Acta Cryst. (1999). B**55**, 591–600

Crystal engineering using bisphenols and trisphenols. Complexes with 1,10-phenanthroline: hydrogen-bonded chains in adducts with 4,4′-biphenol (1/1) and 4,4′-sulfonyldiphenol (2/3), π–π stacked chains in the (1/2) adduct with 4,4′-thiodiphenol, and pairwise-interwoven nets in 1,1,1-tris(4-hydroxyphenyl)ethane–1,10-phenanthroline–methanol (1/1/1)

George Ferguson,[a] Christopher Glidewell[b]* and Emma S. Lavender[b]

[a]*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and* [b]*School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland. E-mail: cg@st-andrews.ac.uk*

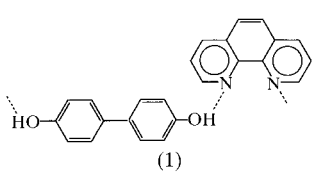
(*Received 28 August 1998; accepted 9 February 1999*)

Abstract

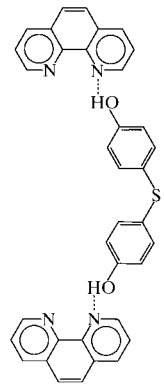
In 4,4′-biphenol–1,10-phenanthroline (1/1) [systematic name: 4,4′-biphenyldiol–1,10-phenanthroline (1/1)] the diphenol molecules lie across centres of inversion and the phenanthroline molecules lie across twofold rotation axes; the phenanthroline molecules act as chain-building units and the molecular components are linked into steeply zigzag $C(16)$ chains parallel to [101] by means of O—H···N hydrogen bonds. In the structure of 4,4′-thiodiphenol–1,10-phenanthroline (1/2) the phenanthroline molecules act as chain-terminating units; the supramolecular aggregation is finite, with the bisphenol linked to each phenanthroline molecule by means of a single O—H···N hydrogen bond. π–π stacking interactions between the phenanthroline molecules in neighbouring hydrogen-bonded aggregates serve to link these aggregates into a continuous two-dimensional array. The phenanthroline molecules in 4,4′-sulfonyldiphenol–1,10-phenanthroline (2/3) play two roles: molecules in general positions act as chain-terminating units and are linked to the sulfonyldiphenol molecules by means of three-centre O—H···$(N)_2$ hydrogen bonds, while those lying across twofold rotation axes act as chain builders and are linked to two different sulfonyldiphenol molecules by means of a two-centre O—H···N hydrogen bond in each case; the resulting U-shaped five-component aggregates are further linked by C—H···O═S hydrogen bonds into a $C_3^3(17)[R_2^2(12)]$ 'chain of rings' along [001]. In 1,1,1-tris(4-hydroxyphenyl)ethane–1,10-phenanthroline–methanol (1/1/1) [systematic name: 4,4′,4″-ethylidynetriphenol–1,10-phenanthroline–methanol (1/1/1)] the phenanthroline molecules again act as chain-terminating units: the trisphenol molecules and the methanol molecules are linked by O—H···O hydrogen bonds into two-dimensional nets built from $R_6^6(42)$ rings, and pairs of these nets are interwoven. The formation of each net utilizes two hydroxyl groups per trisphenol molecule as hydrogen-bond donors and the remaining hydroxyl group acts as donor to the phenanthroline molecule in a three-centre O—H···$(N)_2$ hydrogen bond.

