The preparation and structure of novel sulfimide systems; X-ray crystal structures of 1,4-$(\mathrm{PhS\{NH\}})_2\mathrm{C_6H_4}$ (and dihydrate), 1,2-$(\mathrm{PhS\{NH\}})(\mathrm{PhS})\mathrm{C_6H_4{\cdot}H_2O}$ and of $[\mathrm{Ph_2SNH}]$ and its hydrate

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***Received (in London, UK) 8th April 2001, Accepted 4th January 2002
First published as an Advance Article on the web***

Treatment of 1,4-$(\mathrm{PhS})_2\mathrm{C_6H_4}$ and 1,2-$(\mathrm{PhS})_2\mathrm{C_6H_4}$ with the appropriate amount of *O*-mesitylsulfonylhydroxylamine (MSH) yields the corresponding protonated sulfimides, both of which may be deprotonated with DBU to give the hydrated free sulfimides 1,4-$(\mathrm{PhS\{NH\}})_2\mathrm{C_6H_4{\cdot}2H_2O}$ **1a** and 1-$(\mathrm{PhS\{NH\}})$-2-$(\mathrm{PhS})\mathrm{C_6H_4{\cdot}H_2O}$ **2a**. The X-ray crystal structures of both **1a** and **2a**, together with that of the well-known sulfimide $\mathrm{Ph_2SNH{\cdot}H_2O}$ **3a**, all reveal extended hydrogen-bonded arrays involving the N–H units and the waters of crystallisation. Crystals of **1b**, the dehydrated form of **1a**, also readily form, while removal of the water from **3a** *in vacuo* followed by slow evaporation of a solution in diethyl ether under anaerobic conditions leads to crystals of $\mathrm{Ph_2SNH}$ **3b**; the X-ray crystal structures of both **1b** and **3b** also reveal extended arrays formed from N–H···N interactions. In contrast, dehydration of **2a** breaks down the extended structure resulting in the formation of an oil.

We have recently reported on the reactivity of *S*,*S′*-diphenylsulfimide, $\mathrm{Ph_2SNH}$, towards a number of metal centres.[1] A significant feature of the products of such reactions has been the tendency of the coordinated sulfimide to exhibit strong hydrogen-bonding towards counter-ions; thus we see significant cation–anion interactions in $[\mathrm{Cu(Ph_2SNH_2)_6}]\mathrm{Cl_2}$[2] and in $[\mathrm{Co(Ph_2SNH_2)_6}]\mathrm{Cl_2}$[3] for example. This observation alerted us to the possibility of similar interactions occurring in metal-free environments, involving not only $\mathrm{Ph_2SNH}$ but also a range of new sulfimide systems.

Although the chemistry of sulfimide systems has been the focus of a great deal of work over the past few decades,[4] we can find no evidence for previous systematic investigations into their formation starting from polysulfide systems. In the light of the excellent ligand properties of $\mathrm{Ph_2SNH}$ it follows that species bearing more than one sulfimide unit or a mixture of sulfimide/sulfide units would constitute a potentially important new class of chelating ligand. We have now completed the first stage of investigations into this possibility by isolating the first examples of such systems; in doing so we have confirmed their potential for hydrogen-bonding *via* observation of the extended arrays they and their hydrates form. In addition, prompted by such observations we have returned to our original sulfimide $\mathrm{Ph_2SNH}$ and its hydrate and performed the first X-ray crystallographic studies on them, again revealing array structures.

Experimental

Both 1,4-$(\mathrm{PhS})_2\mathrm{C_6H_4}$ and 1,2-$(\mathrm{PhS})_2\mathrm{C_6H_4}$ were prepared by reaction of the appropriate dibromobenzene with a mixture of KOH and PhSH in boiling dimethylacetamide for seven days, followed by addition of water to precipitate an oil; pure crystalline materials were then isolated by addition of methanol to an $\mathrm{Et_2O}$ solution of the oil. *O*-Mesitylsulfonylhydroxylamine (MSH) was prepared by the literature route.[5] DBU, 1,8-Diazabicyclo[5.4.0]undec-7-ene, was used as received (Aldrich). Microanalyses were performed by the Loughborough Departmental service. IR spectra were run on a Perkin-Elmer PE2000 spectrometer; NMR on a Bruker AC250 spectrometer.

