)		104.3(1)		110.8(1)
	N	2	1	1.414(2)	121.4(1)	102.6(1)	1.743(2)	110.4(1)
	N	2	2	1.420(2)		103.6(1)		110.6(1)
	O	3	1	1.414(3)	122.4(2)	109.2(1)	1.740(3)	109.4(2)
	O	3	2	1.400(3)		98.5(1)		110.1(1)
(5)	O	1	1	1.466(3)[f]	112.2(2)	110.5(2)	1.770(4)	105.3(2)
	O	1	2	1.441(3)[f]		114.4(2)		106.9(2)
	O	1	3	1.444(3)[f]				107.0(2)
	N	2	1	1.414(3)	121.6(2)	103.9(2)	1.753(4)	108.5(2)
	N	2	2	1.427(3)[e]		104.3(2)		108.9(2)

[a]C = Compound. [b]A = N1 or O13 designated N or O, respectively. [c]Atom label where $1 \leq X \leq 3$. [d]Atom label where $1 \leq Y \leq 3$. [e]Oxygen atom involved in hydrogen bond. [f]Sulfonate S=O has resonance contributions from S-O^-.

While increasing substitution at the hydroxylamine core lengthens the N1-S bonds, no systematic effect is observed on the N1-O13 bonds. Substitution has no significant effect on the N1-O13 bond length in **1**, **2**, and **4**, but this bond in **3** is about 0.015Å longer than in the others. It is interesting to note that the O13 lone pairs of **3** are involved in dπ-pπ bonding to a greater extent than in **4** as evidenced by the shorter O13-S3 bond in **3**. The extent to which hydrogen bonding, dπ-pπ bonding, and inductive effects influence the N1-O13 bond lengths remains unclear.

The crystal packing of **5** involves a cylindrically shaped H-bonded network which is insulated by the phenyl groups. The circumference of this cylinder is an eight membered H-bonded, (N2-H2A···O11) and (N2-H2C···O11), ring which consists of a dimer of the two asymmetric units containing both enantiomers of the hydrazinium group (cf. Figure 10). The length of the cylinder, up the A-axis, is defined by a stack in which each dimer is H-bonded, N2-H2A···O12 and N2-H2B···O13, to its nearest neighbors (cf. Figure 11).

The bond length and inner bond angle data for the phenyl rings, as well as the average S-O bond length of the sulfonate group agree nicely with those reported in the literature[32]. Since O11 is involved in two H-bonds, while

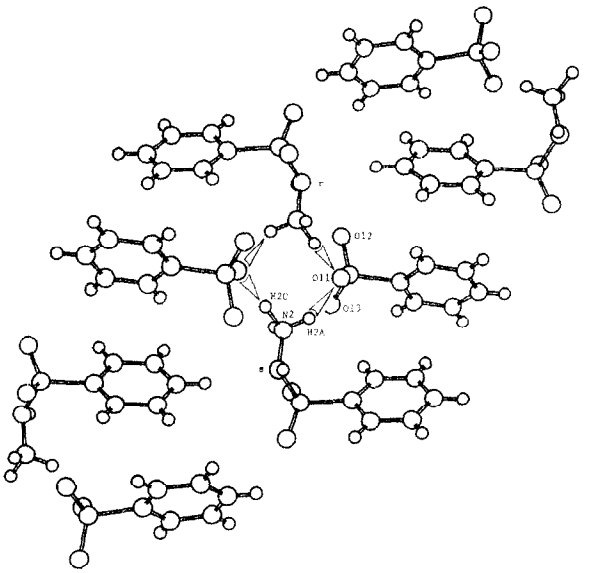


Figure 10: Ball and stick drawing showing the crystal packing of **5**. The sulfonate groups on the left half of the drawing reside about the plane of the page. All hydrazinium groups reside about the same plane beneath the page. The sulfonate groups on the right half of the drawing reside beneath the plane of the hydrazinium groups. The wedges indicate the perspective of the N2-H2A··O11 and N2-H2C··O11 H-bonds.

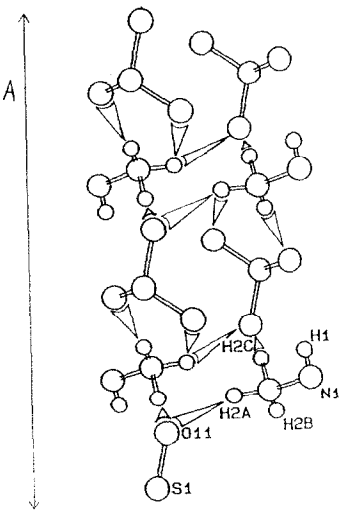


Figure 11: Ball and stick drawing showing the crystal packing of the molecules of **5** which contain atoms within the axis limits of $0 \leq A \leq 3$, $1/4 \leq B \leq 3/4$, and $0 \leq C \leq 1$ omitting the phenyl and phenylsulfonyl groups of the sulfonyl and hydrazinium moieties, respectively. The wedges indicate the perspective of the H-bonds. The omitted phenyl and phenylsulfonyl groups of the atoms on the left half of the drawing would be projected above the page, while those on the right half would be projected beneath the page.