1. Introduction

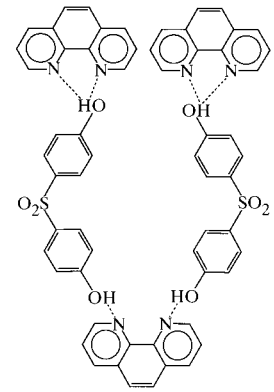
In supramolecular structures dominated by hydrogen bonding the structural role of 4,4′-bipyridyl, in which the separation of the two hard (Braga *et al.*, 1995) hydrogen-bond acceptors is essentially fixed at *ca* 7.2 Å, is primarily that of a builder of chains or large rings (Bényei *et al.*, 1998; Coupar *et al.*, 1996; Ferguson *et al.*, 1999; Sharma & Zaworotko, 1996). In contrast the 2,2′ isomer, where there is effectively free rotation about the central C—C bond with a corresponding variability in both the distance between, and the mutual orientation of, the two hydrogen-bond acceptors, often behaves as a pendent unit with a *trans* planar conformation (Lavender *et al.*, 1998*a*,*b*). 1,10-Phenanthroline is analogous to 2,2′-bipyridyl in terms of the three-bond separation of the hydrogen-bond acceptor atoms, but is constrained by the presence of the additional carbocyclic ring to have the separation of the N atoms fixed at *ca* 2.8 Å; the nitrogen lone pairs point inwards, along two of the edges of an equilateral triangle of side *ca* 2.8 Å. The behaviour of this diamine in hydrogen-bonded systems in thus not readily predictable; it could act as a chain-building unit, with the introduction of very sharp turns in the chain direction, or it could act as a chain-terminating unit by formation of a three-centre hydrogen bond in which a single donor unit *D*—H interacts with both of the nitrogen acceptors, thus *D*—H···$(N)_2$. In order to delineate the behaviour patterns of 1,10-phenanthroline in hydrogen-bonded systems with reasonably strong hydrogen-bond donors, we have now investigated its behaviour with a representative selection of bisphenols, 4,4′-biphenol, HOC_6H_4-C_6H_4OH, 4,4′-thiodiphenol, $S(C_6H_4OH)_2$, and 4,4′-sulfonyldiphenol, $O_2S(C_6H_4OH)_2$, and with the trisphenol 1,1,1-tris(4-hydroxyphenyl)ethane, CH_3C-$(C_6H_4OH)_3$, to give the products (1)–(4).



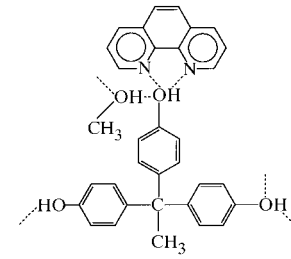
(1)



(2)



(3)



(4)

2. Experimental

2.1. *Synthesis*

Aliquots of 1,10-phenanthroline and the appropriate bis- or trisphenol were separately dissolved in methanol, and the solutions were mixed to give molar ratios of phenol:phenanthroline in the range 1:2 to 2:1. The solutions were then set aside to crystallize, producing analytically pure samples of compounds (1)–(4). Within the range of reaction stoichiometries investigated only a single product was obtained from each phenol. Analyses: compound (1) found C 78.6, H 5.0, N 7.7, $C_{24}H_{18}N_2O_2$ requires C 78.7, H 5.0, N 7.7%; compound (2) found C 74.6, H 4.2, N 9.6, $C_{36}H_{26}N_4O_2S$ requires C 74.7, H 4.5, N 9.7%; compound (3) found C 69.3, H 4.2, N 8.0, $C_{60}H_{44}N_6O_8S_2$ requires C 69.2, H 4.3, N 8.1%; compound (4) found C 76.4, H 5.8, N 5.4, $C_{33}H_{30}N_2O_4$ requires C 76.4, H 5.8, N 5.4%. 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 collection and refinements are summarized in Table 1. For compounds (1) and (3), the systematic absences permitted the choice of space groups *Cc* or *C*2/*c*; for each compound space group *C*2/*c* was chosen and confirmed by successful structure solution and refinement. Compound (2) is triclinic and space group $P\bar{1}$ was chosen and confirmed by the successful refinement. For compound (4) the space group *Pbca* was uniquely assigned from the systematic absences.

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 *ORTEP*II (Johnson, 1976) and *PLATON*. Details of the hydrogen-bonding and selected molecular dimensions are given in Tables 2, 3 and 4.† Figs. 1, 3, 6 and 8 show the asymmetric units in compounds (1)–(4), and Figs. 2, 4, 5, 7 and 9 show aspects of the connectivity within the crystal structures of these compounds.

3. Results and discussion

3.1. *Co-crystallization behaviour*

Co-crystallization of methanol solutions containing 1,10-phenanthroline and one of 4,4′-biphenol, 4,4′-thiodiphenol, 4,4′-sulfonyldiphenol or 1,1,1-tris(4-hydroxyphenyl)ethane, with molar ratios of phenol: phenanthroline in the range 1:2 to 2:1, yielded a single analytically pure product for each phenol. With 4,4′-biphenol, a 1:1 product $HOC_6H_4C_6H_4OH{\cdot}C_{12}H_8N_2$, (1), was obtained, whereas with 4,4′-thiodiphenol and 4,4′-sulfonyldiphenol, products of 1:2 and 2:3 stoichiometry, respectively, were formed: $S(C_6H_4OH)_2{\cdot}2C_{12}H_8N_2$, (2), and $2O_2S(C_6H_4OH)_2{\cdot}3C_{12}H_8N_2$, (3). With 1,1,1-tris(4-hydroxyphenyl)ethane, a methanol-solvated 1:1 product was isolated: $CH_3C(C_6H_4OH)_3{\cdot}C_{12}H_8N_2{\cdot}$MeOH, (4).

