

**Crystal engineering using bisphenols: interwoven ladders, sheet and framework structures in the binary adducts of 4,4'-sulfonyldiphenol with pyrazine (2/1), 4,4'-bipyridyl (1/1), *trans*-1,2-bis(4-pyridyl)ethene (1/1), 1,2-bis(4-pyridyl)ethane (1/1) and 4,4'-trimethylenedipiperidine (1/1), and in 4,4'-sulfonyldiphenol–4,4'-trimethylenedipiperidine–water (2/2/1)**

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(Received 28 August 1998; accepted 9 February 1999)

### Abstract

The structures of six hydrogen-bonded adducts of 4,4'-sulfonyldiphenol with heteroaromatic amines have been determined. In 4,4'-sulfonyldiphenol–pyrazine (2/1) the pyrazine molecules lie across centres of inversion. The bisphenol molecules are linked into  $C(8)$  chains parallel to [100] by means of  $O-H \cdots O=S$  hydrogen bonds, and antiparallel pairs of these chains are cross-linked by the pyrazine molecules, via  $O-H \cdots N$  hydrogen bonds, to form molecular ladders containing  $R_6^6(50)$  rings between the rungs of the ladders. Each ladder is interwoven with two neighbouring ladders, thus producing a continuous two-dimensional sheet. The structure of 4,4'-sulfonyldiphenol–4,4'-bipyridyl (1/1) consists of spiral  $C_2^2(21)$  chains parallel to [010] containing alternating bisphenol and bipyridyl molecules linked by  $O-H \cdots N$  hydrogen bonds: these chains are linked by two types of  $C-H \cdots O$  hydrogen bonds which form  $C(5)$  chains along [001] and  $C_2^2(10)$  chains along [101], thus generating two interconnected nets characterized in the one case by a chequerboard pattern of  $R_6^6(44)$  and  $R_6^6(52)$  rings, and in the other by a single type of  $R_6^6(46)$  ring. 4,4'-Sulfonyldiphenol–*trans*-1,2-bis(4-pyridyl)ethene (1/1) [systematic name: 4,4'-sulfonyldiphenol–*trans*-4,4'-vinylenedipiperidine (1/1)] and 4,4'-sulfonyldiphenol–1,2-bis(4-pyridyl)ethane (1/1) [systematic name: 4,4'-sulfonyldiphenol–*trans*-4,4'-ethylenedipiperidine (1/1)] are isomorphous: the 1,2-bis(4-pyridyl)ethane component exhibits orientational disorder, corresponding approximately to a 180° rotation of *ca* 23% of the molecules about the  $N \cdots N$  vector; in each compound the structure is built from  $C_2^2(23)$  chains of alternating bisphenol and bis(pyridyl) molecules connected by  $O-H \cdots N$  hydrogen bonds, running parallel to [112] and generated by translation. The [112] chains are linked by  $C-H \cdots O$  hydrogen bonds which generate  $C_2^2(12)$  chains parallel to [101], so forming a two-dimensional net built from  $R_6^6(50)$  rings. The structure of 4,4'-sulfonyldiphenol–4,4'-trimethylenedipiperidine (1/1) consists of  $C_2^2(24)$  chains parallel to [100] generated by translation and consisting

of alternating bisphenol and bis(pyridyl) molecules linked by  $O-H \cdots N$  hydrogen bonds. Pairs of such chains are coiled together to form double helices, and pairs of such double helices, of opposite hand, are linked together by paired  $C-H \cdots O$  hydrogen bonds in  $R_2^2(10)$  rings to form pairs of interwoven ladders in which the  $C_2^2(24)$  chains form the uprights and the  $R_2^2(10)$  rings form the rungs, between which are  $R_6^6(50)$  rings: an  $R_2^2(10)$  ring belonging to one ladder lies at the centre of an  $R_6^6(50)$  ring belonging to the other. 4,4'-Sulfonyldiphenol–4,4'-trimethylenedipiperidine–water (2/2/1) is a salt,  $2C_{13}H_{27}N_2^+ \cdot 2C_{12}H_9O_4S^- \cdot H_2O$ , containing two independent singly protonated diamine cations, two independent bisphenolate anions, and neutral water molecules. The two independent diamine cations are linked by  $N-H \cdots N$  hydrogen bonds into  $C_2^2(24)$  chains running parallel to [001] and generated by translation, and each type of bisphenolate anion forms an independent spiral  $C(12)$  chain, also parallel to [001]. The three types of chain are linked by the water molecules: the two types of bisphenolate chain are linked by water molecules acting as double donors in  $O-H \cdots O^-$  hydrogen bonds in a  $C_6^4(32)$  chain parallel to [100], thus generating a two-dimensional net built from  $R_6^6(56)$  rings; the diamine chains are linked to these nets by means of  $N-H \cdots O$  hydrogen bonds in which the water molecules act as acceptors and further hydrogen bonds, of  $N-H \cdots O^-$  and  $N-H \cdots O=S$  types, link these two-dimensional nets into a continuous three-dimensional framework.

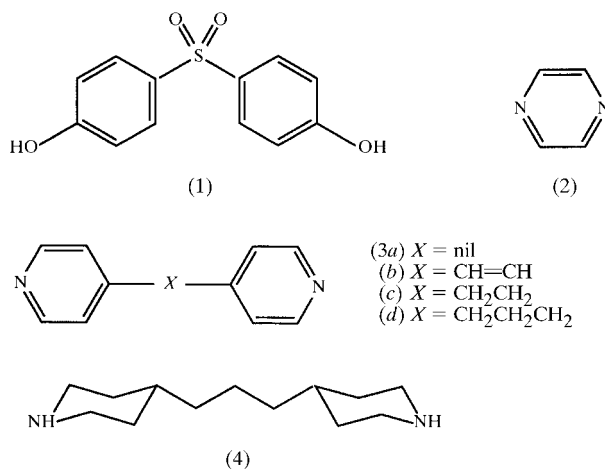
### 1. Introduction

The bisphenol 4,4'-sulfonyldiphenol,  $O_2S(C_6H_4OH)_2$ , is an extremely versatile building block for the purposes of crystal engineering. That this would be so became evident from the crystal structure of the pure substance (Glidewell & Ferguson, 1996): each of the hydroxyl O atoms acts as a hydrogen-bond donor, and each of the sulfone O atoms acts as a hydrogen-bond

acceptor, so that each molecule is hydrogen-bonded to four others. The resulting supramolecular arrangement is thus of square  $R_4^2(32)$  (Etter, 1990; Bernstein *et al.*, 1995) nets, which are pairwise interwoven in {4, 2, 1} mode (Ferguson *et al.*, 1998c). In this structure, the numbers of hard (Braga *et al.*, 1995) hydrogen-bond donors and acceptors are identical, but in two-component systems containing this bisphenol and another hydrogen-bond acceptor, such as a tertiary amine, and thus having an excess of hard acceptors over hard donors, the formation of soft hydrogen bonds (Braga *et al.*, 1995) of type  $C-H \cdots O=S$  may be expected in addition to hard  $O/N-H \cdots O/N$  hydrogen bonds. Thus in the 1:1 compound with hexamethylenetetramine,  $(CH_2)_6N_4$  (HMTA), the bisphenol acts as a double donor to HMTA in  $O-H \cdots N$  hydrogen bonds, so forming a very simple zigzag  $C_2^2(16)$  chain containing alternating bisphenol and HMTA molecules (Coupar *et al.*, 1997): these chains are linked together by rather strong  $C-H \cdots O=S$  hydrogen bonds in which one of the sulfone O atoms acts as a double acceptor.

In the presence of more basic amines, proton transfer from the bisphenol to the amine is possible (Coupar *et al.*, 1996b; Ferguson *et al.*, 1998b). The resulting formation of the phenolate anion  $HOC_6H_4SO_2C_6H_4O^-$  leads to a radically different mode of supramolecular aggregation: instead of chains built of alternating bisphenol and amine molecules, linked by neutral  $O-H \cdots N$  hydrogen bonds, the dominant mode of aggregation is that of phenolate anions linked together by means of the much stronger ionic (Aakeröy & Seddon, 1993; Gilli *et al.*, 1994)  $O-H \cdots O^-$  hydrogen bonds. In the 2:1 compound formed with piperazine, which is in fact the salt  $[H_2N(CH_2)_4NH_2]^{2+} \cdot 2HOC_6H_4SO_2C_6H_4O^-$  (Coupar *et al.*, 1996b), pairs of phenolate anions form  $R_2^2(24)$  rings. The rings are joined together by the cations, by means of ionic  $N^+-H \cdots O=S$  and  $N^+-H \cdots O^- - C$  hydrogen bonds, to form stacks which enclose linear channels. By contrast, the 2:1 compound formed by the bisphenol with 1,4,8,11-tetraazacyclotetradecane,  $C_{10}H_{24}N_4$  (cyclam), is again a salt,  $C_{10}H_{26}N_4^{2+} \cdot 2HOC_6H_4SO_2C_6H_4O^-$ , which contains infinite  $C(12)$  chains of bisphenolate anions linked by  $O-H \cdots O^-$  hydrogen bonds (Ferguson *et al.*, 1998b); pairs of these chains are cross-linked by the cyclam  $H_2^{2+}$  cations to form molecular ladders in which the chains form the uprights and the cations form the rungs. The ladders are themselves linked into a continuous bundle by means of  $C-H \cdots O=S$  hydrogen bonds.

These examples indicate the potential richness of the supramolecular behaviour of 4,4'-sulfonyldiphenol. In order to explore further this behaviour in a more systematic manner, we have now studied the behaviour of this bisphenol (1) with pyrazine (2), with a range of 4,4'-bipyridyls (3) including some chain-extended examples, and with the chain-extended dipiperidine (4).



By analogy with piperazine, it was expected that (4) would effect proton transfer with formation of the bisphenolate anion  $HOC_6H_4SO_2C_6H_4O^-$ ; on the other hand, 4,4'-bipyridyl (3a) does not show any evidence of proton transfer in its adduct with 1,3,5-trihydroxybenzene (Coupar *et al.*, 1996a), and hence it was not expected that the aromatic diamines (3) would lead to phenolate anion formation: the outcome with (2) was not readily predictable. In each of (2), (3a) and *trans*-(3b), the distance between the two N atoms, acceptors of hard hydrogen bonds, is effectively fixed at *ca* 2.8, 7.0 and 9.2 Å, respectively. However, the chain-extended bipyridyls (3c) and (3d) have additional torsional degrees of freedom which can lead to flexibility in the molecular conformation, and thus to variation in the distance between the two acceptor sites; likewise the dipiperidine (4). We have commented previously on the fact that in hydrogen-bonded systems of this general type, soft hydrogen bonds can play a key role in determining the overall supramolecular structure provided that there is reasonable conformational flexibility in the components, but where there is little or no such flexibility the soft hydrogen bonds have little influence (Ferguson *et al.*, 1997). Moreover, the building blocks (2) and (3a)–(3d) all offer the possibility of  $\pi-\pi$  stacking of aryl rings as a significant determinant of supramolecular structure in the resulting adducts with (1). The series of adducts formed by (1) with (2), (3) and (4) provide a further test of all these ideas. Co-crystallization of (1) with (2) leads to the 2:1 product (5); (1) with (3a)–(3d) leads to a series of crystalline products, (6a)–(6d), respectively, all of 1:1 stoichiometry, while with (4) a hemihydrate (7) was isolated.