1,4-$(\mathrm{PhS\{NH\}})_2\mathrm{C_6H_4{\cdot}2H_2O}$ 1a

A solution of 1,4-$(\mathrm{PhS})_2\mathrm{C_6H_4}$ (0.61 g, 2.07 mmol) in $\mathrm{CH_2Cl_2}$ (10 ml) was added to a solution of MSH (20.89 g, 4.14 mmol) in an equal volume of the same solvent, with stirring. After stirring for 24 hours the solution was filtered and the resulting solid washed with $\mathrm{CH_2Cl_2}$ (3×20 ml) then dried *in vacuo*; the resulting white solid was then recrystallised from $\mathrm{MeOH/Et_2O}$ to give pure $[1,4\text{-}(\mathrm{PhS\{NH_2\}})_2\mathrm{C_6H_4}][2,4,6\text{-}\mathrm{Me_3C_6H_2SO_3}]_2$. Yield 1.296 g (86%). *m*/*z* (FAB) ($\mathrm{M} = [(\mathrm{PhS\{NH_2\}})_2\mathrm{C_6H_4}]$): 525 $[\mathrm{M} + \mathrm{Me_3C_6H_2SO_3SO_3})^+$, 325 $[\mathrm{M} - \mathrm{H}]^+$, 310 $[\mathrm{M} - \mathrm{NH_2}]^+$. ^{1}H NMR (dmso): δ 7.25–7.65 (14H, m, Ph), 6.28 (4H, s(br), mes CH), 2.03 (12H, s, Me), 1.71 (6H, s, Me). IR: 3161 [ν N–H], 846 cm^{-1} [ν N–S]. Found: C, 58.3; H, 5.4; N, 3.9: Calc. for $\mathrm{C_{36}H_{40}N_2S_4O_6{\cdot}H_2O}$: C, 58.2; H, 5.7; N, 3.8%. Mp: 212–214 °C.

A suspension of the above product (0.524 g, 0.67 mmol) in $\mathrm{CH_2Cl_2}$ (10 ml) was treated with a solution of DBU (1.471 g, 9.66 mmol) in an equal volume of the same solvent with vigorous stirring. During addition the solid at first dissolved and then by the time addition was complete a precipitate had appeared. After stirring for three hours the solvent was removed *in vacuo* and the product triturated with water to give **1a** as a white solid. Yield 0.100 g (40%). *m*/*z* (FAB) ($\mathrm{M} = [(\mathrm{PhS\{NH\}})_2\mathrm{C_6H_4}]$): 325 $[\mathrm{MH}]^+$, 310 $[\mathrm{M} - \mathrm{N}]^+$, 200 $[\mathrm{M} - \mathrm{PhSNH}]^+$.^{1}H NMR (dmso): δ 7.00–7.32 (14H, m, Ph). IR: 3111 [ν N–H], 928 cm^{-1} [ν N–S]. Microanalysis after complete dehydration to **1b** *in vacuo*: Found: C, 66.4; H, 4.9; N, 8.5: Calc. for $\mathrm{C_{18}H_{16}N_2S_2}$: C, 66.6; H, 5.0; N, 8.6%. MP: 194 °C (decomp.).

1-$(\mathrm{PhS\{NH\}})$-2-$(\mathrm{PhS})\mathrm{C_6H_4{\cdot}H_2O}$ 2a

A solution of 1,2-$(\mathrm{PhS})_2\mathrm{C_6H_4}$ (3.56 g, 0.012 mol) in $\mathrm{CH_2Cl_2}$ (10 ml) was treated with a solution of MSH (2.6 g, 0.012 mol)

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in an equal volume of the same solvent, added slowly with stirring. After stirring for a further 24 hours the solution was filtered through Celite, the volume of the filtrate reduced to 5 ml *in vacuo* and the crude product precipitated by addition of Et_2O (50 ml). Recrystallisation by addition of Et_2O to a methanol solution resulted in pure [1-(PhS{NH})-2-(PhS)C_6H_4][2,4,6-$Me_3C_6H_2SO_3$] as a white solid. Yield 3.23 g (87%). *m*/*z* (FAB) (M = [(PhS{NH_2})(PhS)C_6H_4]): 310 $[M]^+$, 294 $[M - NH_2]^+$. ^1H NMR ($CDCl_3$): δ 8.50–8.53 (1H, m, Ph), 6.94–7.70 (13H, m, Ph), 6.75 (2H, s(br), mes CH) , 3.1 (1H, br, NH), 2.55 (6H, s, Me), 2.20 (3H, s, Me). IR: 3084 [ν N–H], 847 cm^{-1} [ν N–S]. Found: C, 62.9; H, 5.2; N, 2.5: Calc. for $C_{27}H_{27}NS_3O_3$: C, 63.6; H, 5.3; N 2.8%. MP: 132–134 °C.