3.2. *Description of the structures*

3.2.1. *Compound (1)*. Compound (1) crystallizes in space group *C*2/*c* with $Z' = 0.5$ (Brock & Dunitz, 1994): the 4,4′-biphenol molecules lie across centres of inversion and the 1,10-phenanthroline molecules lie across twofold axes. The biphenol molecules act as double donors of O—H···N hydrogen bonds and each phenanthroline molecule acts as a double acceptor (Fig. 1). The resulting supramolecular structure is dominated by the formation of steeply zigzag chains, stacked in register along the [010] direction (Fig. 2). The biphenol

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF0005). Services for accessing these data are described at the back of the journal.

Table 1. *Experimental details*

	(1)	(2)	(3)	(4)
Crystal data				
Chemical formula	$C_{12}H_{10}O_2{\cdot}C_{12}H_8N_2$	$C_{12}H_{10}O_2S{\cdot}2C_{12}H_8N_2$	$2C_{12}H_{10}O_4S{\cdot}{\cdot}3C_{12}H_8N_2$	$C_{20}H_{18}O_3{\cdot}{\cdot}C_{12}H_8N_2{\cdot}CH_4O$
Chemical formula weight	366.4	578.69	1041.13	518.59
Cell setting	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$C2/c$	$P\bar{1}$	$C2/c$	$Pbca$
a (Å)	13.0288 (17)	7.7342 (5)	15.8692 (16)	22.811 (3)
b (Å)	12.1865 (10)	13.3624 (14)	24.3728 (17)	22.029 (3)
c (Å)	12.0778 (12)	14.9843 (11)	13.0952 (9)	10.7965 (10)
α (°)	—	110.514 (6)	—	—
β (°)	105.199 (9)	95.195 (6)	102.362 (8)	—
γ (°)	—	95.895 (7)	—	—
V (Å^3)	1850.6 (3)	1429.3 (2)	4947.5 (7)	5425.3 (12)
Z	4	2	4	8
D_x (Mg m^{-3})	1.315	1.345	1.398	1.270
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.7107	0.7107	0.7107	0.7107
No. of reflections for cell parameters	25	25	25	25
θ range (°)	9.82–18.79	9.64–18.56	10.21–18.28	9.93–15.7
μ (mm^{-1})	0.085	0.155	0.175	0.084
Temperature (K)	294 (1)	294 (1)	294 (1)	294 (1)
Crystal form	Lath	Plate	Plate	Plate
Crystal size (mm)	0.42 × 0.31 × 0.12	0.42 × 0.35 × 0.22	0.42 × 0.38 × 0.10	0.42 × 0.42 × 0.14
Crystal colour	Colourless	Colourless	Colourless	Colourless
Data collection				
Diffractometer	Enraf–Nonius CAD-4	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	$\theta/2\theta$ scans
Absorption correction	None	Gaussian	Gaussian	None
T_{min}	—	0.9455	0.9367	—
T_{max}	—	0.9696	0.9833	—
No. of measured reflections	1748	5184	4636	5200
No. of independent reflections	1678	5184	4434	4861
No. of observed reflections	915	3431	3182	2178
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.012	—	0.006	0.008
θ_{max} (°)	25.19	25.2	25.14	25.15
Range of h, k, l	$-15 \rightarrow h \rightarrow 15$ $0 \rightarrow k \rightarrow 14$ $0 \rightarrow l \rightarrow 14$	$-9 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 16$ $-17 \rightarrow l \rightarrow 16$	$-18 \rightarrow h \rightarrow 18$ $0 \rightarrow k \rightarrow 29$ $0 \rightarrow l \rightarrow 15$	$0 \rightarrow h \rightarrow 27$ $0 \rightarrow k \rightarrow 26$ $0 \rightarrow l \rightarrow 12$
No. of standard reflections	3	3	3	3
Frequency of standard reflections	Every 120 min	Every 120 min	Every 120 min	Every 120 min
Intensity decay (%)	0	0	1.7	1.6
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.0334	0.0351	0.0408	0.0388
$wR(F^2)$	0.0989	0.1004	0.1040	0.1075
S	0.976	1.035	1.034	0.874
No. of reflections used in refinement	1678	5184	4434	4861
No. of parameters used	129	391	346	358
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0561P)^2 + 0.0505P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 1.3074P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0580P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.001	<0.001	0.001	<0.001
$\Delta\rho_{max}$ (e Å^{-3})	0.140	0.203	0.221	0.158
$\Delta\rho_{min}$ (e Å^{-3})	−0.127	−0.203	−0.298	−0.143
Extinction method	*SHELXL*97 (Sheldrick, 1997*b*)	*SHELXL*97 (Sheldrick, 1997*b*)	*SHELXL*97 (Sheldrick, 1997*b*)	*SHELXL*97 (Sheldrick, 1997*b*)