## 2. Experimental

### 2.1. Preparation of the compounds

Equimolar quantities of the bisphenol (1) and each of the diamines (2), (3) and (4) were separately dissolved in methanol, then mixed to give in each case a

phenol:diamine stoichiometric ratio of 1:1, and then set aside to crystallize. The resulting colourless crystals were isolated by filtration and were dried briefly over silica gel. In this manner the following compounds were obtained: 4,4'-sulfonyldiphenol-pyrazine (2/1), (5); 4,4'-sulfonyldiphenol-4,4'-bipyridyl (1/1), (6a); 4,4'-sulfonyldiphenol-*trans*-1,2-bis(4-pyridyl)ethene (1/1), (6b); 4,4'-sulfonyldiphenol-1,2-bis(4-pyridyl)ethane (1/1), (6c); 4,4'-sulfonyldiphenol-4,4'-trimethylenedipyridine (1/1), (6d); and 4,4'-sulfonyldiphenol-4,4'-trimethylene-dipiperidine-water (2/2/1), (7). Analyses: for (5) found C 58.4, H 4.1, N 4.8%,  $C_{28}H_{24}N_2O_8S_2$  requires C 57.9, H 4.2, N 4.8%; for (6a) found C 64.3, H 4.4, N 6.5%,  $C_{22}H_{18}N_2O_4S$  requires C 65.0, H 4.5, N 6.9%; for (6b) found C 66.9, H 4.5, N 6.4%,  $C_{24}H_{20}N_2O_4S$  requires C 66.7, H 4.6, N 6.5%; for (6c) found C 66.8, H 5.0, N 6.5%,  $C_{24}H_{22}N_2O_4S$  requires C 66.3, H 5.1, N 6.5%; (6d) found C 67.3, H 5.4, N 6.3%,  $C_{25}H_{24}N_2O_4S$  requires C 66.9, H 5.4, N 6.3%; for (7) found C 63.9, H 8.0, N 5.9,  $C_{50}H_{74}N_4O_9S_2$  requires C 63.9, H 7.9, N 6.0%. In all cases, crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

## 2.2. Single-crystal X-ray diffraction

Details of the X-ray experimental conditions, unit-cell data, data collections and refinements are summarized in Table 1.† For compounds (5), (6a), (6d) and (7), the space groups  $P2_1/a$ ,  $P2_1/n$ ,  $P2_1/c$  and  $P2_12_12_1$ , respectively, were assigned uniquely from the systematic absences. Compounds (6b) and (6c) are both triclinic and are, indeed, isomorphous: space group  $P\bar{1}$  was chosen and confirmed by the successful refinement. The solution and refinement for compound (6b) proceeded smoothly to  $R = 0.048$ , but at this point a difference map (Fig. 10) showed two substantial electron-density maxima, one on either side of the central C=C double bond of the *trans*-1,2-bis(4-pyridyl)ethene fragment, although the rest of the map was devoid of any significant features. The analytical purity of the starting components and of (6b) itself, together with the crystallization conditions employed in the formation of (6b), suggested that the only plausible interpretation of these two maxima was in terms of orientational disorder of the *trans*-1,2-bis(4-pyridyl)ethene unit such that the pyridyl rings in the two orientations were more or less coincident, but with the central  $-\text{CH}=\text{CH}-$  fragment adopting two quite distinct locations: subsequent refinement of such a model indicated major and minor orientations of the 1,2-bis(4-pyridyl)ethene with site-occupation factors of 0.771 (5) and 0.229 (5) (Fig. 12). The lack of other significant electron-density maxima around the pyridyl rings in the difference map (Fig. 10) calculated for the single-occupancy model was asso-

ciated with the unusual anisotropic displacement parameters calculated for this model. The correct enantiomorph of the selected crystal of compound (7) was established by refinement of the Flack parameter (Flack, 1983).

For all refinements, a weighting scheme based upon  $P = (F_o^2 + 2F_c^2)/3$  was employed to reduce statistical bias (Wilson, 1976). Supramolecular structures were analysed with the aid of *PLATON* (Spek, 1998). The figures were prepared with the aid of *ORTEPII* (Johnson, 1976) and *PLATON*. Details of the hydrogen bonding and selected molecular dimensions are given in Tables 2 and 3, respectively. Figs. 1, 4, 8, 11, 13 and 16 show the molecular aggregates in compounds (5), (6a)–(6d) and (7), and Figs. 2, 3, 5–7, 9, 10, 12, 14, 15 and 17–21 show aspects of the crystal structures of these compounds.

## 3. Results and discussion

### 3.1. Crystal and molecular structures of compounds (5), (6) and (7)

3.1.1. 4,4'-Sulfonyldiphenol-pyrazine (2/1), (5). The asymmetric unit of compound (5) (Fig. 1) consists of one molecule of the bisphenol lying in a general position and one half of a molecule of pyrazine, which lies across a centre of inversion. The bisphenol molecules are linked by  $\text{O}-\text{H}\cdots\text{O}=\text{S}$  hydrogen bonds into chains, generated by translation along [100], so that this structure thus retains one of the main structural motifs found in the pure bisphenol (Glidewell & Ferguson, 1996); pairs of these chains related by centres of inversion are linked into ladders by the pyrazine molecules using  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds. This very simple molecular ladder (Fig. 2), generated solely by translation and inversion, utilizes only one half of the contents of the unit cell, the bisphenols at  $(x, y, z)$  and  $(-x, -y, -z)$  and the pyrazine

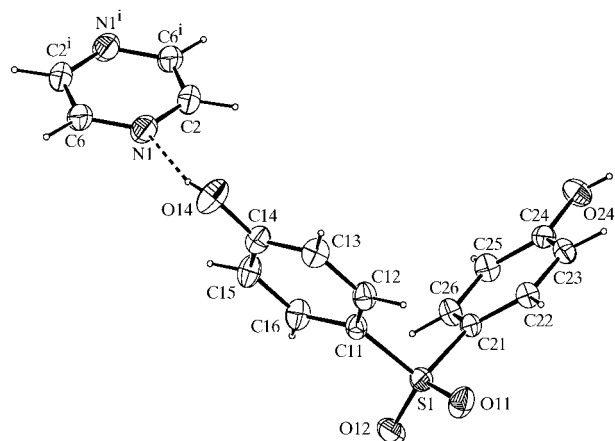


Fig. 1. The molecular aggregate in compound (5), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 30% probability level. Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF0004). Services for accessing these data are described at the back of the journal.

Table 1. *Experimental details*

	(5)	(6a)	(6b)
Crystal data			
Chemical formula	$2C_{12}H_{10}O_4S \cdot C_4H_4N_2$	$C_{12}H_{10}O_4S \cdot C_{10}H_8N_2$	$C_{12}H_{10}O_4S \cdot C_{12}H_{10}N_2$
Chemical formula weight	580.64	406.44	432.48
Cell setting	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/a$	$P2_1/n$	$P\bar{1}$
$a$ (Å)	8.3506 (9)	7.5765 (10)	7.3981 (8)
$b$ (Å)	18.0102 (17)	23.9154 (10)	12.7472 (15)
$c$ (Å)	9.6360 (14)	11.225 (2)	13.0006 (13)
$\alpha$ (°)	—	—	115.037 (8)
$\beta$ (°)	110.869 (8)	105.921 (10)	102.398 (10)
$\gamma$ (°)	—	—	94.239 (10)
$V$ (Å <sup>3</sup> )	1354.1 (3)	1955.9 (4)	1065.9 (2)
$Z$	2	4	2
$D_x$ (Mg m <sup>-3</sup> )	1.424	1.380	1.347
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.7107	0.7107	0.7107
No. of reflections for cell parameters	25	25	25
$\theta$ range (°)	9.49–20.35	9.50–18.76	9.92–18.19
$\mu$ (mm <sup>-1</sup> )	0.251	0.197	0.186
Temperature (K)	294 (1)	294 (1)	294 (1)
Crystal form	Plate	Needle	Needle
Crystal size (mm)	0.42 × 0.35 × 0.25	0.42 × 0.22 × 0.18	0.42 × 0.28 × 0.24
Crystal colour	Colourless	Colourless	Colourless
Data collection			
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans
Absorption correction	Gaussian	Gaussian	Gaussian
$T_{\min}$	0.9153	0.9522	0.9487
$T_{\max}$	0.9505	0.9706	0.9667
No. of measured reflections	3271	3774	3829
No. of independent reflections	3102	3504	3829
No. of observed reflections	2431	2461	2948
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\text{int}}$	0.008	0.011	—
$\theta_{\text{max}}$ (°)	27.4	25.11	25.19
Range of $h, k, l$	–10 → $h$ → 10 0 → $k$ → 23 0 → $l$ → 12	–9 → $h$ → 8 0 → $k$ → 28 0 → $l$ → 13	–8 → $h$ → 8 0 → $k$ → 15 –15 → $l$ → 14
No. of standard reflections	3	3	3
Frequency of standard reflections	Every 240 min	Every 120 min	Every 120 min
Intensity decay (%)	0	0	0
Refinement			
Refinement on	$F^2$	$F^2$	$F^2$
$R[F^2 > 2\sigma(F^2)]$	0.0356	0.0392	0.0357
$wR(F^2)$	0.0966	0.0984	0.1002
$S$	1.035	1.053	0.980
No. of reflections used in refinement	3102	3504	3829
No. of parameters used	183	265	330
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.2603P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 0.0855P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.2472P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	<0.001	<0.001	0.001
$\Delta\rho_{\text{max}}$ (e Å <sup>-3</sup> )	0.248	0.226	0.207
$\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	–0.221	–0.247	–0.200
Extinction method	None	SHELXL97 (Sheldrick, 1997b)	SHELXL97 (Sheldrick, 1997b)
Extinction coefficient	—	0.0043 (9)	0.0143 (18)
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1 (*cont.*)