A solution of the above product (3.43 g, 6.74 mmol) in CH_2Cl_2 (10 ml) was treated with a solution of DBU (3.59 g, 23.59 mmol) in an equal volume of the same solvent. After stirring for one hour the solvent was removed *in vacuo* and the product triturated with water to give **2a** as a white solid. Microanalysis indicates the presence of one water of hydration which may be removed from the product *in vacuo* yielding an oil. Yield 1.40 g (67%). *m*/*z* (FAB) (M = [(PhS{NH})(PhS)C_6H_4]): 310 $[MH]^+$, 294 $[M-NH]^+$. ^1H NMR ($CDCl_3$): δ 7.94–7.97 (1H, m, Ph), 7.17–7.53 (13H, m, Ph), 1.61 (s, water). IR: 3129 [ν N–H], 919 cm^{-1} [ν N–S]. Found: C, 66.2; H, 5.0; N, 3.9: Calc. for $C_{18}H_{15}NS_2{\cdot}H_2O$: C, 66.0; H, 5.2; N, 4.3%. MP: 48–50 °C.

Crystallography

All measurements were made on a Bruker SMART 1000 CCD diffractometer at 150 K using ω-rotation and narrow frames. Data were corrected for absorption semi-empirically from equivalent reflections. These corrections were sometimes hampered by the extreme crystal shapes, especially for compounds **1a** and **2a**, which led to larger than usual R_{int} and final difference map features. All structures were solved by direct methods. In **1a** the molecule sits on an inversion centre. In **1b** the molecule sits on an inversion centre and the N*H* atom is disordered across two positions. The crystals of **2a** were particularly challenging crystallographically, exhibiting extreme crystal shape (very thin needles), weak diffraction, and having two molecules in the asymmetric unit. Hydrogen atoms could not be located reliably for one of the two unique water molecules in this case (in all other cases all N–H and O–H hydrogens were located from the difference map; their coordinates were refined and U_{iso} values tied to the carrier atom). In **3b** there are two molecules in the asymmetric unit. Programs used were Bruker SMART,[6a] SAINT,[6a] SHELXTL[6b] and local programs. Crystallographic parameters for all the compounds are listed in Table 1.

CCDC reference numbers 157265, 157266, 162725–162727. See http://www.rsc.org/suppdata/nj/b1/b103502a/ for crystallographic data in CIF or other electronic format.

Results and discussion

Preparation of sulfimides

Reaction of MSH (*O*-mesitylsulfonylhydroxylamine)[7] with 1,4-$(PhS)_2C_6H_4$ (molar ratio 2 : 1) in dichloromethane results in the formation of [1,4-(PhS{NH_2})$_2C_6H_4$][2,4,6-$Me_3C_6H_2SO_3$]$_2$ from which 1,4-(PhS{NH})$_2C_6H_4$ **1** forms after deprotonation with the base DBU (see Scheme 1). To the best of our knowledge **1** constitutes the first reported example of a free bis-sulfimide; it forms as a dihydrate **1a** after water is used to wash excess DBU from the crude product. Crystallisation of the product by slow diffusion of Et_2O vapour into a methanol solution results in the formation of two distinct crystal types: a long, thin needle form and a block morphology. As we will show in the structural section these correspond to the dihydrate **1a** and the water-free form **1b** respectively.