Table 1 (*cont.*)

	(1)	(2)	(3)	(4)
Extinction coefficient	0.0049 (9)	0.030 (2)	0.00124 (18)	0.0025 (3)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs				
Data collection	*CAD*-4-*PC Software* (Enraf–Nonius, 1992)	*CAD*-4-*PC Software* (Enraf–Nonius, 1992)	*CAD*-4-*PC Software* (Enraf–Nonius, 1992)	*CAD*-4-*PC Software* (Enraf–Nonius, 1992)
Cell refinement	*SET*4 and *CELDIM* (Enraf–Nonius, 1992)	*SET*4 and *CELDIM* (Enraf–Nonius, 1992)	*SET*4 and *CELDIM* (Enraf–Nonius, 1992)	*SET*4 and *CELDIM* (Enraf–Nonius, 1992)
Data reduction	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)
Structure solution	*SHELXS*97 (Sheldrick, 1997*a*)	*SHELXS*97 (Sheldrick, 1997*a*)	*SHELXS*97 (Sheldrick, 1997*a*)	*SHELXS*97 (Sheldrick, 1997*a*)
Structure refinement	*NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*b*)	*NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*b*)	*NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*b*)	*NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*b*)
Preparation of material for publication	*NRCVAX*96, *SHELXL*97 and *PRPCIF*97 (Ferguson, 1997)	*NRCVAX*96, *SHELXL*97 and *PRPCIF*97 (Ferguson, 1997)	*NRCVAX*96, *SHELXL*97 and *PRPCIF*97 (Ferguson, 1997)	*NRCVAX*96, *SHELXL*97 and *PRPCIF*97 (Ferguson, 1997)

molecules lying across the inversion centres at ($\frac{1}{4}$, $\frac{1}{4}$, 0) and ($\frac{3}{4}$, $\frac{1}{4}$, $\frac{1}{2}$) both act as donors to a phenanthroline molecule lying across the twofold axis ($\frac{1}{2}$, y, $\frac{1}{4}$), and propagation of these hydrogen bonds generates a $C(16)$ chain (Bernstein *et al.*, 1995) running parallel to the [101] direction.

3.2.2. *Compound (2)*. The asymmetric unit of compound (2) contains one molecule of 4,4′-thiodiphenol and two molecules of 1,10-phenanthroline (Fig. 3). Each hydroxyl group of the bisphenol acts as hydrogen-bond donor to one N atom of a phenanthroline molecule; O14 acts as donor towards N31, and O24 acts as donor towards N51. The two other N atoms, one in each phenanthroline molecule, take no part in the hydrogen bonding: there are no soft hydrogen bonds involving N41 or N61. Hence, with each phenanthroline molecule utilizing one hydroxyl group, the 1:2 stoichiometry means that the hydrogen bonding is finite and cannot give rise to any chain formation.

Although the dihedral angle between the two independent aromatic rings of the bisphenol is 74.0 (1)°, the mean planes of the two independent phenanthroline molecules in the asymmetric unit (molecule *A* containing N31 and N41, and molecule *B* containing N51 and N61) are almost parallel [dihedral angle between planes 3.0 (1)°]; multiple, although weak, π–π interactions between phenanthroline molecules in neighbouring hydrogen-bonded aggregates separated by *ca* 3.6 Å serve to link these aggregates into a continuous two-dimensional array.

