A 1:1 molecular complex of bis(4-aminophenyl) disulfide and 4-aminothiophenol

Venu R. Vangala,[a] **Gautam R. Desiraju,**[a]* **Ram K. R. Jetti,**[b] **Dieter Bläser**[b] **and Roland Boese**[b]

[a]School of Chemistry, University of Hyderabad, Hyderabad 500 046, India, and
[b]Institut für Anorganische Chemie der Universität-GH Essen, Universitätsstraße 3-5, D-45117 Essen, Germany
Correspondence e-mail: desiraju@uohyd.ernet.in

The centrosymmetric crystal structure of the title complex, $C_{12}H_{12}N_2S_2 \cdot C_6H_7NS$, is built up of dimers of the constituent molecules and stabilized by a herring-bone geometry between the phenyl rings. The structure reveals an N—H···N—H···N—H···S co-operative hydrogen-bonded chain, and C—H···S and N—H···π hydrogen bonds. The S—H group forms an uncommon S—H···π interaction.

Comment

Crystals of the title complex, (I), were obtained during an investigation of 4-aminothiophenol. Aerial oxidation of this compound leads to the disulfide, which cocrystallizes with the original thiophenol to give the present 1:1 molecular complex.
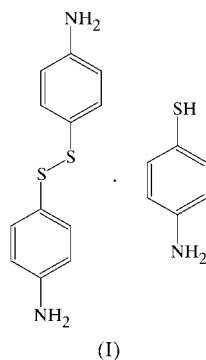
Complex (I) illustrates a situation wherein a crystal structure is stabilized by the interplay of strong and also weak intermolecular interactions. The molecular geometry and numbering of (I) are given in Fig. 1. The S—S distance of 2.0645 (7) Å is normal and is comparable with the length of 2.074 (1) Å reported for bis(4-aminophenyl) disulfide (Vittal & Anjali, 1998). The C—S—S—C torsion angle in (I) is 94.8 (1)° [80.2 (1)° in bis(4-aminophenyl) disulfide]. Fig. 2 shows a packing diagram of (I) viewed down the [010] axis.

The geometry of the intermolecular interactions is given in Table 1.

The structure of (I) is stabilized by a finite co-operative chain of N3—H3A···N2—H2B···N1—H1A···S2 hydrogen bonds in the *ac* plane. The weak C2—H2···S2 interaction is antico-operative with respect to the above set of interactions. Other antico-operative interactions, namely N3—H3B···π and C3—H3···π, are also seen. A weak C15—H15···π interaction exists between screw-related molecules.

Although the S—H group is considered to be one of the classical hydrogen-bonding groups, it does not form S—H···X interactions very often (Desiraju & Steiner, 1999; Allen *et al.*,
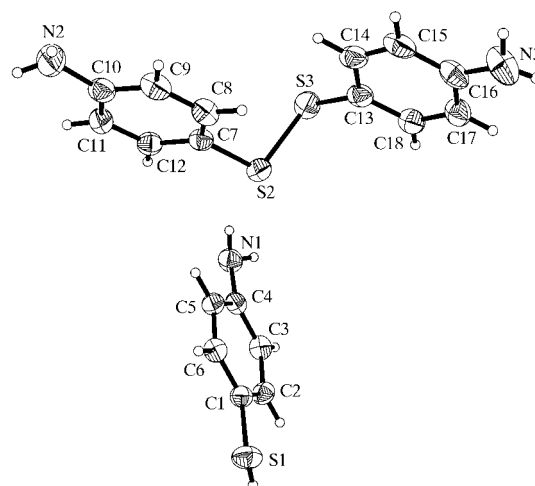

Figure 1
A view of the molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
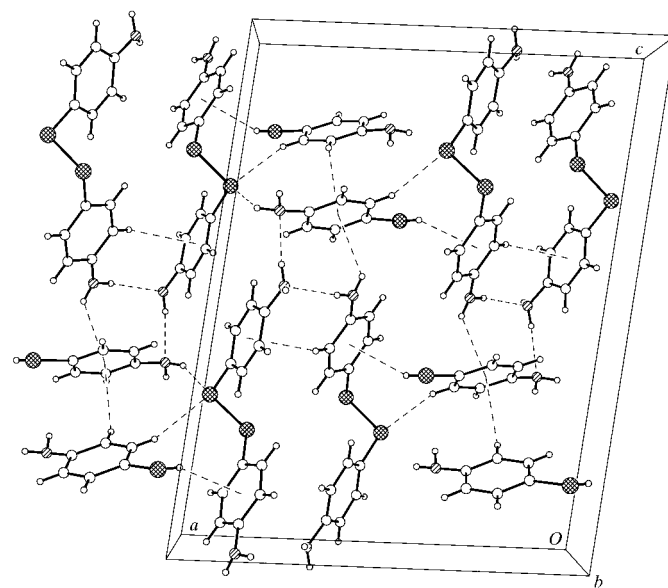

Figure 2
The packing of (I), viewed down [010]. N and S atoms are shaded differently for clarity, and hydrogen bonds are shown as dotted lines. Note the N—H···N—H···N—H···S chain and the S—H···π interactions.