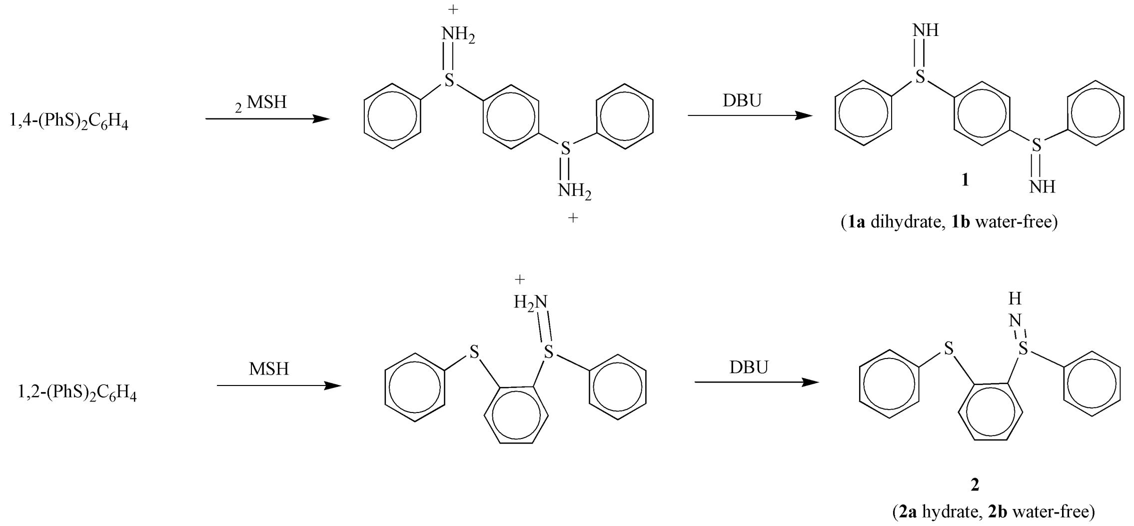
Yields of the corresponding 1,2-bis-sulfimide are very low, at least under analogous conditions; the mixed sulfide/sulfimide 1-(PhS{NH})-2-(PhS)C_6H_4 may be generated in good yield, however, by treatment of 1,2-$(PhS)_2C_6H_4$ with one equivalent of MSH (giving [1-(PhS{NH})-2-(PhS)C_6H_4][2,4,6-$Me_3C_6H_2SO_3$]) followed by treatment with DBU (see Scheme 1). Again this material may be crystallised from Et_2O/MeOH; X-ray crystallography confirms the resulting needles to be the monohydrate 1-(PhS{NH})-2-(PhS)$C_6H_4{\cdot}H_2O$ **2a**. In contrast to **1a**, however, dehydration *in vacuo* results in the formation of 1-(PhS{NH})-2-(PhS)C_6H_4 **2b** as an oil, which reverts to solid **2a** upon standing under water.

Diphenylsulfimide may be readily prepared by a modification of the traditional literature route recently reported by us.[2] This gives rise to the hydrate $Ph_2SNH{\cdot}H_2O$ **3a** which may be crystallised from warm diethyl ether in air; here we report the first crystallographic investigation into this material. If samples of crystalline **3a** thus prepared are ground to a powder and

Table 1 Summary of crystal data and structure determination for compounds **1a**, **1b**, **2a**, **3a** and **3b**

Compound	**1a**	**1b**	**2a**	**3a**	**3b**
Formula	$C_{18}H_{16}N_2S_2{\cdot}2H_2O$	$C_{18}H_{16}N_2S_2$	$C_{18}H_{15}NS_2{\cdot}H_2O$	$C_{12}H_{11}NS{\cdot}H_2O$	$C_{12}H_{11}NS$
M	360.48	324.45	327.45	219.29	201.28
Crystal size/mm	0.17 × 0.05 × 0.01	0.37 × 0.26 × 0.21	0.85 × 0.05 × 0.02	1.12 × 0.08 × 0.04	0.76 × 0.09 × 0.06
Crystal colour, habit	Colourless, lath	Colourless, block	Colourless, needle	Colourless, needle	Colourless, needle
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/n$	$P2_1/c$	*Pbca*	$P2_1/c$
a/Å	15.9838(16)	5.5099(2)	20.698(6)	5.1467(4)	5.6702(4)
b/Å	5.2038(5)	8.5604(4)	28.122(8)	20.1417(14)	8.9745(6)
c/Å	20.426(2)	16.5197(7)	5.5475(15)	21.4008(14)	40.530(3)
β/°	90	92.699(2)	94.837(5)	90	90.970(2)
V/Å^3	1698.9(3)	778.32(6)	3217.5(15)	2218.5(3)	2062.2(2)
Z	4	2	8	8	8
μ/mm^{-1}	0.327	0.339	0.332	0.263	0.270
Reflections measured	13 039	6503	18 565	17 699	16 687
Unique reflections {observed $F^2 > 2\sigma(F^2)$}	1943 {1152}	1844 {1790}	4187 {2259}	2712 {2111}	4872 {4159}
R_{int}	0.1024	0.0112	0.2399	0.0252	0.0257
R [$F^2 > 2\sigma(F^2)$][a]	0.0527	0.0399	0.0995	0.0321	0.0479
$wR2$ [all data][b]	0.1278	0.0982	0.2570	0.0898	0.0973
Largest difference map features/e Å^{-3}	0.718, −0.472	0.560, −0.267	0.835, −0.667	0.376, −0.271	0.415, −0.340

[a] $R = \sum| |F_o| - |F_c| |/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.