Phenanthroline molecule *A* at (x, y, z) overlaps and π-stacks with phenanthroline molecule *B* at (x, y, 1 + z), and repetition of this interaction generates by translation a chain running parallel to the [001] direction (Fig.

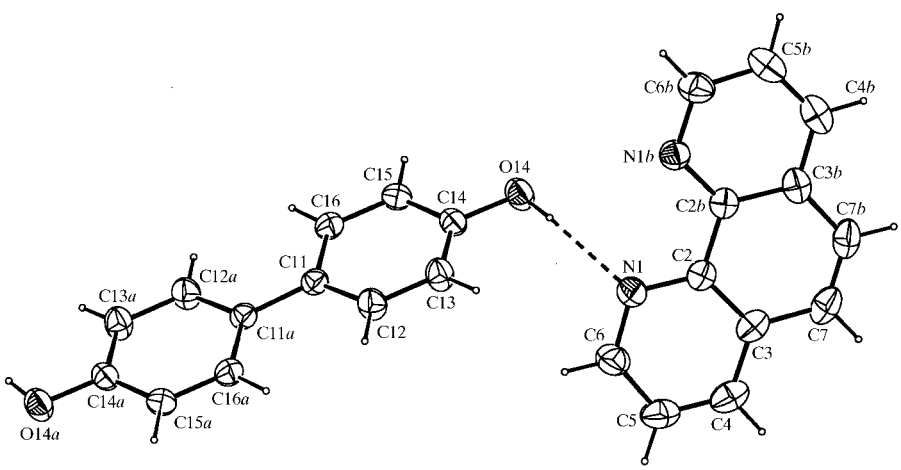


Fig. 1. The molecular components of compound (1), showing the asymmetric unit and the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 2. *Hydrogen-bond dimensions (Å, °)*

(1)			
O14···N1	2.878 (2)	O14—H14···N1	159
C12···O14^{i}	3.403 (2)	C12—H12···O14^{i}	148
(2)			
O14···N31	2.741 (2)	O14—H14···N31	153
O24···N51	2.757 (2)	O24—H24···N51	151
(3)			
O14···N31	2.861 (2)	O14—H14···N31	171
O24···N41	2.896 (2)	O24—H24···N41	159†
O24···N51	3.015 (3)	O24—H24···N51	124†
C15···O12^{ii}	3.406 (3)	C15—H15···O12^{ii}	153
(4)			
O51···O14	2.708 (3)	O51—H51···O14	170
O24···O34^{iii}	2.824 (2)	O24—H24···O34^{iii}	169
O34···O51^{iv}	2.633 (2)	O34—H34···O51^{iv}	165
O14···N41	2.835 (3)	O14—H14···N41	150‡
O14···N412	3.112 (3)	O14—H14···N412	137‡
C44···O24^{v}	3.432 (4)	C44—H44···O24^{v}	156

Symmetry codes: (i) $x, 1-y, -\frac{1}{2}+z$; (ii) $1-x, 1-y, -z$; (iii) $x, y, -1+z$; (iv) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$. † N41 and N51 are the acceptors in a three-centre hydrogen bond; the angle N41···H24···N51 is 72°. ‡ N41 and N412 are the acceptors in a three-centre hydrogen bond; the angle N41···H14···N412 is 72°.

4). Similarly, phenanthroline *A* at (x, y, z) also interacts with phenanthroline *B* at $(1 + x, y, 1 + z)$; the effect of this is to produce a continuous stack of phenanthroline molecules, parallel to [100], with types *A* and *B* alternating along the stack (Fig. 5). These two chain-forming motifs thus generate a two-dimensional sheet normal to (010).

3.2.3. *Compound (3)*. In compound (3), the hydrogen-bonded molecular aggregate contains two molecules of 4,4′-sulfonyldiphenol and three molecules of 1,10-phenanthroline; the whole aggregate lies across a twofold rotation axis so that the asymmetric unit contains one complete molecule of each component lying in general positions together with one half of a phenanthroline molecule lying across the axis (Fig. 6). The combination of O—H···N hydrogen bonds and π–π stacking interactions between phenanthroline molecules within the molecular aggregate gives this aggregate the shape of a molecular pincer (Fig. 7).

