Investigation and Rationalisation of Hydrogen Bonding Patterns in Sulfonylamino Compounds and Related Materials: Crystal Structure Determination of Microcrystalline Solids from Powder X-Ray Diffraction Data

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The crystal structures of three sulfonylamino compounds have been solved *ab initio* using powder diffraction data collected using a conventional laboratory X-ray diffractometer, and refined using Rietveld profile-refinement techniques. 4-Toluenesulfonamide (**1**) is monoclinic, $P2_1/n$, with a = 7.7030(3), b = 16.4656(7), c = 6.5861(3) Å, β = 92.411(2)°; benzenesulfonylhydrazine (**2**) is monoclinic, $P2_1/c$, with a = 8.0924(2), b = 8.6082(2), c = 11.7122(4) Å, β = 108.591(2)°; and 4-toluenesulfonylhydrazine (**3**) is monoclinic, $P2_1/n$, with a = 18.6021(6), b = 5.6406(2), c = 8.5356(3) Å, β = 106.222(2)°. The structures of **1** and **2** were solved from powder X-ray diffraction data by direct methods, using the SHELXS and SIR88 programs respectively; the structure of **3** was solved from powder X-ray diffraction data by the combined maximum entropy and likelihood method. The hydrogen bonding patterns in these crystals, and in the crystal structures of some related sulfonylamino compounds, are analysed and classified according to recently developed methods based on graph set analysis. For **1**, the hydrogen bonding is described by the graph set **C**(4)**C**(4); for **2**, the graph set for the first-order network is N_1 = **C**(5)**S**(5)**C**(4), and there are second-order networks $\mathbf{R}^4_4(14)$ and $\mathbf{R}^4_4(18)$; for **3**, the first-order network is N_1 = **C**(5)**S**(5)**C**(4).

In organic molecular crystals, hydrogen bonds often constitute the strongest intermolecular forces, and hence often dictate the preferred packing arrangement of the molecules. The general principles underlying hydrogen bond formation are reasonably well understood, and the structures of hydrogen bonded crystals can often be rationalised and codified in terms of preferred combinations of hydrogen bond donors and acceptors.[1-3] At present, however, there are few, if any, reliable methods for predicting the detailed hydrogen bonding and molecular packing arrangements in specific cases, and these patterns must usually be derived from experimental data. Although in certain special cases high-resolution solid-state NMR spectroscopy can be used[4] to probe the structural features of hydrogen bonding patterns in the solid state, the elucidation of these patterns generally requires full crystal structure determination from X-ray or neutron diffraction data.

For many molecular systems containing potential hydrogen bond donors and acceptors, crystals of suitable size and quality for single crystal X-ray diffraction studies are not available; for such systems, direct structure determination using high resolution powder X-ray diffraction data from a conventional laboratory X-ray diffractometer provides a highly attractive alternative experimental approach. Here we report the crystal structure determinations of three sulfonylamino compounds using data measured in this way, combined with a variety of structure solution techniques. From these results, and from previously reported crystal structures, we discuss and classify the hydrogen bonding patterns in sulfonamides, sulfonylhydrazines and sulfonylhydroxylamines. Preliminary accounts of two of these structure determinations have been published.[5,6]

The hydrogen bonding patterns in the materials investigated in this paper are discussed using the graph set approach, which was introduced as a classificatory tool by Etter.[1,2] This approach considers hydrogen bonding patterns on a purely topological basis, viewing them as intertwined nets, with the molecules as the nodes and the hydrogen bonds as the internodal connections. Graph sets can be applied to motifs[2] and to networks[2] using pattern designators[1,2] of the general type $\mathbf{G}^a_d(r)$. The descriptor **G** may be **C** (chain), **D** (dimer or other finite set), **R** (ring), or **S** (self) (*i.e.* an intramolecular hydrogen bond). The degree r represents the total number of atoms in a ring or in the repeating unit of a chain, the superscript a indicates the number of hydrogen bond acceptors, and the subscript d indicates the number of hydrogen bond donors. Thus, for example, the hydrogen bond pattern in the familiar carboxylic acid dimer is represented as $\mathbf{R}^2_2(8)$.