Scheme 1

placed under a 0.1 mmHg vacuum for two days the water is removed. Slow evaporation of a dry ethereal solution of this material under strictly anaerobic conditions results in the formation of crystalline Ph_2SNH **3b** and we have now been able to investigate its structure using X-ray crystallography.

Structure of sulfimides 1–3

Although $Ph_2SNH{\cdot}H_2O$ **3a** has been known for many years, searches of the literature and of the Cambridge Structural Database[8] suggest that its structure has not been determined before. Fig. 1(a) reveals the expected molecular structure from which an extended array is generated *via* two features: (i) N–H···N contacts between neighbouring sulfimides and (ii) O–H···N and O–H···O contacts from the waters of hydration. Fig. 1(b) highlights the resulting infinite 1-D kinked-ladder arrangement that results.

In view of the integral part water plays in this array structure we were interested to determine whether or not a similar array still forms in the absence of water. Weight-loss experiments confirm that after 48 hours under a 0.1 mmHg vacuum all of the water has been removed from the structure. This dehydrated form, **3b**, readily re-hydrates in the solid phase (see below) while addition of a drop of water to a diethyl ether solution, followed by brief mixing, provokes almost instantaneous crystallisation of the hydrate. If **3b** is dissolved in Et_2O (in which it is substantially more soluble than **3a**) and the solution allowed to evaporate under a stream of nitrogen, X-ray crystallography confirms that the resulting crystalline product is indeed water free. In this case a similar array of N–H···N contacts is seen but now the channels within which the waters of **3a** were located are effectively removed by a contraction of the packing. The impetus for the latter effect appears to be the close approach of each nitrogen to a C–H hydrogen atom of an adjacent phenyl group; in effect this interaction replaces the O–H···N interaction seen in the hydrate. The resulting H–N distance of 2.613 Å (C–N = 3.548 Å) is within the accepted parameters for a weak hydrogen-bond;[9] Fig. 2 highlights the result this has on the packing within the structure.

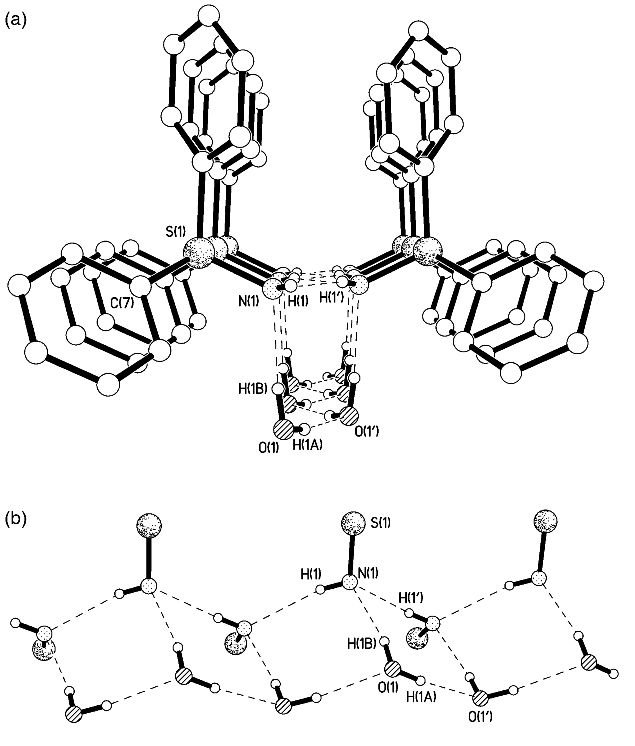


Fig. 1 (a) The X-ray crystal structure of **3a** showing the molecular structure of the sulfimide and its stacking with water molecules within the array. Selected bond distances (Å) and angles (°): S(1)–N(1) 1.5767(12), N(1)-H(1B) 2.05(2), H(1A)-O(1A) 2.03(2); C(1)-S(1)-C(7) 98.29(6), C(1)-S(1)-N(1) 111.88(6), C(7)-S(1)-N(1) 110.34(6), S(1)-N(1)-H(1) 110(2). (b) A side-on view of the array highlighting the overall kinked-ladder arrangement (phenyl groups omitted for clarity).