The phenanthroline lying across the rotation axis acts as a double acceptor of O—H···N hydrogen bonds, one from each of two bisphenol molecules, with O14 acting as donor to N31; the two bisphenol molecules are thus bound to the same edge of this phenanthroline mole-

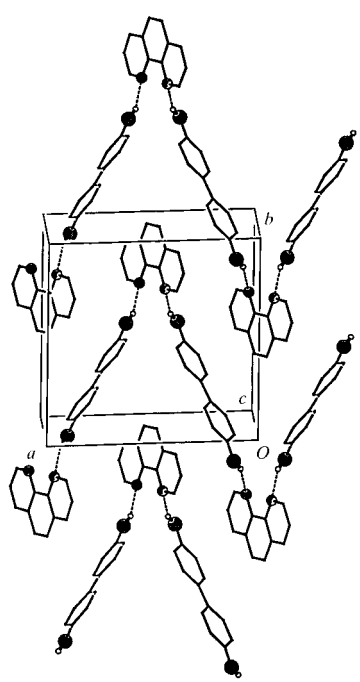


Fig. 2. View of part of the crystal structure of compound (1) showing the stacking of the [101] chains. H atoms bonded to C are omitted for the sake of clarity.

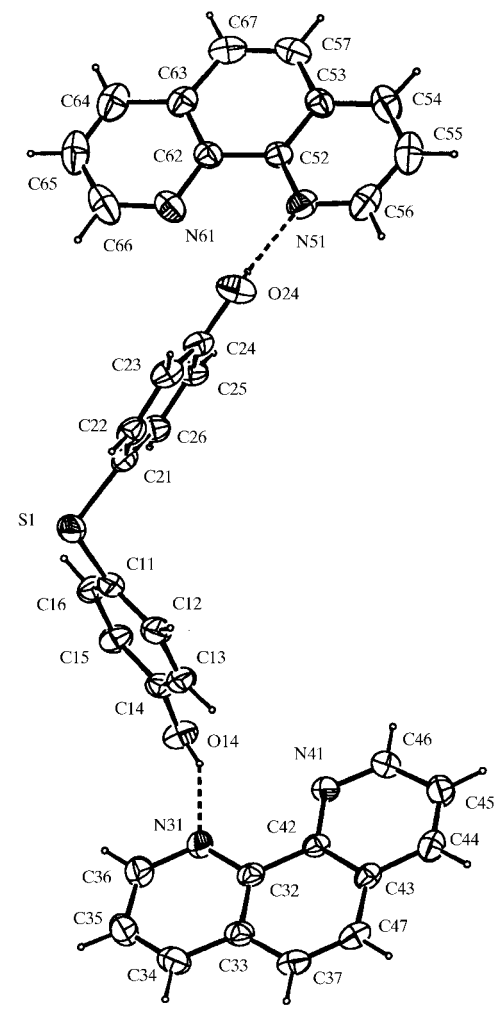


Fig. 3. The asymmetric unit of compound (2), showing the atom-labelling scheme. Atoms are depicted as in Fig. 1.

cule, forming a U-shaped fragment. The other hydroxyl group of the bisphenol, that containing O24, forms a three-centred hydrogen bond employing both N41 and N51 as acceptors. The interaction with N41 is clearly much the stronger, as judged from both the O···N and H···N distances, and the O—H···N angle. The sum of the angles around H24 is 355°, close to the most commonly observed value of 360° (Jeffrey & Saenger, 1991).

The two phenanthroline molecules in this hydrogen-bonded aggregate that are related by the twofold rotation axis describe parallel planes, and their positions are such that there are very extensive π–π stacking interactions between them (Fig. 7): the phenanthroline units are themselves very slightly puckered, but the mean perpendicular distance between them is only *ca* 3.45 Å. It is possible that these π–π interactions play the key role in establishing the very compact conformation of the supramolecular aggregate defined by the hard (Braga *et al.*, 1995) hydrogen bonds.