	(5)	(6a)	(6b)
Computer programs			
Data collection	<i>CAD-4-PC Software</i> (Enraf–Nonius, 1992)	<i>CAD-4-PC Software</i> (Enraf–Nonius, 1992)	<i>CAD-4-PC Software</i> (Enraf–Nonius, 1992)
Cell refinement	<i>SET4</i> and <i>CELDIM</i> (Enraf–Nonius, 1992)	<i>SET4</i> and <i>CELDIM</i> (Enraf–Nonius, 1992)	<i>SET4</i> and <i>CELDIM</i> (Enraf–Nonius, 1992)
Data reduction	<i>DATRD2</i> in <i>NRCVAX96</i> (Gabe <i>et al.</i> , 1989)	<i>DATRD2</i> in <i>NRCVAX96</i> (Gabe <i>et al.</i> , 1989)	<i>DATRD2</i> in <i>NRCVAX96</i> (Gabe <i>et al.</i> , 1989)
Structure solution	<i>SHELXS97</i> (Sheldrick, 1997a)	<i>SHELXS97</i> (Sheldrick, 1997a)	<i>SHELXS97</i> (Sheldrick, 1997a)
Structure refinement	<i>NRCVAX96</i> and <i>SHELXL97</i> (Sheldrick, 1997b)	<i>NRCVAX96</i> and <i>SHELXL97</i> (Sheldrick, 1997b)	<i>NRCVAX96</i> and <i>SHELXL97</i> (Sheldrick, 1997b)
Preparation of material for publication	<i>NRCVAX96</i> , <i>SHELXL97</i> and <i>PRPCIF97</i> (Ferguson, 1997)	<i>NRCVAX96</i> , <i>SHELXL97</i> and <i>PRPCIF97</i> (Ferguson, 1997)	<i>NRCVAX96</i> , <i>SHELXL97</i> and <i>PREP8</i> (Ferguson, 1998)
	(6c)	(6d)	(7)
Crystal data			
Chemical formula	C <sub>12</sub> H <sub>10</sub> O <sub>4</sub> S·C <sub>12</sub> H <sub>12</sub> N <sub>2</sub>	C <sub>12</sub> H <sub>10</sub> O <sub>4</sub> S·C <sub>13</sub> H <sub>14</sub> N <sub>2</sub>	2C <sub>13</sub> H <sub>27</sub> N <sub>2</sub> <sup>+</sup> ·2C <sub>12</sub> H <sub>9</sub> O <sub>4</sub> S <sup>-</sup> ·H <sub>2</sub> O
Chemical formula weight	434.5	448.52	939.25
Cell setting	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	7.7599 (9)	10.0292 (10)	12.2739 (10)
<i>b</i> (Å)	12.4866 (16)	15.579 (2)	19.454 (2)
<i>c</i> (Å)	12.914 (2)	15.0208 (10)	20.6251 (13)
$\alpha$ (°)	114.003 (14)	—	—
$\beta$ (°)	104.694 (14)	105.4699 (10)	—
$\gamma$ (°)	93.690 (13)	—	—
<i>V</i> (Å <sup>3</sup> )	1085.7 (3)	2261.9 (4)	4924.7 (8)
<i>Z</i>	2	4	4
<i>D</i> <sub>x</sub> (Mg m <sup>-3</sup> )	1.329	1.317	1.267
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
Wavelength (Å)	0.7107	0.7107	0.7107
No. of reflections for cell parameters	25	10602	25
$\theta$ range (°)	9.84–22.45	2.6–30.3	9.45–17.50
$\mu$ (mm <sup>-1</sup> )	0.183	0.177	0.167
Temperature (K)	294 (1)	150 (1)	294 (1)
Crystal form	Plate	Block cut from larger piece	Plate
Crystal size (mm)	0.42 × 0.42 × 0.32	0.30 × 0.30 × 0.30	0.40 × 0.38 × 0.19
Crystal colour	Colourless	Colourless	Colourless
Data collection			
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius KappaCCD	Enraf–Nonius CAD-4
Data collection method	$\theta/2\theta$ scans	$\omega$ scans	$\theta/2\theta$ scans
Absorption correction	Gaussian	None	Gaussian
<i>T</i> <sub>min</sub>	0.9335	—	0.9431
<i>T</i> <sub>max</sub>	0.9506	—	0.9718
No. of measured reflections	4973	10 602	9558
No. of independent reflections	4973	5465	8866
No. of observed reflections	3905	3828	5888
Criterion for observed reflections	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )
<i>R</i> <sub>int</sub>	—	0.031	0.019
$\theta$ <sub>max</sub> (°)	27.42	30.2	25.2
Range of <i>h</i> , <i>k</i> , <i>l</i>	–10 → <i>h</i> → 9 0 → <i>k</i> → 16 –16 → <i>l</i> → 15	–12 → <i>h</i> → 12 –19 → <i>k</i> → 19 –19 → <i>l</i> → 19	0 → <i>h</i> → 14 0 → <i>k</i> → 23 –24 → <i>l</i> → 24
No. of standard reflections	3	—	3
Frequency of standard reflections	Every 120 min	—	Every 120 min
Intensity decay (%)	0	0	2.2
Refinement			
Refinement on	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	0.0418	0.0405	0.0416
<i>wR</i> ( <i>F</i> <sup>2</sup> )	0.1225	0.1151	0.1031
<i>S</i>	1.072	1.039	1.031

Table 1 (cont.)

	(6c)	(6d)	(7)
No. of reflections used in refinement	4973	5465	8866
No. of parameters used	283	292	595
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	Some H-atom parameters constrained, some refined independently
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.2544P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0620P)^2 + 0.2027P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 0.2197P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001	0.001	<0.001
$\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	0.434	0.269	0.213
$\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	-0.318	-0.358	-0.174
Extinction method	SHELXL97 (Sheldrick, 1997b)	SHELXL97 (Sheldrick, 1997b)	None
Extinction coefficient	0.015 (2)	0.0066 (14)	—
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs			
Data collection	CAD-4-PC Software (Enraf-Nonius, 1992)	KappaCCD Control Program (Enraf-Nonius, 1997)	CAD-4-PC Software (Enraf-Nonius, 1992)
Cell refinement	SET4 and CELDIM (Enraf-Nonius, 1992)	DENZO (Enraf-Nonius, 1997)	SET4 and CELDIM (Enraf-Nonius, 1992)
Data reduction	DATRD2 in NRCVAX96 (Gabe <i>et al.</i> , 1989)	DENZO (Enraf-Nonius, 1997)	DATRD2 in NRCVAX96 (Gabe <i>et al.</i> , 1989)
Structure solution	SHELXS97 (Sheldrick, 1997a)	SHELXS97 (Sheldrick, 1997a)	SHELXS97 (Sheldrick, 1997a)
Structure refinement	NRCVAX96 and SHELXL97 (Sheldrick, 1997b)	NRCVAX96 and SHELXL97 (Sheldrick, 1997b)	NRCVAX96 and SHELXL97 (Sheldrick, 1997b)
Preparation of material for publication	NRCVAX96, SHELXL97 and PREP8 (Ferguson, 1998)	NRCVAX96, SHELXL97 and PREP8 (Ferguson, 1998)	NRCVAX96, SHELXL97 and PRPCIF97 (Ferguson, 1997)

centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ; thus there are two such ladders running through each unit cell with the second based upon the pyrazine centred at  $(0, 1, \frac{1}{2})$ . The supramolecular complexity arises from the interweaving of the adjacent ladders: the two ladders based upon pyrazine molecules centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  and  $(\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$  are each separately interwoven with the ladder based upon the pyrazine centred at  $(0, 1, \frac{1}{2})$  (Fig. 3). In this way, each ladder along [100] is interwoven with its two neighbouring ladders in the [010] direction, so producing two-dimensional sheets parallel to the (001) plane. These sheets are then linked into a three-dimensional framework by the action of C—H...O hydrogen bonds: C13 in the bisphenol at  $(x, y, z)$  acts as donor to the hydroxyl O atom O24 at  $(1+x, y, 1+z)$ , so linking the (001) sheets.

3.1.2. *4,4'-Sulfonyldiphenol-4,4'-bipyridyl (I/I)*, (6a). The asymmetric unit in (6a) (Fig. 4) contains one molecule each of the bisphenol and of 4,4'-bipyridyl; the hydroxyl H atoms are fully ordered and there is no evidence for any proton transfer from the bisphenol to the bipyridyl. Each molecule of the bisphenol acts as a donor in two O—H...N hydrogen bonds and each bipyridyl molecule thus acts as a double acceptor to give a simple chain of alternating bisphenol and bipyridyl units (Fig. 5).

Within the asymmetric unit, the hydroxyl O atom O14 acts as hydrogen-bond donor to N31: the other hydroxyl

O atom O24 at  $(x, y, z)$  acts as donor to N41 at  $(\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z)$ , thus providing a spiral chain running parallel to [010] and generated by the  $2_1$  screw axis along  $(\frac{3}{4}, y, \frac{3}{4})$  (Fig. 5). This chain utilizes one half of the contents of the unit cell, and the unit cell is completed by a second chain, related to the first by the action of centres of inversion, around the screw axis at  $(\frac{1}{4}, y, \frac{1}{4})$ .

Despite the very wide diameter of these spirals, the two independent chains within the unit cell are not intertwined, but adjacent spirals are linked by two different types of C—H...O hydrogen bonds (Table 2) to form a two-dimensional aggregate. Atom C12 (Fig. 4) at  $(x, y, z)$  acts as donor to the sulfone O atom O12 at  $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ , while C12 at  $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$  in turn acts as donor to O12 at  $(1+x, y, 1+z)$ , so leading to formation of a chain parallel to [101], generated by the  $n$ -glide plane: atom C42 at  $(x, y, z)$  acts as donor to the hydroxyl O atom O14 at  $(1+x, y, 1+z)$ , generating a similar chain by simple translation. The effect of these two types of C—H...O hydrogen bond is to tie adjacent [101] spirals into a raft parallel to the  $(10\bar{1})$  plane.

3.1.3. *4,4'-Sulfonyldiphenol-trans-1,2-bis(4-pyridyl)ethene (I/I)*, (6b), and *4,4'-sulfonyldiphenol-1,2-bis(4-pyridyl)ethane (I/I)*, (6c). Compounds (6b) and (6c) are isomorphous in space group  $P\bar{1}$  with (6c) having a unit-cell volume larger than that of (6b) by ca 2% (Table 1). Because of the orientational disorder exhibited by the

Table 2. Hydrogen-bond dimensions ( $\text{\AA}$ ,  $^\circ$ )

(5)			
O14...N1	2.792 (2)	O14—H14...N1	167
O24...O12 <sup>i</sup>	2.732 (2)	O24—H24...O12 <sup>i</sup>	174
C13...O24 <sup>ii</sup>	3.353 (2)	C13—H13...O24 <sup>ii</sup>	161
(6a)			
O14...N31	2.721 (3)	O14—H14...N31	167
O24...N41 <sup>iii</sup>	2.731 (3)	O24—H24...N41 <sup>iii</sup>	176
C12...O12 <sup>iv</sup>	3.376 (3)	C12—H12...O12 <sup>iv</sup>	165
C42...O14 <sup>ii</sup>	3.487 (3)	C42—H42...O14 <sup>ii</sup>	167
(6b)			
O14...N31	2.743 (4)	O14—H14...N31	171
O14...N51	2.730 (7)	O14—H14...N51	172
O24...N41 <sup>v</sup>	2.688 (5)	O24—H24...N41 <sup>v</sup>	173
O24...N61 <sup>v</sup>	2.714 (7)	O24—H24...N61 <sup>v</sup>	174
(6c)			
O14...N31	2.735 (2)	O14—H14...N31	170
O24...N41 <sup>v</sup>	2.706 (2)	O24—H24...N41 <sup>v</sup>	174
C46...O14 <sup>vi</sup>	3.476 (3)	C46—H46...O14 <sup>vi</sup>	164
(6d)			
O14...N31	2.6514 (19)	O14—H14...N31	171
O24...N41 <sup>viii</sup>	2.6850 (18)	O24—H24...N41 <sup>viii</sup>	166
C12...O11 <sup>viii</sup>	3.428 (2)	C12—H12...O11 <sup>viii</sup>	160
(7)			
O9...O44	2.790 (3)	O9—H91...O44	162 (3)
O9...O14	2.766 (3)	O9—H92...O14	163 (4)
O24...O14 <sup>ix</sup>	2.499 (3)	O24—H24...O14 <sup>ix</sup>	167
O34...O44 <sup>x</sup>	2.629 (3)	O34—H44...O44 <sup>x</sup>	169
N51...O9	3.148 (3)	N51—H51...O9	133
N61...N71 <sup>xi</sup>	2.809 (3)	N61—H61B...N71 <sup>xi</sup>	173
N61...O44 <sup>xii</sup>	2.810 (3)	N61—H61A...O44 <sup>xii</sup>	175
N81...N51	2.742 (4)	N81—H81B...N51	172
N81...O21 <sup>xiii</sup>	3.148 (3)	N81—H81A...O21 <sup>xiii</sup>	153 <sup>†</sup>
N81...O22 <sup>xiii</sup>	3.337 (4)	N81—H81A...O22 <sup>xiii</sup>	145 <sup>†</sup>
C33...O9 <sup>x</sup>	3.397 (4)	C33—H33...O9 <sup>x</sup>	164

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $1 + x, y, 1 + z$ ; (iii)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (iv)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (v)  $1 + x, 1 + y, 2 + z$ ; (vi)  $x - 1, y, z - 1$ ; (vii)  $2 + x, y, z$ ; (viii)  $-x, -y, -z$ ; (ix)  $\frac{1}{2} - x, -y, \frac{1}{2} + z$ ; (x)  $-\frac{1}{2} - x, -y, z - \frac{1}{2}$ ; (xi)  $x, y, 1 + z$ ; (xii)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (xiii)  $\frac{1}{2} + x, \frac{1}{2} - y, -z$ . <sup>†</sup> The angle O21<sup>xiii</sup>...H81A...O22<sup>xiii</sup> is  $61^\circ$ ; the sum of angles at H81A is  $359^\circ$ .

diamine component of (6b) (see §2.2), it is convenient to discuss first the supramolecular structure of compound (6c).