As we have already noted, samples of **3b** formed by dehydration of **3a** in the solid state prove to be hygroscopic. In addition, if the crystals of **3b** obtained from Et_2O (with the structure shown in Fig. 2) are ground up they also take up water in a similar manner. A number of features of both observations are worthy of note. Firstly, the water uptake is quite rapid. For example, when spread on a watch-glass in air, 857 mg of the material formed by the *in vacuo* dehydration of $Ph_2SNH{\cdot}H_2O$ gained half (31 mg) of its eventual total water uptake in just 14 minutes (by 12 hours into the experiment the rate of uptake was negligible). In addition, both materials ultimately only take up some 80% of the expected amount of water *i.e.* neither appear to fully return to the formula $Ph_2SNH{\cdot}H_2O$ by re-hydration in the solid state. The X-ray powder patterns of both solids after taking on as much water as they appear able are effectively identical but show some significant differences to that of $Ph_2SNH{\cdot}H_2O$. From this we can conclude that the solid state re-hydration results in a new phase; future studies will aim to identify this new phase and to assess the mechanism of, and structural response to, solid-state dehydration and re-hydration of **3a**.

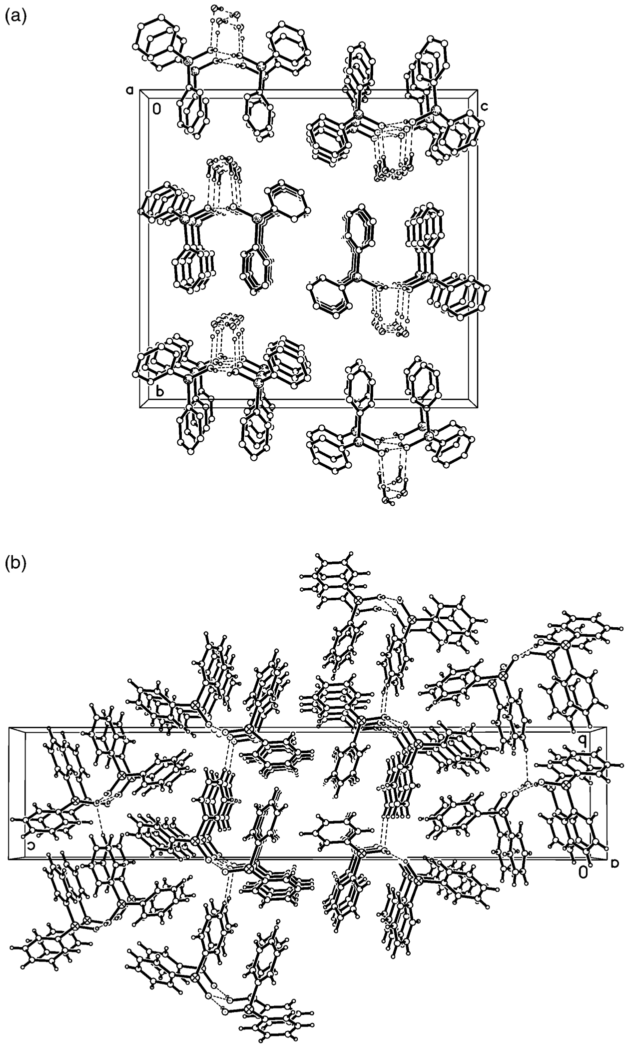


Fig. 2 Comparison of the hydrogen-bonding arrangements in **3a** (a) with those in **3b** (b) highlighting the contraction brought about by dehydration and the formation of close C–H···N interactions (H···N = 2.613 Å). Note the N–H···N interactions in **3b** show average H···N distances of 2.37 Å and N–H–N angles of 160°.