In addition to the hydrogen bonds of O—H···N type and the π–π stacking interactions, there is one further type of intermolecular bonding. Soft (Braga *et al.*, 1995) hydrogen bonds, of C—H···O═S type, serve to link the hard hydrogen-bonded aggregates into continuous chains. Carbon C15 in the bisphenol at (x, y, z) acts as donor to the sulfone O atom O12 at $(1-x, 1-y, -z)$, while C15 at $(1-x, 1-y, -z)$ acts as donor to O12 at (x, y, z), thus generating a centrosymmetric $R_2^2(12)$ ring (Bernstein *et al.*, 1995) lying around the inversion centre at $(\frac{1}{2}, \frac{1}{2}, 0)$. The symmetry-related C15 in the same hydrogen-bonded aggregate is at $(1-x, y, \frac{1}{2}-z)$ and this C atom acts as donor to O12 in the bisphenol at $(x, 1-y, \frac{1}{2}+z)$, generating a second $R_2^2(12)$ ring centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Of these two hydrogen-bonded rings, the first links the aggregate lying across the twofold axis at $(\frac{1}{2}, y, \frac{1}{4})$ to that lying across $(\frac{1}{2}, y, -\frac{1}{4})$, while the second ring links the aggregates generated by twofold axes at $(\frac{1}{2}, y, \frac{1}{4})$ and $(\frac{1}{2}, y, \frac{3}{4})$; propagation of these hydrogen bonds by translation generates $C_3^3(17)$ chains running parallel to [001], in which alternate U-shaped components have the

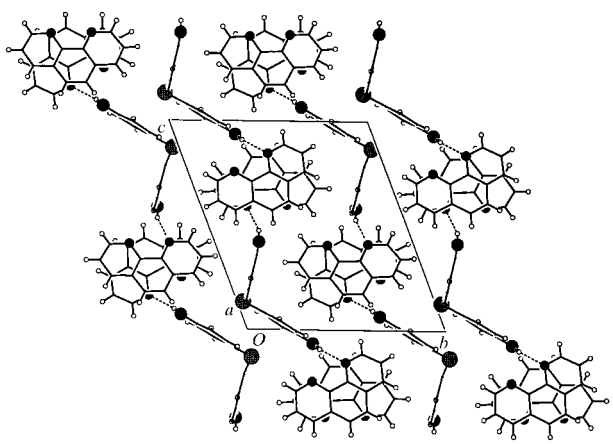


Fig. 4. View of part of the crystal structure of compound (2) showing the [001] chains.

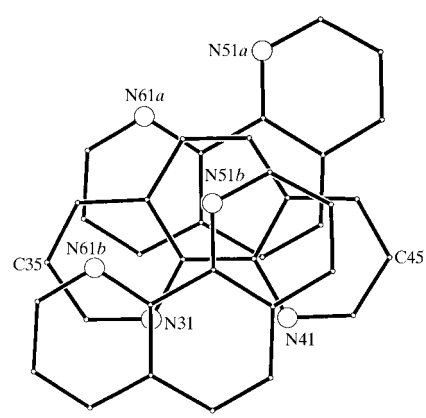


Fig. 5. Schematic view of the stacking of 1,10-phenanthroline molecules in compound (2). Atoms N31, N51*a* and N51*b* are in the molecules at (x, y, z), $(x, y, 1+z)$ and $(1+x, y, 1+z)$, respectively.

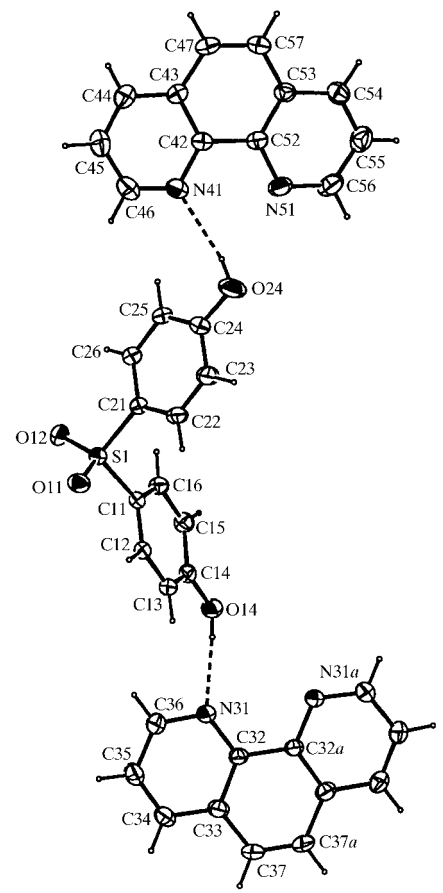


Fig. 6. The molecular components of compound (3), showing the asymmetric unit and the atom-labelling scheme. Atoms are depicted as in Fig. 1.