Experimental

Powder X-ray diffraction data for 4-toluenesulfonamide (p-$CH_3C_6H_4SO_2NH_2$, **1**), benzenesulfonylhydrazine ($PhSO_2NHNH_2$, **2**), and 4-toluenesulfonylhydrazine (p-$CH_3C_6H_4$-SO_2NHNH_2, **3**) were collected in the following way. Polycrystalline samples were ground and then mounted in a disc between two layers of transparent tape. Powder diffraction data were collected in transmission mode on a Stoe STADI/P high-resolution powder X-ray diffractometer, using Ge-monochromatised Cu-Kα_1 radiation and a linear position-sensitive detector covering 6° in 2θ. Data collection times were approximately 15 h. Further details of data collection, structure solution and structure refinement are given in Table 1.

Details of the methods used for crystal structure determination of **1** and **3** have been described previously,[5,6] and involved conventional direct methods, and maximum entropy and likelihood methods, respectively.

For **2**, the powder diffractogram was indexed using the program TREOR,[7] and the space group was determined unambiguously as $P2_1/c$. Integrated intensities were extracted from the diffractogram using a modified Rietveld method,[8,9] and a partial structure solution was obtained using direct methods (SIR88 program[10]). Our experience to date suggests that structures of this type may be determined using a correctly located sulfur atom as the initial structural model for Rietveld refinement. Hence the highest peak (sulfur atom) in the output

Table 1 Details of powder X-ray diffraction data collection, and crystal structure solution and refinement for **1**, **2** and **3**

	1	**2**	**3**
Data range (Cu-Kα_1 radiation) in $2\theta/°$	10–70	10–90	7.5–80
Number of reflections used in structure solution	109	149	175
Number of reflections used in structure refinement	371	633	530
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/Å	7.7030(3)	8.0924(2)	18.6021(6)
b/Å	16.4656(7)	8.6082(2)	5.6406(2)
c/Å	6.5861(3)	11.7122(4)	8.5356(3)
β/°	92.411(2)	108.591(2)	106.222(2)
V/Å^3	834.60(8)	773.31(5)	859.98(6)
R_{wp} (%)	7.0	12.2	7.8
Program used for structure solution	SHELXS	SIR88	MICE

Table 2 Final refined atomic parameters for the crystal structure of **2** ($PhSO_2NHNH_2$). In structure refinement, the values of U_{iso} were constrained according to atom type

Atom	x/a	y/b	z/c	U_{iso}/Å^2
S	0.8999(6)	0.4141(6)	0.7171(4)	0.033(2)
N(1)	1.079(2)	0.345(1)	0.691(1)	0.038(2)
N(2)	1.005(2)	0.310(1)	0.559(1)	0.038(2)
O(1)	0.820(1)	0.554(1)	0.6400(9)	0.038(2)
O(2)	0.967(1)	0.423(1)	0.8447(9)	0.038(2)
C(1)	0.703(2)	0.302(2)	0.682(1)	0.006(2)
C(2)	0.687(1)	0.176(2)	0.755(1)	0.006(2)
C(3)	0.540(2)	0.091(2)	0.727(1)	0.006(2)
C(4)	0.411(1)	0.098(2)	0.616(1)	0.006(2)
C(5)	0.446(2)	0.202(2)	0.533(1)	0.006(2)
C(6)	0.584(2)	0.304(1)	0.562(1)	0.006(2)

Table 3 Selected bond distances (Å) and angles (°) for the crystal structure of **2** ($PhSO_2NHNH_2$). Constrained values are indicated by an asterisk