O12 and O13 are involved in one, the S1-O11 bond is longer than either the S1-O12 or S1-O13 bonds due to less donation of the O11 lone pairs to the 3d orbital of S1. The S=O bond lengths of the hydrazinium group are similar to those of the (phenylsulphonyl)hydroxylamines (cf. Table 4).

In summary, all of the stable benzenesulfonylhydroxylamines can be prepared either by reaction of benzenesulfonyl chloride with the appropriate hydroxylamine or by oxidation of other benzenesulfonylhydroxylamines. These compounds, as well as the benzenesulfonylhydrazine salt **5** formed as a byproduct in the preparation of Piloty's acid, have been characterized by X-ray crystallography, elemental analysis, and ^{13}C NMR. Hydrogen bonding plays a crucial role in the crystal structure of these compounds.

Experimental

General: ^{13}C NMR spectra were recorded at 75.469 MHz and ambient temperature using a Bruker AM-300 spectrometer while IR spectra were taken on a Perkin Elmer model 1330 spectrometer. Melting points were run on a Mel-Temp apparatus, which was calibrated with known compounds. Physical constants and spectral data are given in Table 5. Crystals of **1** suitable for X-ray structure determination were grown from acetonitrile while crystals of **2**, **3**, and **4** were grown by diffusion of hexane into saturated ethyl acetate, and **5** by diffusion of ether into saturated methanol. Intensity data were collected on a Rigaku AFC5S diffractometer with graphite-monochromated Mo Kα radiation, $\lambda = 0.71069$Å, in the $4° \leq 2\Theta \leq 50°$ range (cf. Table 6). The structures were

Table 5: Physical Constants and Spectral Data

Cmp'd	Melting Range (°C)	Elemental Analysis	C	H	N	^{13}C NMR Solvent	C1	C2[a]	C3[a]	C4	IR (cm^{-1})
(1)	109-10	Obs.	41.9	3.9	8.1	DMSO-d_6	137.5 (s)	128.0 (d)	128.8 (d)	133.0 (d)	3450 (OH)
		Calc.	41.6	4.1	8.1						3215 (NH)
(2)	124-5[b]	Obs.	45.9	3.4	4.2	DMSO-d_6	134.9 (s)	128.7 (d)	129.0 (d)	134.6 (d)	3280 (br, OH)
		Calc.	46.0	3.5	4.5						
(3)	155-6	Obs.	45.8	3.4	3.9	DMSO-d_6	135.8 (s)	128.2 (d)	129.5 (d)	134.4 (d)	3190 (NH)
		Calc.	46.0	3.5	4.5		133.0 (s)	129.1 (d)	129.4 (d)	135.2 (d)	
(4)	93-4	Obs.	47.8	3.3	3.0	DMSO-d_6	134.2 (s)	129.2 (d)	129.6 (d)	135.9 (d)[c]	
		Calc.	47.7	3.3	3.1		133.2 (s)	128.9 (d)	129.8 (d)	136.1 (d)	
(5)	167-9[b]	Obs.[d]	43.6	4.1	8.4	DMSO-d_6	144.6 (s)	126.9 (d)	129.2 (d)	131.6 (d)	3245 (NH)
		Calc.	43.6	4.3	8.5		139.4 (s)	128.9 (d)	129.9 (d)	134.2 (d)	2600 (br, OH)
						D_2O[e]	142.6	125.8	129.4	132.1	
							135.3	128.3	130.2	135.2	
Benzenesulfonyl hydrazinium[f]						D_2O	135.1	128.4	130.3	135.5	
Benzenesulfonic acid						D_2O	142.6	125.8	129.4	132.1	
Benzenesulfonyl hydrazide						D_2O	135.5	128.2	130.0	134.6	

[a]Assignments based on calculated chemical shifts. [b]Melting point determined in a sealed tube. [c]The four resonances in this row were roughly twice as intense as those in the next row. [d]C, H, & N values are the average of four determinations. A single O determination gave obs. 22.9, calc. 24.2. [e]All shifts in D_2O were referenced to MeCN methyl carbon at 1.30 ppm. 5 µl MeCN / 0.5 ml D_2O. [f]Obtained by mixing equimolar H_2SO_4 and benzenesulfonyl hydrazide.