In compound (6c) (Fig. 8) the bisphenol acts as a double donor of O—H...N hydrogen bonds and the diamine as a double acceptor but, as in (6a), there is no proton transfer from the bisphenol to the diamine. The principal supramolecular motif is, as in (6a), a chain of alternating bisphenol and diamine units; however, unlike the corresponding chain in (6a), which is a spiral generated by the action of a  $2_1$  screw axis (see §3.1.2), the chain in (6c) is generated simply by translation: atom O24 in the bisphenol at  $(x, y, z)$  (Fig. 9) acts as a donor to N41 at  $(1 + x, 1 + y, 2 + z)$ . The fact that the repeat unit of this chain spans two unit cells in the [001] direction means that there are in fact four such chains running

through each cell, a pair generated by a unit translation along [001] and a second pair generated from the first by the action of the centres of inversion. These [112] chains are linked into sheets by means of soft C—H...O hydrogen bonds. Atom C46 in the bipyridyl at  $(x, y, z)$  (Fig. 8) acts as donor to the hydroxyl O atom O14 at  $(-1 + x, y, -1 + z)$  to generate, again by translation, a chain running parallel to [101]; the interaction of these two types of chain, parallel to the [112] and [101] directions, produces a two-dimensional net, four of which are necessary to generate the entire unit-cell contents.

The supramolecular architecture in compound (6b) (Fig. 11) is essentially the same as for (6c), with only minor differences consequent upon the change from a  $-\text{CH}_2\text{CH}_2-$  spacer to  $-\text{CH}=\text{CH}-$ . As indicated earlier (see §2.2) the 1,2-bis(4-pyridyl)ethene component exhibits orientational disorder. Rotation of the whole bis(pyridyl) unit through  $180^\circ$  about the N...N vector provides an alternative configuration in which all the atoms in the pyridyl rings are in sites close to those of the original orientation, but with the C—C bond of the central  $-\text{CH}=\text{CH}-$  unit almost at right angles to its original location (Fig. 12). The difference map calculated after the initial refinements, based on a structural model involving only one orientation of this unit, was devoid of any significant features in the vicinity of the pyridyl rings because the slight difference in the atom positions had been obscured by the highly aniso-

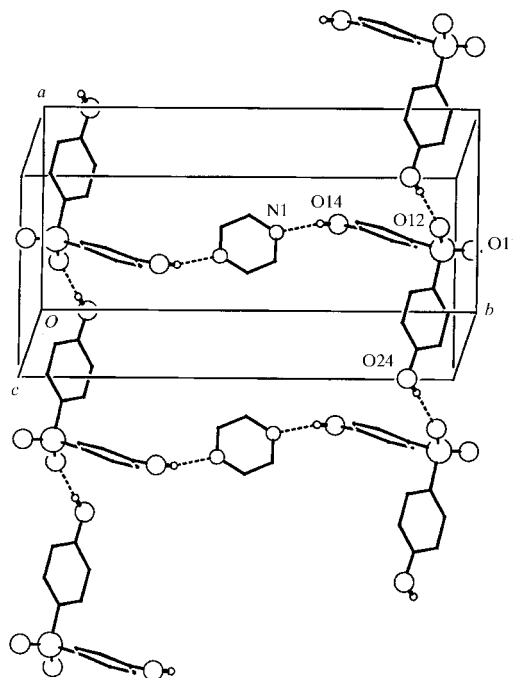


Fig. 2. View of part of the crystal structure of (5), showing the formation of a single molecular ladder. H atoms bonded to C are omitted for the sake of clarity.

tropic displacement parameters that resulted from the use of this model. However, this model not only gave the two large electron-density maxima corresponding to the second orientation, but also gave some unexpected bond angles at atoms C34 and C44 (*cf.* Fig. 10). Inclusion of two orientations in the structural model allowed a clear distinction to be made between the two sets of occupied sites for the ring atoms, and showed clearly the sources of the unusual parameter values found for the single-orientation model.

3.1.4. *4,4'-Sulfonyldiphenol-4,4'-trimethylenedipyridine (1/1), (6d)*. The asymmetric unit of (6d) contains

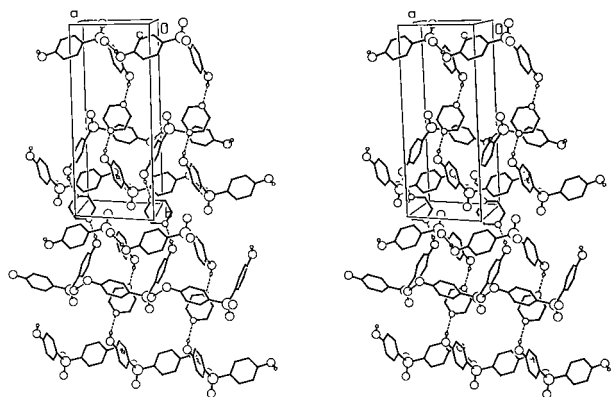


Fig. 3. Stereoview of part of the crystal structure of (5), showing the continuous interweaving of adjacent ladders. H atoms bonded to C are omitted for the sake of clarity.

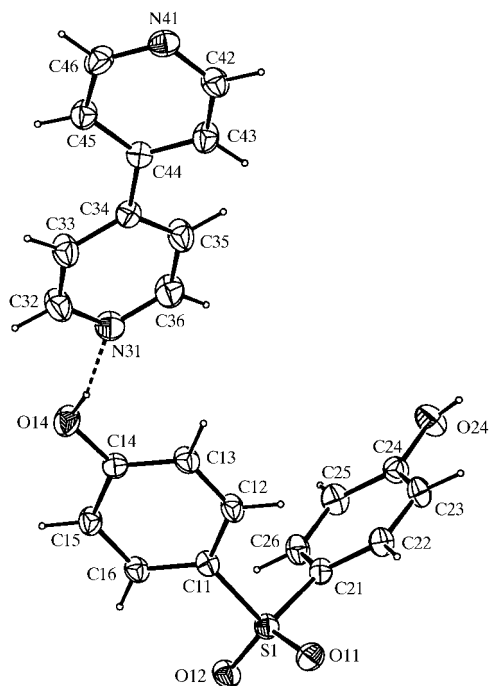


Fig. 4. The asymmetric unit in compound (6a). Atoms are depicted as in Fig. 1.

one molecule each of 4,4'-trimethylenedipyridine and 4,4'-sulfonyldiphenol (Fig. 13); the diphenol acts as a double donor and the dipyridine as a double acceptor in the formation of intermolecular O—H···N hydrogen bonds. Atom O14 of the diphenol acts as donor to atom N31 of the dipyridine within the asymmetric unit at  $(x, y, z)$ , while atom O24 of the diphenol acts as donor to N41 of the dipyridine at  $(2 + x, y, z)$ , thus forming chains parallel to the  $[100]$  direction. Such a chain involves molecular components from only every other unit cell in the  $a$  direction and hence there is an entirely similar, but independent, chain based upon the asymmetric unit at  $(1 + x, y, z)$ . These two chains are not connected, either covalently or by any intermolecular hydrogen bonds, but are nonetheless coiled together to form a double helix, which utilizes just one of the four molecular aggregates per unit cell. A second double helix, related to the first double helix by the action of the inversion centre at the origin, and thus of opposite hand, is linked to the first by pairs of C—H···O hydrogen bonds: atom C12 (Fig. 13) in the diphenol at  $(x, y, z)$  acts as hydrogen-bond donor to the sulfone O atom O11 in the diphenol at  $(-x, -y, -z)$ , while the corresponding C—H bond at  $(-x, -y, -z)$  forms a hydrogen bond with the sulfone O

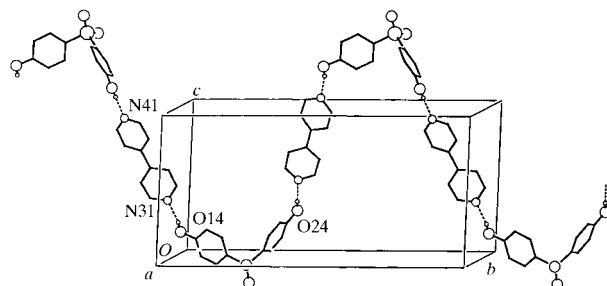


Fig. 5. View of one of the molecular spirals in (6a). H atoms bonded to C are omitted for the sake of clarity.

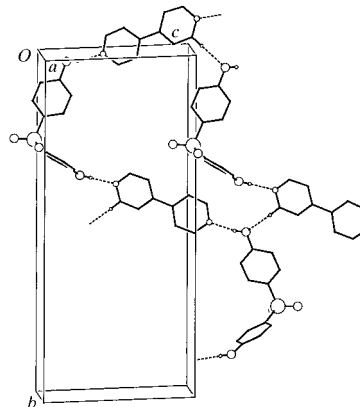


Fig. 6. View of part of the crystal structure of (6a), showing the  $C_2^2(21)$  and  $C_2^2(10)$  chains along  $[101]$  and  $[101]$ , respectively, interacting to generate  $R_2^0(46)$  rings. H atoms bonded to C but not involved in hydrogen bonding are omitted for the sake of clarity.



atom O11 at  $(x, y, z)$ , thus generating a cyclic centrosymmetric motif.

These cyclic motifs may be regarded as the rungs of a ladder running parallel to  $[100]$  (Fig. 14). Alternatively, the supramolecular structure may be regarded as two interwoven ladders, each of which is based on single-strand uprights and having rungs at intervals of  $2a$ : rungs centred at  $(n, 0, 0)$  for even  $n$  link the pair of uprights generated by the asymmetric unit at  $(x, y, z)$ , while rungs centred at  $(n, 0, 0)$  for odd  $n$  link the pairs of uprights generated by the asymmetric unit at  $(1 + x, y, z)$  (Fig. 15). If the structure is regarded as a single molecular ladder, then this has barley-sugar (Fleming *et al.*, 1980; Brown, 1993) uprights consisting of an enantiomeric pair of double helices.

Each supramolecular ladder pair, however it is described, utilizes just half the contents of the unit cell: the ladder pair generated from the units at  $(x, y, z)$  and  $(-x, -y, -z)$  lies largely in the half of the cell having  $-\frac{1}{4} < z < \frac{1}{4}$ , and there is an identical ladder pair in the domain  $\frac{1}{4} < z < \frac{3}{4}$ , generated from the first by the action of the glide plane. Between individual ladder pairs, related either by translation along the  $[010]$  direction or by the action of the glide plane, there are no intermolecular contacts significantly shorter than the sum of the van der Waals radii.