S–O(1)	1.52(1)	O(1)–S–O(2)	122(1)
S–O(2)	1.42(1)	O(1)–S–N(1)	114(1)
S–N(1)	1.68(1)	O(1)–S–C(1)	96(1)
S–C(1)	1.79(2)	O(2)–S–N(1)	99(1)
N(1)–N(2)	1.49(2)	O(2)–S–C(1)	121(1)
		N–S–C(1)	100(1)
C(1)–C(2)	1.42(2)*	C(6)–C(1)–C(2)	116(1)*
C(2)–C(3)	1.35(2)*	C(1)–C(2)–C(3)	121(2)*
C(3)–C(4)	1.38(2)*	C(2)–C(3)–C(4)	123(2)*
C(4)–C(5)	1.42(2)*	C(3)–C(4)–C(5)	115(2)*
C(5)–C(6)	1.38(2)*	C(4)–C(5)–C(6)	124(2)*
C(6)–C(1)	1.42(2)*	C(5)–C(6)–C(7)	119(1)*
		S–C(1)–C(7)	119(1)
		S–C(1)–C(2)	120(1)

Table 4 Final refined atomic parameters for the crystal structure of **1** (p-$CH_3C_6H_4SO_2NH_2$). In structure refinement, the values of U_{iso} were constrained according to atom type

Atom	x/a	y/b	z/c	U_{iso}/Å^2
S	0.3622(6)	0.2792(3)	0.7186(8)	0.051(2)
N	0.185(2)	0.2247(8)	0.756(2)	0.083(4)
O(1)	0.433(2)	0.3038(5)	0.931(2)	0.083(4)
O(2)	0.452(2)	0.2239(6)	0.584(2)	0.083(4)
C(1)	0.317(2)	0.378(1)	0.625(2)	0.012(2)
C(2)	0.319(2)	0.457(1)	0.703(3)	0.012(2)
C(3)	0.280(2)	0.531(1)	0.589(3)	0.012(2)
C(4)	0.217(2)	0.512(1)	0.402(3)	0.012(2)
C(5)	0.207(2)	0.441(1)	0.292(3)	0.012(2)
C(6)	0.251(2)	0.3676(8)	0.390(2)	0.012(2)
C(7)	0.167(2)	0.5925(8)	0.253(2)	0.012(2)

Table 5 Final refined atomic parameters for the crystal structure of **3** (p-$CH_3C_6H_4SO_2NHNH_2$). In structure refinement, the values of U_{iso} were constrained according to atom type

Atom	x/a	y/b	z/c	U_{iso}/Å^2
S	0.6835(3)	0.1583(9)	0.4085(7)	0.056(2)
N(1)	0.752(1)	0.345(2)	0.516(1)	0.021(3)
N(2)	0.729(1)	0.478(2)	0.640(1)	0.021(3)
O(1)	0.671(1)	−0.008(2)	0.536(1)	0.077(3)
O(2)	0.690(1)	0.071(2)	0.261(1)	0.077(3)
C(1)	0.596(1)	0.332(2)	0.329(2)	0.034(2)
C(2)	0.595(1)	0.531(2)	0.223(2)	0.034(2)
C(3)	0.528(1)	0.648(2)	0.166(2)	0.034(2)
C(4)	0.457(1)	0.613(2)	0.201(2)	0.034(2)
C(5)	0.466(1)	0.392(3)	0.289(2)	0.034(2)
C(6)	0.528(1)	0.244(2)	0.352(2)	0.034(2)
C(7)	0.391(1)	0.735(2)	0.122(2)	0.034(2)

from the direct methods calculation was used in this manner as the initial structural model. This partial structure was developed by Rietveld refinement and difference Fourier techniques until all the non-hydrogen atoms had been located. During the final refinement cycles, soft constraints were imposed on the benzenoid ring such that C–C = 1.40 Å and ∠C–C–C = 120°. Final refined atomic coordinates for **2** are given in Table 2, and bond distances and angles are given in Table 3. The final refined atomic coordinates for **1** and **3** are given in Tables 4 and 5. The final powder X-ray diffraction profiles from the Rietveld refinements for **1**, **2** and **3** are given in Fig. 1.