1997; Steiner, 2000). In (I), there is a well characterized S—H···π interaction, which is uncommon. In the Cambridge Structural Database (CSD, Version 5.23; Allen & Kennard, 1993), there are only eight crystal structures [refcodes HIPMUO (Zhu-Ohlbach et al., 1998), SIZBAE (Bernardinelli et al., 1991), TASPOS (Slusarchyk et al., 1995), TAXMUA (Nishio et al., 1996), VOPBEH (Garbarczyk & Krolikowska, 1992), YOMWAY01 (Gibbs et al., 1995), and YULZOU and YULZUA (Sellmann et al., 1995)], containing 12 thiol groups, wherein such S—H···π interactions are seen. Not many crystal structures of aminothiols have been reported to date. The present structure is in contrast with that of 6-amino-pyridine-1-thiol (Sabino et al., 2002), where N—H···N hydrogen bonds are preferentially formed.

Experimental

Aerial oxidation of 4-aminothiophenol leads to the disulfide, which cocrystallizes with the original thiophenol, leading to yellow crystals of the 1:1 molecular complex, (I).

Crystal data

$C_{12}H_{12}N_2S_2 \cdot C_6H_7NS$	$D_x = 1.389$ Mg m^{-3}
$M_r = 373.54$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 5202
$a = 15.210$ (3) Å	reflections
$b = 6.0099$ (11) Å	$\theta = 2.7$–$28.3°$
$c = 19.683$ (4) Å	$\mu = 0.42$ mm^{-1}
$\beta = 96.814$ (3)°	$T = 203$ (2) K
$V = 1786.6$ (6) Å^3	Rod, yellow
$Z = 4$	$0.28 \times 0.08 \times 0.05$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	4410 independent reflections
	3497 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.081$
Absorption correction: empirical (SADABS; Blessing, 1995)	$\theta_{max} = 28.3°$
	$h = -20 \rightarrow 20$
$T_{min} = 0.89$, $T_{max} = 0.99$	$k = 0 \rightarrow 8$
8776 measured reflections	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.070P)^2 + 0.063P]$
$R[F^2 > 2\sigma(F^2)] = 0.050$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.128$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.79$ e Å^{-3}
4410 reflections	$\Delta\rho_{min} = -0.25$ e Å^{-3}
217 parameters	
H-atom parameters constrained	

H atoms on C atoms were refined using a riding model starting from idealized geometries, with $U_{iso}(H) = 1.5U_{eq}(C)$. The positions of H atoms on N and S atoms were taken from a difference Fourier map and these H atoms were also refined as riding, with $U_{iso}(H) = 1.2U_{eq}(N)$ or $1.5U_{eq}(S)$. We note that the geometry around the N1-amino group is pyramidal and this is in accord with previous observations in crystal structures of aromatic amines where the N atom is a hydrogen-bond acceptor (Allen et al., 1997). The maximum/minimum residual electron densities are located close to the S atoms, obviously also influencing the position of the attached H1 atom.

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 2000); program(s) used to solve structure: SHELXTL (Bruker, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Table 1
Hydrogen-bonding geometry (Å, °).

$Cg1$, $Cg2$ and $Cg3$ are the centroids of rings C–C6, C7–C12 and C13–C18, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2B···N1^i	0.87	2.34	3.199 (2)	168
N1—H1A···S2	0.88	2.99	3.7452 (16)	144
N3—H3A···N2^{ii}	0.91	2.52	3.410 (3)	168
C2—H2···S2^{iii}	0.94	2.84	3.7387 (18)	162
S1—H1···$Cg3^{iii}$	0.90	2.89	3.7310 (12)	155
N3—H3B···$Cg1^{iv}$	0.86	2.65	3.312 (2)	135
C3—H3···$Cg1^{iii}$	0.94	2.88	3.544 (2)	129
C15—H15···$Cg2^{ii}$	0.94	2.83	3.614 (2)	142

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

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