3.1.5. *4,4'-Sulfonyldiphenol-4,4'-trimethylenedipiperidine-water (2/2/1), (7)*. The asymmetric unit of (7) (Fig. 16) contains two molecules each of the diamine and the bisphenol, together with one molecule of water, thus confirming the deduction from the elemental analysis of

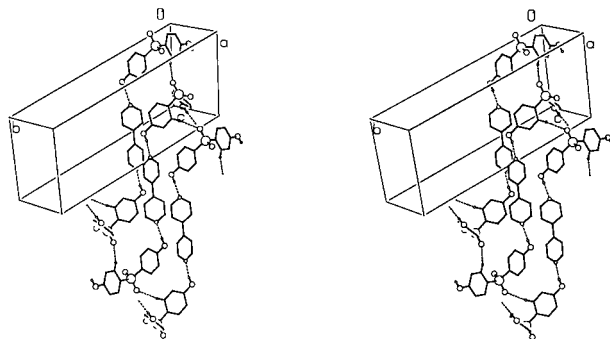


Fig. 7. Stereoview of part of the crystal structure of (6a), showing the formation of a net built from alternating  $R_6^0(44)$  and  $R_6^0(52)$  rings.

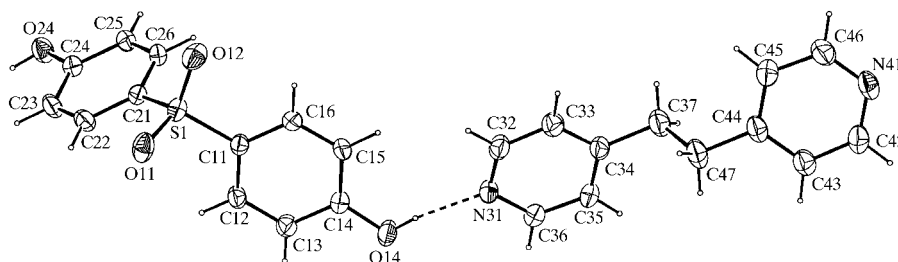


Fig. 8. The asymmetric unit in compound (6c). Atoms are depicted as in Fig. 1.

0.5 molecules of water per diamine/bisphenol pair: all components of the asymmetric unit lie in general positions. The refinement shows clearly that each of the bisphenol units has lost a single H atom, and that each diamine unit has gained one H atom: the water molecule is clearly present still as neutral  $H_2O$ , but the two other components are present as  $[H_2N(CH_2)_4CH(CH_2)_3-CH(CH_2)_4NH]^+$  and  $HOC_6H_4SO_2C_6H_4O^-$ , respectively.

Despite the presence in the asymmetric unit in space group  $P2_12_12_1$  of two units each of the protonated diamine and the bisphenolate anion, any possibility of additional symmetry was readily ruled out by inspection both of the refined coordinates and of the hydrogen-bonding characteristics of the various molecular components (Table 2). In one of the diamine cations, that containing N51 and N61, all three N—H bonds are engaged in hydrogen bonds, while in the other cation only two of the N—H bonds are involved. Similarly, in the bisphenolate anion containing S2, both O atoms of the sulfone group act as acceptors in a three-centre hydrogen bond involving N81 as donor, while in the other anion neither of the sulfone O atoms is involved in a hard (Braga *et al.*, 1995) hydrogen bond.

The supramolecular architecture is dominated by chains of diamine cations, linked together by N—H...N hydrogen bonds, and chains of bisphenolate anions linked together by O—H...O hydrogen bonds, all running parallel to the  $[001]$  direction. The chains built from the two types of components are, however, rather different: there is a single type of chain built from the diamine cations, but there are two types of chain built from bisphenolate anions (Table 2). In the diamine chain (Fig. 17), both types of cation are present with, in each case, a quaternary  $R_2NH_2^+$  N atom in one cation acting as hydrogen-bond donor to a neutral  $R_2NH$  N atom in a neighbouring cation: this chain is built by translation along the  $[001]$  direction. The quaternary N atom N81 acts as donor, *via* H81B, to the neutral N51 within the asymmetric unit, while the quaternary N atom N61 at  $(x, y, z)$  acts as donor, *via* H61B, to the neutral N71 at  $(x, y, 1 + z)$ , thus generating a chain parallel to  $[001]$ . Four such chains run through each unit cell; those running close to the lines  $(0, \frac{1}{4}, z)$  and  $(\frac{1}{2}, \frac{3}{4}, z)$  have the N—H...N hydrogen bonds directed along positive  $z$  and those running close to  $(0, \frac{3}{4}, z)$  and  $(\frac{1}{2}, \frac{1}{4}, z)$  have the N—H...N hydrogen bonds directed along negative  $z$ .

Table 3. Selected molecular dimensions ( $\text{\AA}$ ,  $^\circ$ )

(5)			
O14—C14	1.354 (2)	O24—C24	1.3548 (18)
N1—C2	1.329 (2)	N1—C6	1.323 (2)
C2—C6 <sup>i</sup>	1.372 (3)		
O11—S1—C11—C12	22.0 (2)	O11—S1—C21—C22	-19.5 (2)
(6a)			
O14—C14	1.349 (2)	O24—C24	1.351 (3)
C33—C34	1.378 (3)		
O12—S1—C11—C16	3.4 (2)	O11—S1—C21—C22	-24.8 (2)
Interplanar angle (N31, C32—C36, C44) $\wedge$ (N41, C42—C46, C34)			24.4 (1)
(6b)			
O14—C14	1.349 (2)	O24—C24	1.344 (2)
C34—C37	1.457 (3)	C54—C57	1.456 (5)
C37—C47	1.308 (3)	C57—C67	1.303 (5)
C44—C47	1.464 (3)	C64—C67	1.464 (5)
O11—S1—C21—C22	-0.85 (18)	O12—S1—C11—C16	10.68 (17)
C33—C34—C37—C47	179.8 (4)	C53—C54—C57—C67	174.3 (12)
C43—C44—C47—C37	176.4 (3)	C63—C64—C67—C57	169.4 (10)
(6c)			
O14—C14	1.3528 (19)	O24—C24	1.347 (2)
C34—C37	1.512 (2)	C44—C47	1.515 (2)
C37—C47	1.474 (3)		
O12—S1—C11—C16	4.25 (16)	O11—S1—C21—C22	-2.71 (17)
C33—C34—C37—C47	101.9 (3)	C43—C44—C47—C37	-126.6 (2)
C35—C34—C37—C47	-79.2 (3)	C45—C44—C47—C37	53.9 (3)
C34—C37—C47—C44	179.7 (2)		
(6d)			
O14—C14	1.3426 (19)	O24—C24	1.3477 (18)
C34—C51	1.502 (2)	C44—C53	1.506 (2)
C51—C52	1.520 (2)	C52—C53	1.521 (2)
O11—S1—C11—C12	-24.83 (15)	O12—S1—C21—C26	-12.27 (14)
C33—C34—C51—C52	-28.8 (2)	C45—C44—C53—C52	-23.4 (2)
C34—C51—C52—C53	-178.32 (14)	C51—C52—C53—C44	-173.91 (14)
(7)			
O14—C14	1.302 (3)	O34—C34	1.334 (3)
O24—C24	1.331 (3)	O44—C44	1.313 (3)
N51—C52	1.453 (4)	N71—C72	1.472 (4)
N51—C56	1.471 (4)	N71—C76	1.474 (4)
N61—C62	1.492 (4)	N81—C82	1.477 (4)
N61—C66	1.491 (4)	N81—C86	1.476 (4)
O11—S1—C11—C12	-25.3 (3)	O21—S2—C31—C32	-26.8 (3)
O11—S1—C21—C26	17.1 (3)	O21—S2—C41—C46	32.3 (3)
C54—C57—C58—C59	179.8 (3)	C74—C77—C78—C79	-178.0 (3)
C57—C58—C59—C64	-178.5 (3)	C77—C78—C79—C84	-170.6 (3)
C53—C54—C57—C58	-173.9 (3)	C73—C74—C77—C78	-174.9 (3)
C55—C54—C57—C58	62.9 (4)	C75—C74—C77—C78	-53.1 (4)
C58—C59—C64—C63	-59.9 (4)	C78—C79—C84—C83	-57.1 (4)
C58—C59—C64—C65	176.8 (3)	C78—C79—C84—C85	178.5 (3)

Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .

By contrast, there are two types of chain built from the bisphenolate anions; each type of chain contains just one type of anion. The bisphenolate containing O14 and

O24 forms two spiral chains per unit cell around the  $2_1$  screw axes at  $(\frac{1}{4}, 0, z)$  and  $(\frac{3}{4}, \frac{1}{2}, z)$  while the anion containing O34 and O44 forms similar spirals, again two

per cell, around the  $2_1$  axes at  $(-\frac{1}{4}, 0, z)$  and  $(\frac{1}{4}, \frac{1}{2}, z)$ . Neutral O atom O24 at  $(x, y, z)$  acts as donor to the deprotonated O14 at  $(\frac{1}{2}-x, -y, \frac{1}{2}+z)$  and O24 at  $(\frac{1}{2}-x, -y, \frac{1}{2}+z)$  in turn acts as donor to O14 at  $(x, y, 1+z)$  to generate a spiral around the  $2_1$  axis at  $(\frac{1}{4}, 0, z)$ ; similarly, neutral O34 at  $(x, y, z)$  acts as donor to

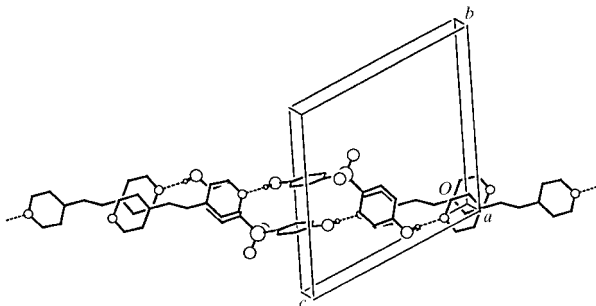


Fig. 9. View of part of the crystal structure of (6c), showing formation of the  $[112]$  chains. H atoms bonded to C are omitted for the sake of clarity.

negative O44 at  $(-\frac{1}{2}-x, -y, -\frac{1}{2}+z)$ , so generating a second spiral, this time around the  $2_1$  axis at  $(-\frac{1}{4}, 0, z)$ . Thus the projection of these various chains onto the (001) plane is a rectangular array of bisphenolate chains, with the diamine chains close to the centres of the rectangles and the water molecules close to the midpoints of their shorter edges.

The  $[001]$  chains, of three different types, are linked together to form a continuous three-dimensional network and the water molecules play an essential role in this. Each water molecule acts as a hydrogen-bond donor towards two deprotonated O atoms, one in each of the two types of bisphenolate chain, and as a hydrogen-bond acceptor from one of the neutral N atoms in the diamine chain, thus serving to link together the three different types of chain. The O atom O9 of the water molecule at  $(x, y, z)$  acts as donor, via H91 and H92, respectively, to the anionic O atoms O44 and O14 within the same asymmetric unit, so linking the two types of bisphenolate chain. Propagation of these hydrogen bonds by means of the screw axes lying along

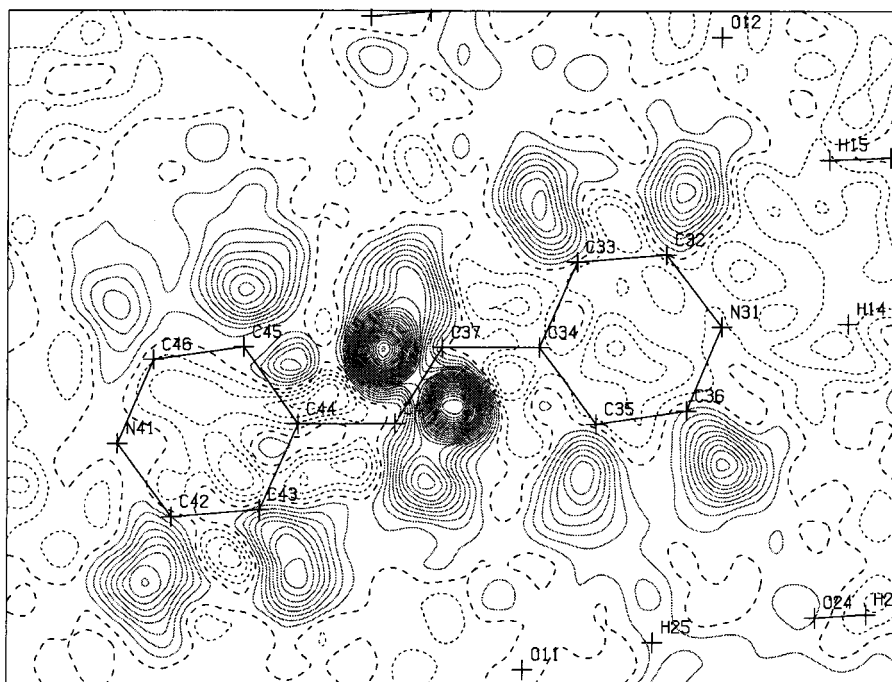


Fig. 10. Difference map calculated for compound (6b) after refinement of the single-orientation model.