Discussion

In the crystal structure of **1**, (p-$CH_3C_6H_4SO_2NH_2$; Fig. 2), there are two independent hydrogen bonding motifs which together employ both potential hydrogen bond donors in the NH_2 group and both potential hydrogen bond acceptors on the SO_2 fragment. Hydrogen bonds formed between O(1) of molecule A [at (x, y, z); see Fig. 2] and an NH donor of molecule B [at $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$] form chains parallel to the a axis with an O $\cdots$ N distance equal to 2.87 Å; the graph set is **C**(4).[2] Similar **C**(4) chains, with an O $\cdots$ N distance of 2.99 Å, are formed parallel to the c axis between O(2) of molecule A and an NH donor of the molecule at $(\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$ (not shown in Fig. 2). Hence the graph set describing the hydrogen bonding in this crystal structure is **C**(4)**C**(4). The O $\cdots$ N distances for the hydrogen bonds in this structure lie comfortably within the range observed for such distances in previous structure determinations [the extremes of this range are established by 2.854(6) Å in $(PhSO_2)_2NH$[11] and 3.24 Å in the γ modification of p-$NH_2C_6H_4SO_2NH_2$[12]]. It is interesting to note that the crystal structure can be regarded to be constructed from two-dimensional hydrogen bonded sheets (*i.e.* two-dimensional networks involving hydrogen bonding between SO_2NH_2 groups) located approximately at $y = \frac{1}{4}$ and $y = \frac{3}{4}$.

The **C**(4) motif, with N–H $\cdots$ O–S hydrogen bonds linking the molecules into infinite chains, is also found in the crystal structures of other sulfonamides; these include