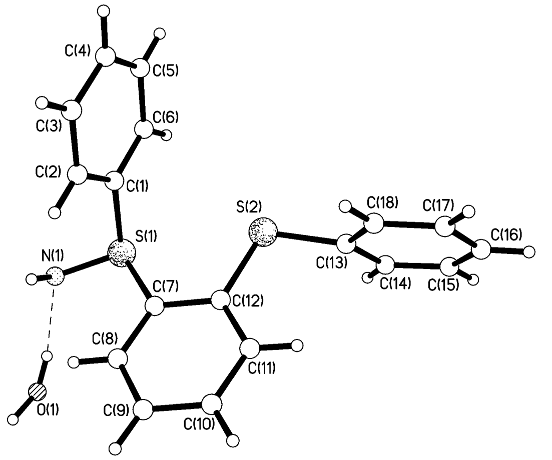


Fig. 3 The molecular structure of **2a**. Selected bond distances (Å) and angles (°): S(1)–N(1) 1.590(8), N(1)-H(1B) 2.00(7); C(1)-S(1)-C(7) 98.6(4), C(1)-S(1)-N(1) 109.8(4), C(7)-S(1)-N(1) 110.3(4), S(1)-N(1)-H(1A) 103(7), C(13)-S(2)-C(12) 105.7(4). The geometry of the other molecule in the asymmetric unit is similar. Note that a similar overall array to that of **3b** builds from the O–H···N interaction shown (2.00(7) Å) and N–H···N interactions of 2.32(9) and 2.17(10) Å.

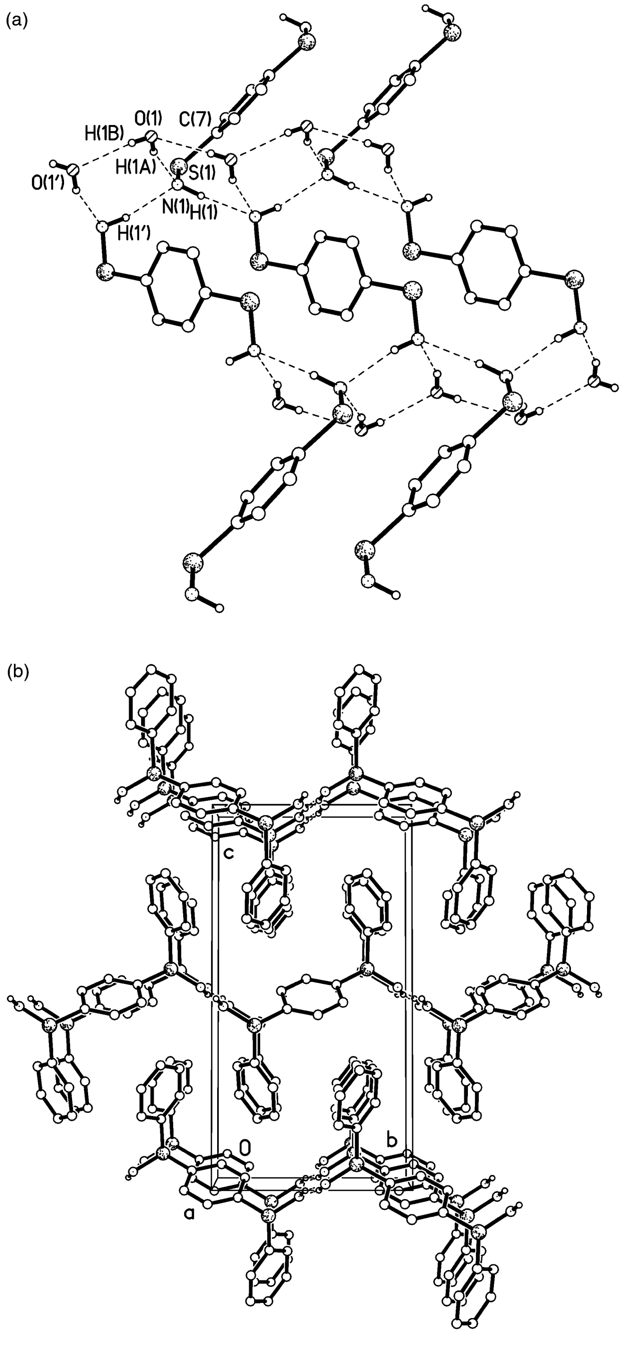


Fig. 4 (a) The X-ray crystal structure of **1a** showing a side-on view of the array highlighting the kinked-ladder arrangements linked into a 2-D sheet (non-bridging phenyl groups omitted for clarity). Selected bond distances (Å) and angles (°): S(1)–N(1) 1.578(3), N(1)-H(1B) 1.99(4), H(1A)-O(1′) 2.19(5); C(1)-S(1)-C(7) 98.72(14), C(1)-S(1)-N(1) 111.86(15), C(7)-S(1)-N(1) 110.06(15), S(1)-N(1)-H(1) 111(4). (b) The stacking array observed in the structure of **1b** viewed along *a*. Note than in contrast to the structure of **3b** (Fig. 2) we see no significant C–H···N interactions. Average H···N distance 2.37 Å, N–H–N angle 166°.