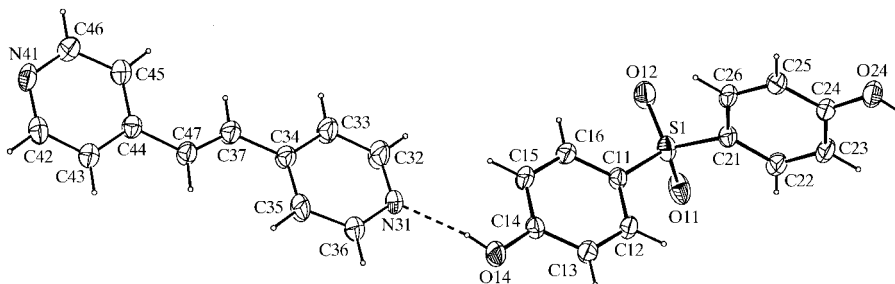


Fig. 11. The asymmetric unit in (6b), showing the major orientation of the *trans*-1,2-bis(4-pyridyl)ethene component. Atoms are depicted as in Fig. 1.

( $\pm \frac{1}{4}, 0, z$ ) generates a two-dimensional net lying parallel to the (010) plane, characterized by a single type of reticulation, and involving within each ring contributions from six bisphenolate anions and two water molecules (Fig. 18). Two such nets, related by the screw axes parallel to [010], run through each unit cell.

At the same time, O9 also acts as an acceptor from the neutral N51 within the same asymmetric unit, thus providing a link between all the different types of chain. The water molecule at  $(x, y, z)$  is linked to the diamine chain running approximately along  $(0, \frac{1}{4}, z)$ , while the water molecule at  $(\frac{1}{2} - x, -y, \frac{1}{2} + z)$  in the same bisphenolate/water sheet is linked to the diamine chain running roughly along the line  $(\frac{1}{2}, -\frac{1}{4}, z)$ . Hence, each such sheet is linked *via* the water molecules to two diamine chains, one on each face of the sheet. The diamine chains run roughly parallel to the bisphenolate chains, with a water molecule providing a connection once per unit-cell translation in the [001] direction; these connections thus give rise to a further type of large ring involving contributions from three bisphenolate anions, three diamines and two water molecules (Fig. 19).

The formation of the diamine chains and their connection to the bisphenolate/water sheets utilizes three of the six independent N—H bonds; of the other three (Table 2), that on the neutral N atom N71 participates in no hydrogen bonds, while one N—H on each of the quaternary N atoms N61 and N81 forms hydrogen bonds which serve to link the (010) sheets into a continuous three-dimensional whole. The quaternary N atom N61 at  $(x, y, z)$  acts as donor, *via* H61A, to the

anionic oxygen O44 at  $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ , thus generating a spiral running parallel to the [010] direction and generated by the action of the  $2_1$  axis along  $(0, y, \frac{1}{4})$  (Fig. 20). This spiral motif links the diamine chain at approximately  $(0, \frac{1}{4}, z)$  to that at approximately  $(0, \frac{3}{4}, z)$ , so joining together neighbouring bisphenolate/water sheets. Finally, N81 at  $(x, y, z)$  acts as donor, *via* H81A, to the two sulfone O atoms O21 and O22 in the bisphenolate at  $(\frac{1}{2} + x, \frac{1}{2} - y, -z)$  as the acceptors in a bifurcated three-centre hydrogen bond. This motif is part of a spiral around the screw axis at  $(x, \frac{1}{4}, 0)$ , again linking neighbouring sheets (Fig. 21): the diamine chain approximately along  $(0, \frac{1}{4}, z)$  is linked by this interaction to that approximately along  $(\frac{1}{2}, \frac{1}{4}, z)$ .

### 3.2. Hydrogen bonding

**3.2.1. Hydrogen-bond dimensions.** It has recently been noted that the criteria for acceptance of non-covalent contacts involving hydrogen as genuine hydrogen bonds seem to be undergoing continual relaxation (Cotton *et al.*, 1997). It therefore seems desirable to specify the acceptance criteria adopted here for the hydrogen bonds listed in Table 2. The hard, two-centre hydrogen bonds, of O—H...O, O—H...N, N—H...O and N—H...N types, exhibit maximum  $D\cdots A$  distances of 2.790 (3), 2.732 (3), 3.148 (3) and 2.809 (3) Å, respectively, and with the exception of a single outlying value of 133° in compound (7), the  $D-H\cdots A$  angles are clustered around 170°, close to the most frequent value of 160° for such two-centre bonds (Jeffrey & Saenger, 1991). For the three-centre hydrogen bond in compound (7), which involves a protonated amine as the donor and the two geminal O atoms of a sulfone as acceptors, the sum of the inter-bond angles at the H atom is close to 360°, as is very frequently found for such systems (Jeffrey & Saenger, 1991). The C—H...O hydrogen bonds in Table 2 all have  $C\cdots O$  distances below 3.5 Å and C—H...O angles not less than 160°: these values are well within the ranges now accepted for such bonds (Desiraju, 1991, 1996; Braga *et al.*, 1995). Beyond these specifications, it is necessary only to note that, as expected, the O...O distances in the ionic O—H...O<sup>-</sup> hydrogen bonds of compound (7) are significantly shorter than the neutral

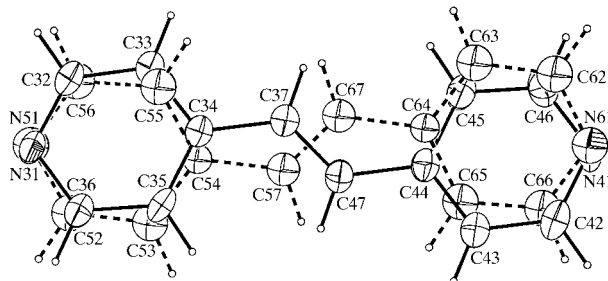


Fig. 12. The major (full lines) and minor (broken lines) orientations of the *trans*-1,2-bis(4-pyridyl)ethene component in compound (6b). Atoms are depicted as in Fig. 1.

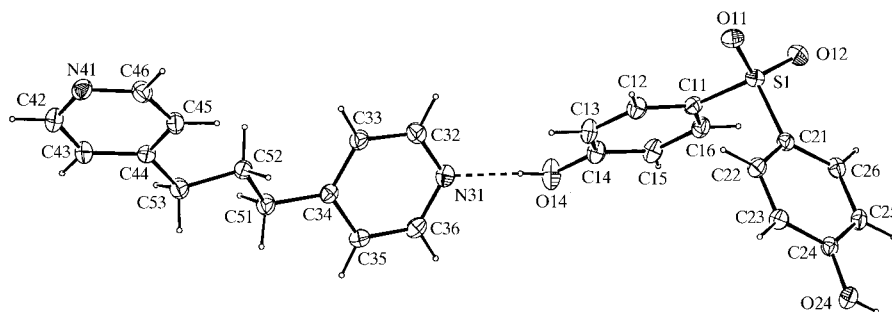


Fig. 13. The asymmetric unit of compound (6d). Atoms are depicted as in Fig. 1.

O—H...O hydrogen bonds listed in Table 2, and that the  $D\cdots A$  distances in the three-centre system in compound (7) are rather long, again as expected.

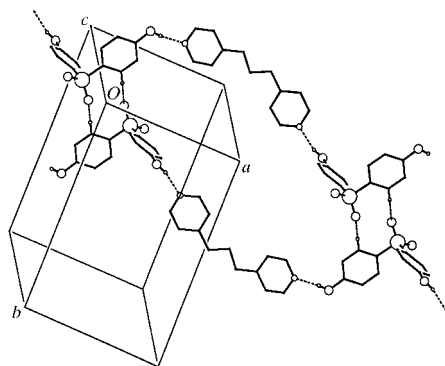


Fig. 14. View of part of the crystal structure of (6d), showing the formation of one molecular ladder containing  $R_2^2(10)$  and  $R_6^6(50)$  rings. H atoms bonded to C but not involved in hydrogen bonding are omitted for the sake of clarity.

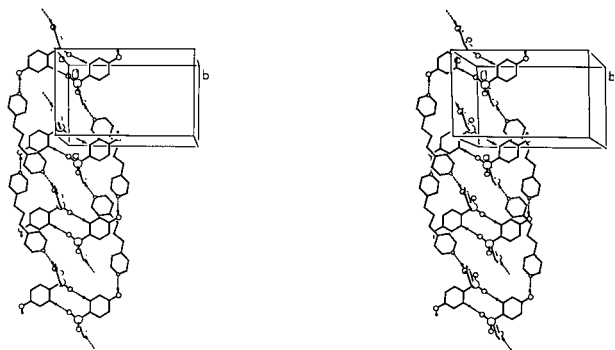


Fig. 15. Stereoview of part of the crystal structure of (6d) showing the pairwise interweaving of the molecular ladders. Atoms are depicted as in Fig. 14.

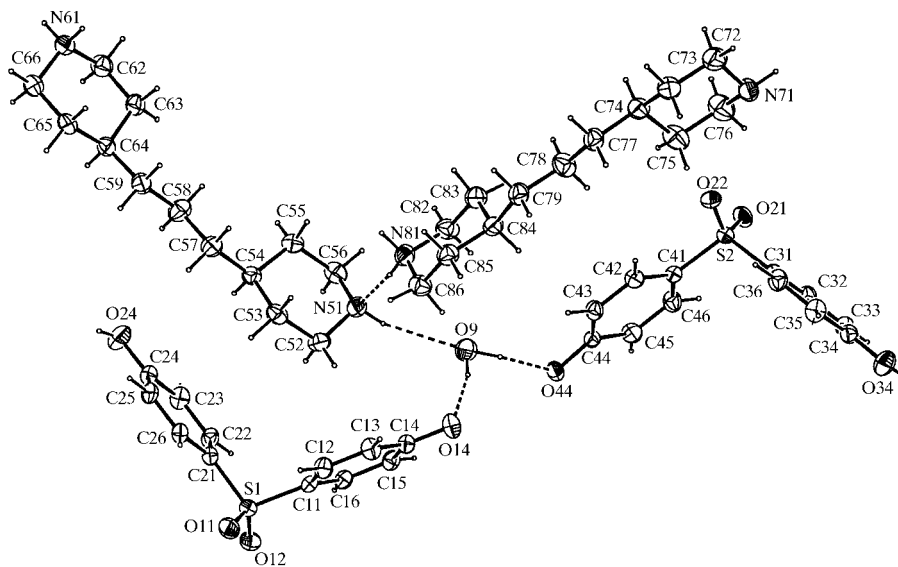


Fig. 16. The asymmetric unit of compound (7). Atoms are depicted as in Fig. 1.