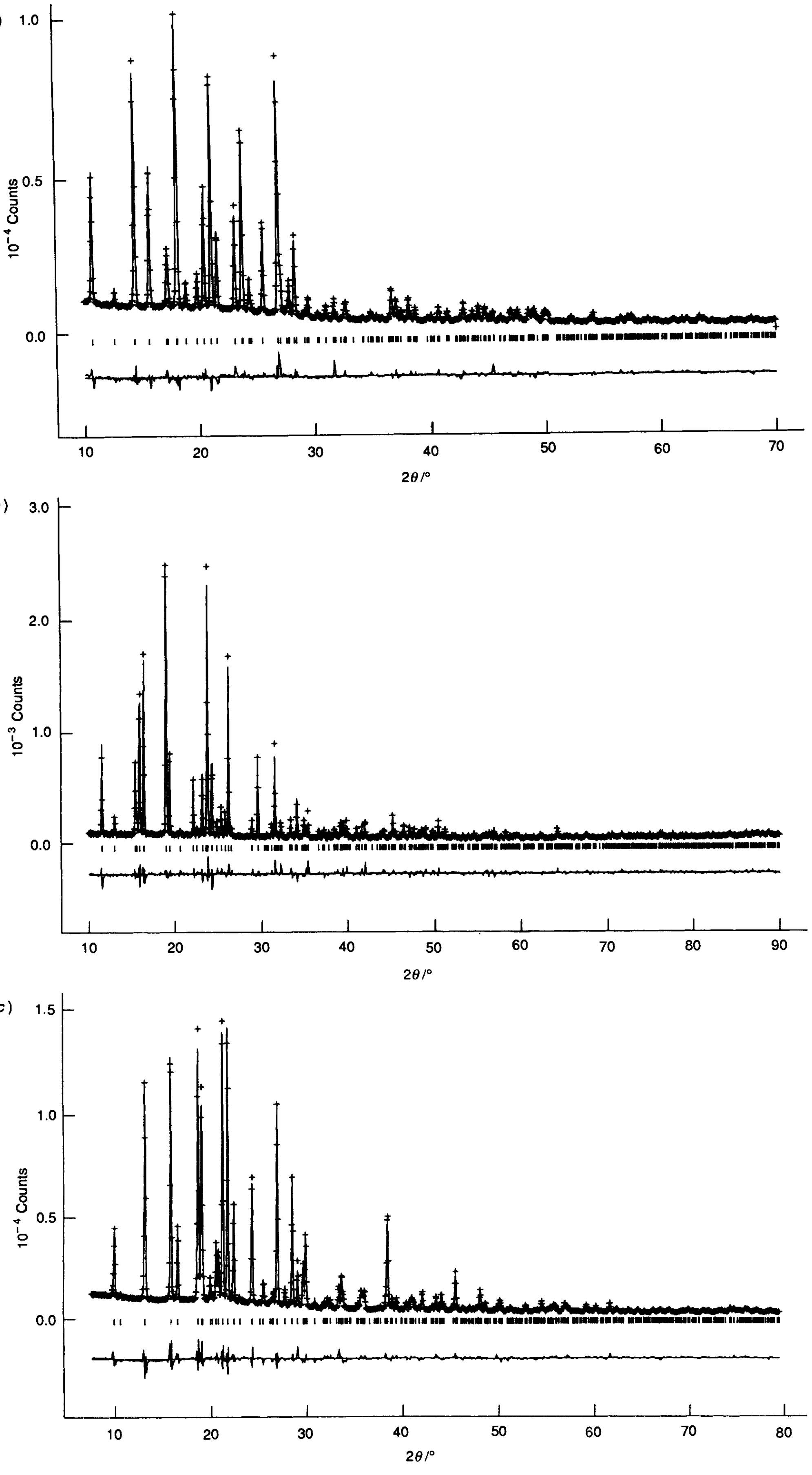

Fig. 1 Final observed (+ marks), calculated (solid line) and difference (below) powder X-ray diffraction profiles for: (*a*) 4-toluenesulfonamide (p-$CH_3C_6H_4SO_2NH_2$, **1**); (*b*) benzenesulfonylhydrazine ($PhSO_2NHNH_2$, **2**); (*c*) 4-toluenesulfonylhydrazine (p-$CH_3C_6H_4SO_2NHNH_2$, **3**)

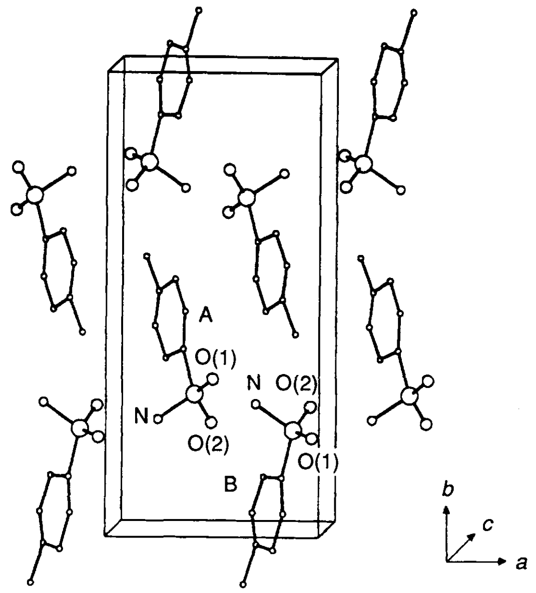

Fig. 2 Crystal structure of 4-toluenesulfonamide (p-$CH_3C_6H_4SO_2$-NH_2; **1**). Hydrogen atoms are not shown.

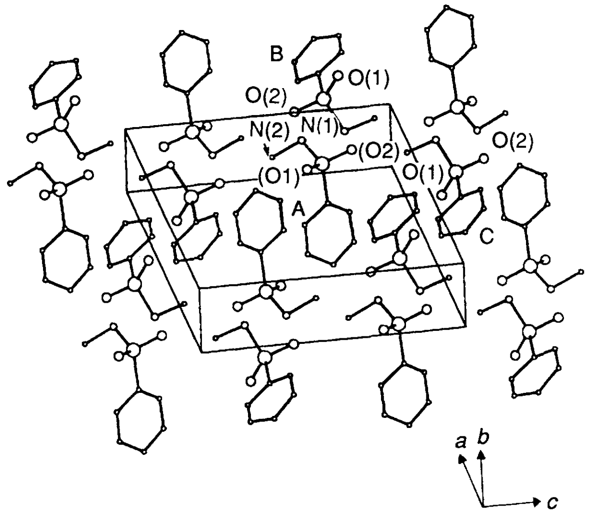

Fig. 3 Crystal structure of benzenesulfonylhydrazine ($PhSO_2NHNH_2$; **2**). Hydrogen atoms are not shown.