Table 6: Crystallographic Data

Compound	(1)	(2)	(3)	(4)	(5)
Formula	$C_6H_7NO_3S$	$C_{12}H_{11}NO_5S_2$	$C_{12}H_{11}NO_5S_2$	$C_{18}H_{15}NO_7S_3$	$C_{12}H_{14}N_2O_5S_2$
M_r	173.19	313.34	313.34	453.50	330.37
Crystal Dimensions (mm)	0.5 x 0.5 x 0.5	0.5 x 0.5 x 0.5	0.5 x 0.5 x 0.5	0.5 x 0.5 x 0.5	0.15 x 0.15 x 0.3
Cell Dimensions:					
a (Å)	16.980 (3)	10.775 (2)	9.745 (2)	12.998 (4)	5.283 (1)
b (Å)	4.976 (1)	11.157 (1)	9.251 (1)	10.641 (1)	17.178 (5)
c (Å)	8.736 (2)	11.254 (2)	15.188 (1)	14.204 (1)	15.724 (3)
β (°)		92.72 (1)	95.00 (1)	90.56 (2)	90.80 (2)
V (Å^3)	738.1 (5)	1351.3 (3)	1364.0 (3)	1964.4 (7)	1427 (1)
Crystal System	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	$Pna2_1$ (#33)	$P2_1/n$ (#14)	$P2_1/a$ (#14)	$P2_1/n$ (#14)	$P2_1/c$ (#14)
Molecules per unit cell	4	4	4	4	4
F(000)	360	648	648	936	688
D_{calc} (g cm^{-3})	1.56	1.54	1.53	1.53	1.54
Linear abs. coeff.(cm^{-1})	3.74	3.94	3.90	4.01	3.79
Scan Width (°)	1.5	0.8	0.8	0.8	0.8
Range of unique h	0 → 11	0 → 14	0 → 13	0 → 17	0 → 7
k	0 → 22	0 → 14	0 → 12	0 → 14	0 → 22
l	0 → 6	-15 → 15	-20 → 20	-18 → 18	-20 → 20
Measured Refl.	1080	3511	3748	5074	3832
Obs'd. Refl. ($I > 3.00\sigma(I)$)	743	2287	1655	3169	1810
Unique Refl. ($I > 3.00\sigma(I)$)	740	2161	1434	3013	1808
Variables	127	225	181	322	246
R (%)	3.8	4.1	4.3	3.9	4.2
R_w (%)	4.6	5.2	5.3	5.4	5.0

solved with either SHELX or the direct methods program MITHRIL in the TEXSAN (v 2.0) Structure Analysis Package (Molecular Structure Corporation). Data were corrected for Lorentz and polarization effects but no absorption corrections were applied.[47,48]

Preparation of 1 and 5: Hydroxylamine hydrochloride (13.9 g, 0.2 mol) was dissolved in a mixture of 30 ml water and 20 ml methanol. This solution was cooled to 0 °C, and then a solution of potassium carbonate (27.7 g, 0.2 mol) in 30 ml water was added dropwise, with vigorous magnetic stirring, during 1 h. Ice cold methanol (200 cc) was added in a single portion followed by dropwise addition of $PhSO_2Cl$ (35.3 g, 0.2 mol) over 1 h. The next day, the mixture was filtered, and the methanol was distilled off the filtrate under reduced pressure. A 100 ml portion of ice-cold water was added to the oily residue and the mixture was stored at 0 °C for 48 h. The resulting solid was filtered off and dried. The crude material (19.7 g) was recrystallized from the minimum volume of acetonitrile to yield **5**, (2.2 g, 6.7 mmol, 6.7%). The filtrate was evaporated to dryness at room temperature, and the resulting solid recrystallized from water to yield **1** (7.0 g, 40 mmol, 20%).

Preparation of authentic 5: A 2.04 g (11.6 mmol) portion of 90% $PhSO_3H$ was added gradually to a solution of 2.00 g (11.6 mmol) $PhSO_2NHNH_2$ in 30 ml EtOH. After a quarter of the $PhSO_3H$ had been added, a white precipitate was observed. The mixture was heated to reflux and EtOH was added to maintain a homogeneous solution. The remaining $PhSO_3H$ was added portionwise, whereupon the mixture was refluxed for 15 min. Upon cooling to room temperature, the precipitated thin white needles (1.70 g, 5.1 mmol) were isolated by gravity filtration. Upon standing, the filtrate yielded more crystals, which were vacuum filtered (1.85 g, 5.6 mmol). The yield was 92.6% based on $PhSO_2NHNH_2$.

N,N-bis(phenylsulfonyl)hydroxylamine (**2**) was prepared by reaction of $PhSO_2Na$ with aqueous nitrous acid[17] while **3** was prepared by the reaction of **1** with one equivalent of benzenesulphonyl chloride and four equivalents of triethylamine in diethyl ether solution.[9] *N,N,O-tris*(phenylsulfonyl)hydroxylamine (**4**) was prepared by oxidation of **2** with PbO_2 in dichloromethane solution.[17]

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