X-Ray crystallography performed upon crystals of **2a**, grown from methanol/water, confirms the presence of both sulfide and sulfimide groups (Fig. 3) and reveals an array structure effectively analogous to that of **3a**. A more substantial difference between the compounds is revealed upon dehydration. In this case the result, **2b**, is an oil; it would appear therefore that the presence of the extra SPh unit mitigates against effective array formation in the absence of the water. In the light of the C–H···N interactions discussed above for **3b** it is possible to speculate that the steric bulk of the sulfide group prevents effective formation of such interactions (it would be much harder to generate the kind of compact arrangement shown in Fig. 2 for example).

As might be expected, **1a** also forms an extended array. In this case the presence of N–H···N, O–H···N and O–H···O interactions at both sulfimide units generates parallel ladder arrangements [Fig. 4(a)] with waters above and below the plane of the nitrogens. The arrays now exhibit an extra dimensionality thanks to the linking phenyl units. The result is a 2-D sheet structure; this is also mirrored within the structure of the dehydrated analogue **1b** [Fig. 4(b)]. Interestingly, in the latter case there appear to be no significant C–H···N interactions of the kind seen in **3b**, and yet the material remains a solid. This presumably stems from the extra structural "rigidity" brought about by having two hydrogen-bonding sulfimide units per molecule and the extra dimensionality this gives the system when compared to monosulfimides such as **2** and **3**. Note that, as with **3a**/**b** there appears to be little change in geometry *within* the sulfimide unit upon dehydration (in both cases the N–S distances are effectively identical, while there is a slight closing of the C–S–C angle of some 4° upon losing the water).

The key to the formation of the water-bearing arrays is undoubtedly the fact that the sulfimide nitrogens can act as H-bond donors *via* the N–H bond and as acceptors from two units: an O–H and an N–H. This presumably reflects both the fact that the nitrogens are relatively sterically unencumbered and that the ylid structure of the sulfimide unit places some degree of negative charge on them.[10] The resulting N_2O_2 rings, which are the building blocks of the kinked ladders of the arrays, are slightly distorted planar squares. Thus within the N_2O_2 rings of **1a**, for example, we see N–N, O–N and O–O distances of 3.1, 2.8 and 2.9 Å respectively, N–N–O and N–O–O angles of 98.5° and 80.4° and a maximum deviation of 0.094 Å from the mean plane. Interestingly, similar, non-sulfimide, systems appear reluctant to exhibit analogous behaviour. For example, Ph_3PNH has been shown to exist as discrete, isolated molecules with no significant intermolecular hydrogen-bonding interactions,[11] while the imine Ph_2CNH does not appear to form a hydrate.

Conclusion

The isolation of **1a**/**b** and **2a**/**b** represents the first preparation and full characterisation of bis-sulfimide and mixed sulfimide/sulfide systems. Like their monosulfimide counterpart, **3**, they interact with water to form hydrates thanks to the sulfimide nitrogen acting as a hydrogen-bond donor and N–H/O–H acceptor. Such interactions with water have a complex dependency upon the precise structure of the molecule; thus within the three systems we have investigated here we find three significantly different responses. Ph_2SNH readily takes up a water of crystallisation in all but the most strictly dry conditions; hydrogen-bonding interactions are, however, strong enough to keep it a solid in the dehydrated form. In contrast while 1-(PhS{NH})-2-(PhS)C_6H_4 is equally hydrophilic, removal of the water destroys the extended array structure. Finally, 1,4-(PhS{NH}$)_2C_6H_4$ is far less hydrophilic and can crystallise in both hydrated and water-free forms from the same solution, indicating that in this case the sheet arrangement of the array provides great stability. Both **1** and **2** have obvious potential as ligands and the observation of their tendency towards array formation strongly suggests that, as with the aforementioned complexes of **3**, their metal complexes will exhibit strong hydrogen-bonding interactions. Work towards assessing such metal coordination chemistry is underway.

Acknowledgements

The authors acknowledge the EPSRC for studentships (K. E. H., J. M. S.) and thank Dr Sandie Dann and Pauline King for useful discussions and help with powder X-ray measurements.

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