$CH_3SO_2NH_2$,[13] $CH_3SO_2NHOCH_3$,[14] $CH_3SO_2NHC_6H_4$-OH[15] and $(PhSO_2)_2NH$.[11] In the crystal structure of p-$CH_3C_6H_4SO_2NHCH_3$ there are four types of N–H ··· O–S hydrogen bond linking the four molecules of the asymmetric unit.[16] On the other hand CH_3SO_2NHPh[17] and $(C_2H_5$-$SO_2)_2NH$[18] both form centrosymmetric cyclic dimers: in each structure, there are rings constructed from two equivalent N–H ··· O–S hydrogen bonds, representing a motif with graph set $\mathbf{R}^2_2(8)$. The steric demands of the substituents have a crucial influence on the formation of the hydrogen bonding network [compare $CH_3SO_2NHOCH_3$ with CH_3SO_2NHPh, and compare $(PhSO_2)_2NH$ with $(C_2H_5SO_2)_2NH$]. This fact is confirmed by the observation that there is no hydrogen bonding in p-$CH_3C_6H_4SO_2NHCH_2Ph$.[19]

Several aryl sulfonamides form hydrogen bonded co-crystals with phosphine oxides. Thus $PhSO_2NH_2$ forms[20] a 1:1 co-crystal with triphenylphosphine oxide, Ph_3PO. This co-crystal contains centrosymmetric aggregates containing two $PhSO_2NH_2$ molecules and two Ph_3PO molecules; in these aggregates, each NH_2 group acts as a hydrogen bond donor to both of the Ph_3PO molecules. The graph set for this motif is $\mathbf{R}^2_4(8)$. On the other hand,[21] p-$CH_3C_6H_4SO_2NH_2$ forms a 3:2 co-crystal with Ph_3PO in which the NH_2 groups of three different p-$CH_3C_6H_4SO_2NH_2$ molecules each act as hydrogen bond donors to a given pair of Ph_3PO molecules, forming a motif with graph set $2\mathbf{R}^2_4(8)$. Identical hydrogen bonding motifs are found in the corresponding co-crystals formed by triphenylarsine oxide.

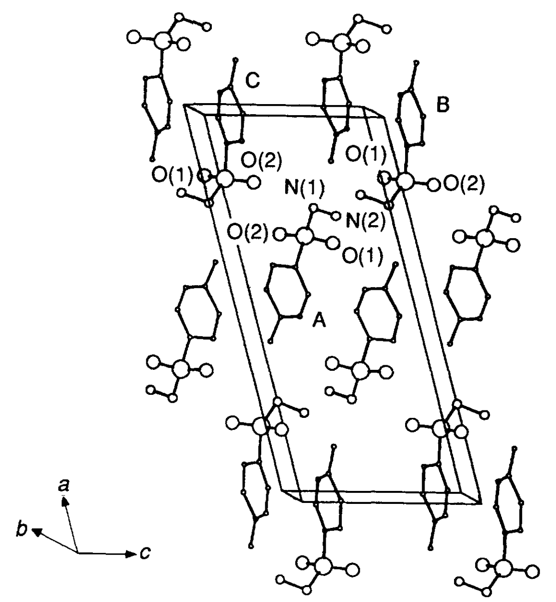

Fig. 4 Crystal structure of 4-toluenesulfonylhydrazine (p-$CH_3C_6H_4$-SO_2NHNH_2; **3**). Hydrogen atoms are not shown.