**3.2.2. Hydrogen-bond motifs.** The chains in compound (5) which form the uprights of the molecular ladders contain a single type of O—H...O=S hydrogen bond, and thus can be characterized by the graph-set descriptor  $C(8)$ : the centrosymmetric rings between the rungs of the ladder are of  $R_6^6(50)$  type. The C—H...O hydrogen bonds which link the (001) sheets form  $C(10)$  chains running parallel to the [101] direction.

The primary chain of alternating bisphenol and bipyridyl units in compound (6a) contains two independent hydrogen bonds, both of O—H...N type, and the graph-set descriptors (Etter, 1990; Bernstein *et al.*, 1995) are thus  $N_1 = DD$ ,  $N_2 = C_2^2(21)$ . These  $C_2^2(21)$  chains along [010] are linked by the soft (Braga *et al.*, 1995) C—H...O hydrogen bonds (Table 2) to give a two-dimensional system of some complexity. The  $C42-H42\cdots O14^{ii}$  [symmetry code: (ii)  $1 + x, y, 1 + z$ ] hydrogen bonds link adjacent chains in a similar  $N_1 = DD$ ,  $N_2 = C_2^2(10)$  motif along [101], and the combination of these two chain motifs gives rise to a two-dimensional net built from  $R_6^6(46)$  rings and involving contributions from three bisphenol and three bipyridyl molecules (Fig. 6). A different mode of linking of the main [010] chains is effected by the  $C12-H12\cdots O12^{iv}$  [symmetry code: (iv)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ] hydrogen bonds: the simple  $C(5)$  chain generated by these bonds, together with the  $C_2^2(21)$  chains along [010] yield a second two-dimensional net, this time built from centrosymmetric  $R_6^6(44)$  and  $R_6^6(52)$  rings, centred at  $(\frac{3}{2}, \frac{1}{2}, \frac{3}{2})$  and  $(1, \frac{1}{2}, 1)$ , respectively, and thus producing a chequerboard pattern (Fig. 7).

In (6b) and (6c) the primary chains along [112] have  $N_1 = DD$ ,  $N_2 = C_2^2(23)$ ; the chains along [101], generated by the  $C46-H46\cdots O14^{vi}$  [symmetry code: (vi)  $-1 + x, y, -1 + z$ ] hydrogen bonds, are of  $C_2^2(12)$  type, and the net generated by the combination of these two chain-

forming motifs is built from a single type of  $R_6^6(50)$  ring, in which each ring contains contributions from three bisphenol molecules and three molecules of the extended bipyridine. These two types of chain and the net arising from them are thus entirely equivalent to a subset of the supramolecular linkages in compound (6a), where there are additional chain and ring motifs arising from the hydrogen bonds involving a sulfone O atom as acceptor. The  $C_2^2(23)$ ,  $C_2^2(12)$  and  $R_6^6(50)$  motifs in (6b) and (6c) are equivalent to the  $C_2^2(21)$ ,  $C_2^2(10)$  and  $R_6^6(46)$  motifs in (6a), when account is taken of the additional two-carbon spacer units in the molecular building blocks (3b) and (3c).

Within the chains in compound (6d) running parallel to [100] and forming the uprights of the supramolecular ladders, there are two types of O—H...N hydrogen bond involving O14 and O24, respectively, as donors: consequently for these chains the binary graph set is  $N_2 = C_2^2(24)$ . The cyclic centrosymmetric motif forming each of the rungs of the ladders has graph set  $R_2^2(10)$ , while the rings between the rungs of the ladders, involving two each of both types of O—H...N hydrogen bonds as well as two C—H...O hydrogen bonds, are of  $R_6^6(50)$  type. Within each interwoven pair of ladders, there is an  $R_2^2(10)$  ring arising from one ladder at the centre of each  $R_6^6(50)$  ring of the other ladder.

In compound (7), the two types of spiral chain built from phenolate anions each contain a single type of hydrogen bond, and so both are characterized by the graph-set descriptor  $C(12)$ : by contrast, the single type of chain built from diamine cations, and generated by translation, contains two types of hydrogen bond so that for this chain  $N_1 = DD$ ,  $N_2 = C_2^2(24)$ . The water mole-

cules link the two types of bisphenolate chain and, in so doing, give rise to a  $C_6^4(32)$  chain motif which is most conveniently traced (Fig. 18) from the asymmetric unit at  $(x, y, z)$  via that at  $(\frac{1}{2} - x, -y, \frac{1}{2} + z)$  to that at  $(1 + x, y, z)$ . The interaction of this  $C_6^4(32)$  chain running parallel to the [100] direction with the two types of  $C(12)$  chain running parallel to the [001] direction generates the two-dimensional net (Fig. 18) built from  $R_8^8(56)$  rings. The linking of the diamine chains to the bisphenolate/water sheets by means of N—H...O hydrogen bonds involving the water molecules as acceptors generates two new types of  $R_8^8(56)$  ring, each involving one diamine chain and one type of bisphenolate chain.

Finally, the spiral linking these compound sheets and running parallel to the [010] direction is of  $C_3^2(16)$  type, while the spiral parallel to the [100] direction and containing the three-centre hydrogen bond with two sulfone O atoms as acceptors can be regarded as a 'chain of rings' (Bernstein *et al.*, 1995), with graph-set descriptor  $C_4^4(14)[R_1^1(4)]$ . Within the resulting three-dimensional network the array of different chain and ring motifs which can be picked out is almost limitless, as is usual in such systems (Ferguson *et al.*, 1998).

### 3.3. $\pi$ - $\pi$ stacking motifs

All of the heteroaromatic amines (2) and (3) have the potential to be involved in  $\pi$ - $\pi$  stacking interactions in their adducts (5) and (6). In compounds (6b) and (6c), where the [112] chains are generated purely by translation, there are several pairs of aryl or heteroaryl rings, related by centres of inversion and therefore parallel to one another, in which both the perpendicular distances between the ring planes and the offset distance between the ring centroids in a direction parallel to the ring planes are consistent with the presence of attractive  $\pi$ - $\pi$  interactions between the rings. In general the C—H bonds in aryl rings are polarized in the sense  $C^{\delta-}-H^{\delta+}$ , while there is a build-up of electron density above and below the plane of each ring, arising from the  $\pi$  orbitals. Hence the most favourable stacking mode for centrosymmetric pairs of parallel rings has the rings not strictly in register, but offset such that an H atom of one ring is

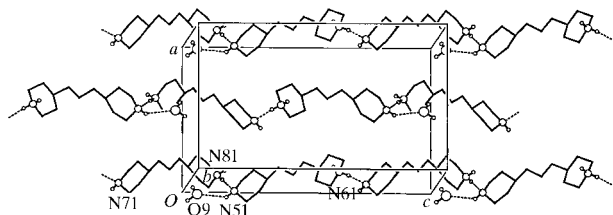


Fig. 17. View of part of the crystal structure of (7), showing the chains built from diamine cations. H atoms bonded to C are omitted for the sake of clarity.

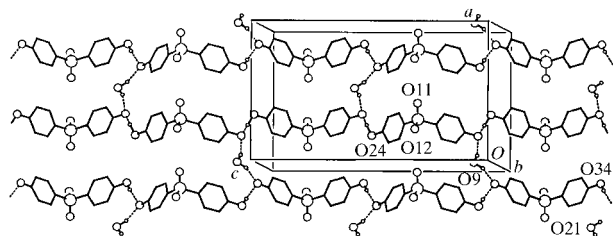


Fig. 18. View of part of the crystal structure of (7), showing the sheets built from bisphenolate anions and water molecules. H atoms bonded to C are omitted for the sake of clarity.

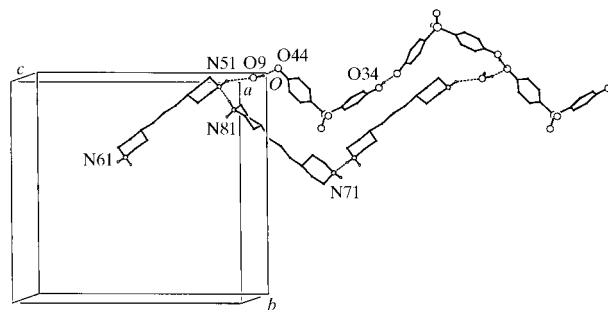


Fig. 19. View of part of the crystal structure of (7), showing how the water molecules link the three types of chain parallel to [001]. H atoms bonded to C are omitted for the sake of clarity.

positioned immediately over the ring centre of the other, and conversely (Hunter, 1994); this condition corresponds to an offset of *ca* 2.5 Å for a single benzenoid ring.

Thus in compound (6c), the (N31, C32–C36) rings in the molecular units at  $(x, y, z)$  and  $(-x, -y, -z)$  exhibit a perpendicular separation of 3.58 Å and an offset of 2.52 Å, close to the ideal; at the same time, the corresponding rings at  $(x, y, z)$  and  $(1 - x, -y, -z)$  show separation and offset values of 3.65 and 1.44 Å, respectively. These values indicate that the (N31, C32–C36) rings in different molecular units, and in different [112] chains, form a parallel stack along the [100] direction with nearly constant perpendicular separation, but with alternating values of the centroid offset. A similar centrosymmetric motif, this time forming an isolated pair rather than part of a continuous stack, is found in the (C21–C26) rings of the bisphenols at  $(x, y, z)$  and  $(1 - x, 1 - y, 2 - z)$ , where the perpendicular separation is 3.43 Å and the offset is 2.52 Å, again close to ideal for an attractive  $\pi$ - $\pi$  interaction between parallel benzenoid rings.

### 3.4. Molecular dimensions and conformations

**3.4.1. Conformations of the bisphenol components.** The heavy-atom skeleton of  $O_2S(C_6H_4OH)_2$  can, in principle, adopt a conformation of  $C_{2v}$  symmetry or of any subgroup of  $C_{2v}$ . Since the independent rotations of the two aryl rings relative to the central  $C_2SO_2$  core of this molecular building block do not alter the positions of the hydroxyl O atoms relative to this central core, then all points in the resulting two-dimensional conformational space should be accessible without affecting the intermolecular hydrogen bonding. However, the structures of compounds (5), (6) and (7) reported here, along with those of pure  $O_2S(C_6H_4OH)_2$  (Glidewell & Ferguson, 1996), as well as the adducts of this bisphenol with HMTA (Coupar *et al.*, 1997) and its salts with

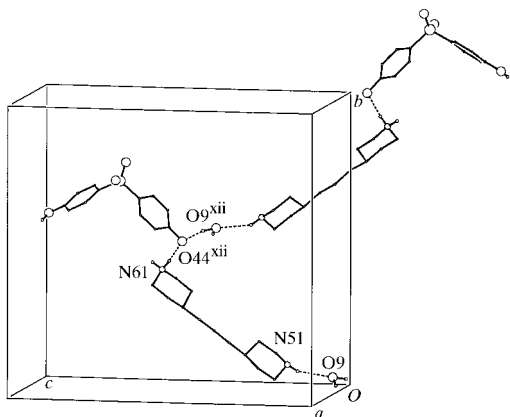


Fig. 20. View of part of the crystal structure of (7) showing the spiral chain along [010] [symmetry code: (xii)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ ]. H atoms bonded to C are omitted for the sake of clarity.

piperazine (Coupar *et al.*, 1996b) and cyclam (Ferguson *et al.*, 1998a), show very clear conformational preferences. So, far from the conformations being randomly distributed, there is a clear preference for conformations in which one or both of the aryl rings are virtually coplanar with a neighbouring C–S=O fragment, with the formation of nearly planar  $S(5) H-C-C-S=O$  ring motifs. The nonbonded C–H...O interactions within these units should not be regarded as hydrogen bonds, as the C–H...O angles are typically around  $105^\circ$ . Rather, these are attractive, purely electrostatic interactions between acidic aromatic C–H bonds, polarized  $C^--H^+$ , and highly polar S=O bonds, polarized  $S^+=O^-$ . Where both aryl rings participate in such interactions with the same S=O bond, the overall heavy-atom conformation of the bisphenol must be close to  $C_s$  molecular symmetry, while if each aryl ring interacts with a different S=O bond, the overall conformation is close to  $C_2$  symmetry.