The crystal structure of **2** ($PhSO_2NHNH_2$; Fig. 3) comprises chains of molecules stacked head-to-tail along the b axis, with adjacent chains oriented in an anti-parallel manner. Within the molecule there are three potential hydrogen bond donors and three potential hydrogen bond acceptors (the two oxygen atoms of the sulfonyl group and the nitrogen atom of the NH_2 group). In the crystal structure, all three hydrogen bond donors in the $NHNH_2$ group and the two hydrogen bond acceptors in the SO_2 group are engaged in hydrogen bonding. There is an intramolecular hydrogen bond between O(1) and the *cis* hydrogen atom of the NH_2 group, with O ··· N distance 2.910(15) Å; the graph set for this motif is S(5). Within a head-to-tail chain there are intermolecular hydrogen bonds between the NH group of molecule A [at (x, y, z)] and O(1) of molecule B [at $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$]. In this chain, the O ··· N distance is 3.135(14) Å and the graph set is **C**(4). In addition, there are hydrogen bonds between adjacent chains of this type; specifically, there is a hydrogen bond between O(2) of molecule A and the *trans* NH_2 hydrogen of molecule C [at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$]. The O ··· N distance in this motif is 3.148(14) Å and the graph set is **C**(5). The crystal structure of **2** can be regarded as being constructed from two-dimensional hydrogen bonded sheets (*i.e.* two-dimensional networks involving hydrogen bonding between SO_2NHNH_2 groups) located approximately at $x = 0$.

In terms of the proposed hydrogen bond priority rules,[2] the relative priorities of the hydrogen bonds in the crystal structure of $PhSO_2NHNH_2$ are: SNH ··· OS > NNH(*cis*) ··· OS > NNH(*trans*) ··· OS. Thus the overall graph set for the first-order network is N_1 = C(5)S(5)C(4). Two second-order networks can be assigned in this structure. One is generated by two **C**(4) motifs and two **C**(5) motifs, forming a centrosymmetric aggregate encompassing all four molecules in the unit cell (Fig. 3), with $N_2 = \mathbf{R}^4_4(18)$. There is another second order network, also encompassing four different molecules and also centrosymmetric, with $N_2 = \mathbf{R}^4_4(14)$.

The hydrogen bonding motifs in **3** (p-$CH_3C_6H_4SO_2NHNH_2$;

Fig. 4) are very similar to those in **2** ($PhSO_2NHNH_2$) despite considerable differences between their crystal structures. There is an intramolecular hydrogen bond with motif **S**(5) and an O(1) ··· N(2) distance of 2.99(1) Å. The same oxygen O(1) of molecule A [at (x, y, z)] is engaged in a hydrogen bond with the *trans* hydrogen atom of the NH_2 group in molecule B [at ($\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$); related to molecule A by the 2_1 axis at ($\frac{3}{4}, y, \frac{3}{4}$)]. This motif has graph set **C**(5) and N ··· O distance 2.87(1) Å. Finally the SNH hydrogen in molecule A is engaged in intermolecular hydrogen bonding to O(2) in molecule C [at ($\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$); related to molecule A by the 2_1 axis at ($\frac{3}{4}, y, \frac{1}{4}$)]. This motif has graph set **C**(4) and N ··· O distance 3.13(1) Å. In terms of the hydrogen bond priority rules, the first order network is N_1 = **C**(5)**S**(5)**C**(4). As with **1** and **2**, the crystal structure of **3** can be regarded as being constructed from two-dimensional hydrogen bonded sheets (*i.e.* two-dimensional networks involving hydrogen bonding between SO_2NHNH_2 groups) located approximately at $x = \frac{1}{4}$ and $x = \frac{3}{4}$.

In $PhSO_2NHNH_2$, the hydrogen bonding patterns defined by the **C**(4) and **C**(5) motifs run parallel to the b and c axes respectively, whereas in p-$CH_3C_6H_4SO_2NHNH_2$ there are two spirals generated by the **C**(4) and **C**(5) motifs, both running parallel to the b axis and having opposite helicity at a common molecule. The similarity of the graph sets for these two very different structures highlights the value of the graph set approach as a convenient means of extracting the key structural attributes of hydrogen bonding patterns in diverse and complex structures.

The influence of the size and shape of the aryl substituent is further demonstrated by the structure of 2-naphthylsulfonylhydrazine.[22] Here the molecules form centrosymmetric dimers with hydrogen bonds between the SNH hydrogen and one of the oxygen atoms of the symmetry-related molecule. Neither the NH_2 group nor the other sulfonyl oxygen atom take part in hydrogen bonding. The overall hydrogen bonding motif has graph set $\mathbf{R}_2^2(8)$.

It is interesting to compare the hydrogen bonding patterns in $ArSO_2NHNH_2$, as described above, with those in the analogous sulfonylhydroxylamines RSO_2NHOH, in which there are two potential hydrogen bond donors (NH and OH) and four potential hydrogen bond acceptors (the two oxygen atoms of the sulfonyl group and the nitrogen and oxygen atoms of the hydroxylamine function). In the crystal structure of CH_3SO_2NHOH,[14] the molecules form centrosymmetric dimers with hydrogen bonds between the OH hydrogen and one oxygen of the sulfonyl group giving a cyclic motif with graph set $\mathbf{R}_2^2(10)$. The NH donor and most of the potential hydrogen bond acceptors do not form hydrogen bonds. By contrast, in $PhSO_2NHOH$,[23] both the NH and OH donors participate in hydrogen bonding. The OH donors form hydrogen bonds to sulfonyl oxygen atoms in neighbouring molecules related by a glide plane to give chains with a **C**(5) motif; between adjacent chains of this type, hydrogen bonds are formed between the NH donors and those sulfonyl oxygen atoms that are not involved in O–H ··· O hydrogen bonding. This gives a further series of chains with **C**(4) motif. The first-order network is N_1 = **C**(4)**C**(5). Together these two sets of chains generate a second-order network characterised by $N_2 = \mathbf{R}_4^4(16)$, analogous to the hydrogen bonded rings (discussed above) in $PhSO_2NHNH_2$.

The application to CH_3SO_2NHOH and $PhSO_2NHOH$ of Etter's postulate[1] that the strongest hydrogen bond donor pairs up with the strongest hydrogen bond acceptor, followed by the next strongest pairing, and so on until all the functionalities are matched, identifies the OH group as the strongest donor in RSO_2NHOH, and the two sulfonyl oxygens as the strongest acceptors (clearly stronger than the hydroxyl oxygen).

The disubstituted hydroxylamine $(PhSO_2)_2NOH$ forms centrosymmetric dimers *via* O–H ··· O hydrogen bonds, giving the same graph set [$\mathbf{R}_2^2(10)$] as CH_3SO_2NHOH; in effect, the passive NH hydrogen in CH_3SO_2NHOH has been replaced in $(PhSO_2)_2NOH$ by a further RSO_2 group. In contrast the isomeric molecule $PhSO_2NHOSO_2Ph$ forms chains with the **C**(4) motif characteristic of sulfonamides.[23]

We have shown that the crystal structures of small molecular systems such as those described here can be solved straightforwardly from powder X-ray diffraction data collected using a conventional laboratory X-ray diffractometer. Moreover, the quality of the refined structure is sufficient to draw meaningful conclusions about hydrogen bonding schemes, despite the fact that hydrogen atoms are, in general, not located. We have recently attempted (as yet unsuccessfully) to extend the present series to further, larger systems [*viz.* 2,4,6-$(CH_3)_3$-$C_6H_2SO_2NHNH_2$, **4**; 2-$CH_3C_6H_4SO_2NH_2$, **5**; and 2,4,6-$(Me_2CH)_3C_6H_2SO_2NH_2$, **6**]. The powder X-ray diffractogram of **4** could not be indexed from the data available. The diffractogram of **5** was indexed as tetragonal with a = 18.69, c = 9.072 Å, and density considerations suggested 16 molecules per unit cell, with probable space group $I4_1/a$. The Laue symmetry $4/m$ gives rise to a severe (greater than 75%) degree of overlap in the diffractogram owing to the fact that the inequivalent reflections (hkl) and (khl) occur at exactly the same values of 2θ. The molecules of **6** are larger than those in the other systems considered here, and its powder diffractogram has been indexed on the basis of the monoclinic cell a = 17.01, b = 8.259, c = 11.90 Å, β = 104.7°. Here, again, there is extensive peak overlap, as a consequence of the large unit cell and low symmetry. Although we have so far failed to solve the crystal structures of the latter two systems, we believe that success may be achieved either by improved instrumental resolution (for example by use of synchrotron X-ray radiation), in the case of **6**, or by improved maximum entropy structure solution software, in both cases.

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