Thus in compounds (6a), (6b), (6c) and (6d) the conformation of the bisphenol is close to  $C_2$ , while in compound (5) it is close to  $C_s$ ; in compound (7) the conformations of both the independent ions are close to  $C_s$ . In pure (2), and in the salt formed with cyclam, the heavy-atom conformations are close to  $C_2$ ; in the HMTA adduct the bisphenol component lies across a crystallographic mirror plane so that it has exact  $C_s$  symmetry; and in the salt with piperazine the heavy-atom conformation of the bisphenolate is close to  $C_s$ .

**3.4.2. Conformations of the diamine components.** The highest possible point symmetry of 4,4'-bipyridyl (3a) is  $D_{2h}$  (*mmm*); while for the extended-reach derivatives (3b)–(3d), the maximum point symmetries are  $C_{2h}$  (*2/m*),  $C_{2h}$  and  $C_s$  (*m*), respectively. Despite this, the bipyridyl components in each of (6a) and (6b) all lie in general positions, so that none of the potential molecular symmetry is utilized. By contrast, 4,4'-bipyridyl lies across centres of inversion in its adduct with ferrocene-1,1'-diylbis(diphenylmethanol) (Glidewell *et al.*, 1994) while one third of the 4,4'-bipyridyl molecules in the adduct with 1,1,1-tris(4-hydroxyphenyl)ethane also lie across centres of inversion (Bényei *et al.*, 1998). Similarly, in pure (3c) the molecules lie across centres of

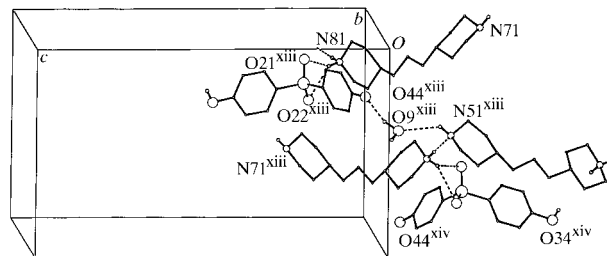


Fig. 21. View of part of the crystal structure of (7), showing the 'chain of rings' parallel to [100]. H atoms bonded to C are omitted for the sake of clarity. Symmetry codes: (xiii)  $\frac{1}{2} + x, \frac{1}{2} - y, -z$ ; (xiv)  $1 + x, y, z$ .

inversion (Ide *et al.*, 1995), as do the molecules of (3b) in the 1:1 adduct with 7,7,8,8-tetracyano-*p*-quinodimethane (Ashwell *et al.*, 1983). In (6c) and (6d) the aliphatic spacer unit adopts the extended-chain, all *transoid* conformation (Table 3), but in each compound the inclination of the pyridyl rings to the mean plane containing this spacer unit effectively destroys any molecular symmetry. In compound (7) the piperidine rings all adopt the chair conformation with the chain-extended  $-(\text{CH}_2)_3-$  spacer units in equatorial sites: the unprotonated N atoms N51 and N71 both have the N—H bond equatorial and the lone pair axial.

**3.4.3. Molecular dimensions.** The bond lengths found in compounds (5), (6) and (7) (Table 3) are generally typical of their types (Allen *et al.*, 1987). It should, however, be noted that the C—O(H) bonds are consistently longer than their C—O<sup>−</sup> counterparts, and that the C—N bonds also show a systematic variation with their local hydrogen-bonding environment. We have noted previously in related systems that C—N bonds are lengthened if the N atom acts as a hydrogen-bond acceptor (Coupar *et al.*, 1997) and, further, that where proton transfer to N takes place, the C—N bond length shows a systematic variation with the degree of proton transfer (Ferguson *et al.*, 1998a). The C—N bond lengths in compound (7) provide an elegant test of this since each of the four independent N atoms exhibits different hydrogen-bonding behaviour. Of the two neutral N atoms, N51 acts as both donor and acceptor of hydrogen bonds, while N71 acts only as an acceptor; of the two cationic N atoms, which cannot of course act as hydrogen-bond acceptors, N61 acts a double donor and N81 as a triple donor. Protonation at N increases the neighbouring C—N bond length, while for both neutral and cationic N acceptance of hydrogen bonds causes an increase in C—N bond length and donation of hydrogen bonds causes a decrease in C—N bond length (Table 3).

#### 4. General comments and conclusions

The results presented here confirm the deduction made previously from more limited data that where proton transfer occurs to generate a bisphenolate anion a major mode of chain formation involves bisphenolate anions linked by O—H $\cdots$ O<sup>−</sup> hydrogen bonds. On the other hand, in the absence of proton transfer from the bisphenol to the diamine the principal mode of chain formation will involve alternation of double-donor bisphenols and double-acceptor diamines linked by O—H $\cdots$ N hydrogen bonds; however, this is now augmented by chain formation by neutral bisphenols linked by O—H $\cdots$ O=S hydrogen bonds, as in compound (5).

In compounds (6a)–(6d), 4,4'-bipyridyl and its chain-extended analogues all act as double acceptors in O—H $\cdots$ N hydrogen bonds. Although 4,4'-bipyridyl acts similarly as a double acceptor in the 3:2 adducts formed with 1,3,5-trihydroxybenzene (Coupar *et al.*, 1996a) and

with 1,1,1-tris(4-hydroxyphenyl)ethane (Bényei *et al.*, 1998), its hydrogen-bonding behaviour is not readily predictable. Thus in the 1:1 adduct formed with phenylphosphonic acid, 4,4'-bipyridyl is mono-protonated but the unprotonated N atom takes no part in the hydrogen bonding (Ferguson *et al.*, 1998a), while in the 1:1 adduct formed with ferrocene-1,1'-diylbis(diphenylmethanol), one half of the bipyridyl molecules act as double acceptors of O—H $\cdots$ N hydrogen bonds, while the other half are merely guests within the structure and participate in no hydrogen bonds at all (Glidewell *et al.*, 1994).

A noteworthy feature of the structure of compound (7) is the formation of chains where the principal mode of intermolecular aggregation involves the formation of N—H $\cdots$ N hydrogen bonds. The formation of such hydrogen bonds in systems of this type, other than intramolecularly as in protonated cyclam (Ferguson *et al.*, 1998b), is extremely uncommon. Piperazine with O<sub>2</sub>S(C<sub>6</sub>H<sub>4</sub>OH)<sub>2</sub> is doubly protonated (Coupar *et al.*, 1996b), so that there are no N atoms capable of acting as hydrogen-bond acceptors, while with S(C<sub>6</sub>H<sub>4</sub>OH)<sub>2</sub> (Coupar *et al.*, 1996c) and CH<sub>3</sub>C(C<sub>6</sub>H<sub>4</sub>OH)<sub>3</sub> (Ferguson *et al.*, 1997), piperazine is unprotonated and acts as an acceptor in O—H $\cdots$ N hydrogen bonds, but without formation of N—H $\cdots$ N hydrogen bonds. Similarly, 1,2-diaminoethane generally acts as an acceptor of O—H $\cdots$ N hydrogen bonds and less frequently as a donor in N—H $\cdots$ O hydrogen bonds, so that its N—H bonds often play no part in any hydrogen bonding (Ferguson *et al.*, 1998, 1998c).

The general weakness of N—H $\cdots$ N compared with O—H $\cdots$ O hydrogen bonds is well illustrated by a comparison of the crystal structures of the isoelectronic and isosteric pairs Ph<sub>3</sub>EOH and Ph<sub>3</sub>ENH<sub>2</sub> for both E = C and E = Si. Ph<sub>3</sub>COH forms almost perfectly tetrahedral tetramers in which the molecules are linked by O—H $\cdots$ O hydrogen bonds in which the four hydroxyl H atoms are mobile over the six O $\cdots$ O edges of the tetrahedron (Ferguson *et al.*, 1992; Aliev *et al.*, 1998), while Ph<sub>3</sub>CNH<sub>2</sub> is monomeric with no intermolecular hydrogen bonds, despite the availability of potential donors and acceptors (Glidewell & Ferguson, 1994). Similarly, Ph<sub>3</sub>SiOH forms cyclic tetramers constructed using O—H $\cdots$ O hydrogen bonds (Puff *et al.*, 1991), but Ph<sub>3</sub>SiNH<sub>2</sub> exhibits no hydrogen bonding (Ruhlandt-Senge *et al.*, 1993). That N—H $\cdots$ N hydrogen bonds play such a major role in the supramolecular structure of compound (7) is an excellent illustration of the additional strength of ionic hydrogen bonds compared with those in which both donor and acceptor are neutral (Aakeröy & Seddon, 1993; Gilli *et al.*, 1994); each molecule of the diamine in compound (7) contains one protonated N atom and one neutral N atom ideal for maximizing the number of ionic N<sup>+</sup>—H $\cdots$ N hydrogen bonds. It is unclear why the molecular building block (4) forms these singly protonated cations so readily



whereas, so far, piperazine has been observed only in the neutral and doubly protonated forms when co-crystallized with bisphenols, although monoprotonated piperazine has been structurally characterized in several salts (Tyršelová *et al.*, 1995; Feng *et al.*, 1995).

The predominant mode of supramolecular aggregation between neutral bisphenols, acting as double donors of hydrogen bonds, and neutral diamines, acting as double acceptors, is the formation of continuous chains, as described both here and elsewhere (Mahmoud & Wallwork, 1979; Coupar *et al.*, 1997). This is so even when the disposition of the donor and acceptor sites on the molecular cores is appropriate for the formation of small cyclic species: for example, the combination of an angular disposition of donor sites, as in the bisphenols  $X(\text{C}_6\text{H}_4\text{OH})_2$  ( $X = \text{O}, \text{S}, \text{SO}_2, \text{CMe}_2$ ) which are approximately tetrahedral at the spacer  $X$ , with a linear disposition of the acceptor sites, as in DABCO, is appropriate for the formation of a finite molecular pentagon of  $A''_2L''_3$  type, where  $A''$  and  $L''$  represent  $n$ -fold donors or acceptors which are angular or linear, respectively (Stang & Olenyuk, 1997). Similarly, the same type of angular bisphenol in combination with HMTA, where the acceptor sites are tetrahedrally disposed, might have been expected to form a molecular square of  $A''_2A''_2$  type. Such finite complexes are known, however, in hydrogen-bonded systems: molecular squares are formed in adducts of nitroanilines with triphenylphosphine oxide (Etter *et al.*, 1991), and both squares and boxes are formed in adducts of sulfonamides with triarylphosphine oxides and triarylsarsine oxides (Ferguson & Glidewell, 1988; Ferguson *et al.*, 1989).

RMG thanks EPSRC (UK) for financial support. We are indebted to Dr J. F. Gallagher and Dublin City University for funds to purchase the X-ray tube used in the data collections for compounds (5), (6a), (6b), (6c) and (7).

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