Table 3. *Selected molecular dimensions for the phenol components (Å, °)*

(1)			
C14—O14	1.364 (2)	C11—C11^{i}	1.484 (3)
O14—C14—C13	122.7 (2)	O14—C14—C15	118.7 (2)
(2)			
O14—C14	1.353 (2)	O24—C24	1.354 (2)
S1—C11	1.775 (2)	S1—C21	1.776 (2)
C11—S1—C21	106.28 (8)	O24—C24—C23	117.0 (2)
O14—C14—C13	122.9 (2)	O24—C24—C25	124.0 (2)
O14—C14—C15	118.3 (2)		
C11—S1—C21—C22	−139.8 (1)	C21—S1—C11—C12	88.1 (2)
C11—S1—C21—C26	47.0 (2)	C21—S1—C11—C16	−99.7 (2)
(3)			
O14—C14	1.352 (2)	O24—C24	1.350 (3)
S1—C11	1.755 (2)	S1—C21	1.750 (2)
S1—O11	1.442 (2)	S1—O12	1.443 (2)
C11—S1—C21	106.51 (9)	O11—S1—O12	117.75 (10)
O14—C14—C13	122.5 (2)	O24—C24—C23	116.2 (2)
O14—C14—C15	117.7 (2)	O24—C24—C25	123.7 (2)
O11—S1—C11—C12	2.0 (2)	O12—S1—C21—C26	−1.4 (2)
C11—S1—C21—C22	−67.3 (2)	C21—S1—C11—C12	118.1 (2)
C11—S1—C21—C26	114.8 (2)	C21—S1—C11—C16	−66.7 (2)
(4)			
C14—O14	1.376 (2)	C24—O24	1.370 (2)
C34—O34	1.380 (2)	O51—C51	1.406 (3)
C13—C14—O14	122.2 (2)	O14—C14—C15	118.3 (2)
C23—C24—O24	118.2 (2)	O24—C24—C25	122.6 (2)
C33—C34—O34	123.2 (2)	O34—C34—C35	117.7 (2)
C2—C1—C11—C12	−119.3 (2)	C2—C1—C11—C16	61.2 (2)
C2—C1—C21—C22	34.8 (2)	C2—C1—C21—C26	−146.9 (2)
C2—C1—C31—C32	−144.8 (2)	C2—C1—C31—C36	37.7 (2)

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, -z$.

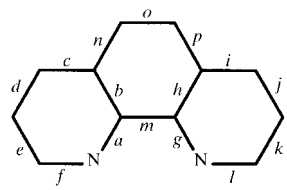
opposite orientation along [010], giving overall a $C_3^3(17)[R_2^2(12)]$ 'chain of rings' (Bernstein *et al.*, 1995).

3.2.4. *Compound (4)*. In the structure of compound (4) (Fig. 8), the 1,10-phenanthroline molecules do not act as chain builders; rather they act as chain terminators so that the overall supramolecular architecture can conveniently be described in terms of the network generated by O—H···O hydrogen bonding between the 1,1,1-tris(4-hydroxyphenyl)ethane and methanol molecules, from which the phenanthroline units are pendent. Atom O24 in the trisphenol at (x, y, z) acts as donor to atom O34 in the trisphenol at (x, y, $-1+z$), thus generating by translation a $C(12)$ chain running parallel to the [001] direction. Atom O34 in the trisphenol at (x, y, z) acts as donor to the methanol O atom O51 at ($-\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$) and this O atom in turn acts as donor to O14 in the trisphenol at ($-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$); repetition of these hydrogen bonds, through the action of a 2_1 screw axis parallel to [100], generates a $C_2^2(14)$ chain along [100]. The interaction of these chains, along [100] and [001], produces a continuous two-dimensional net parallel to (010) and built from a single type of $R_6^6(42)$ ring.

Within the two-dimensional net, O atoms atoms O34 and O51 act as both donors and acceptors of O—H···O hydrogen bonds, O24 acts only as a donor, and O14 acts only as an acceptor. There is a single hydroxyl H atom, H14, which is unused in the formation of this net, and oxygen O14 acts as donor to the pendent phenanthroline molecule, forming a three-centre O—H···N(2) hydrogen bond. As in compound (3), this three-centre system is clearly very asymmetric (Table 2) and the interaction of O14—H14 with N41 is much the stronger of the two: the sum of the bond angles at H14 is 359°.

The formation of this two-dimensional net utilizes only two trisphenol and two methanol molecules per unit cell, and hence four such nets are required to generate the entire structure. Of these four nets, the two

Table 4. *Bond lengths in the phenanthroline components (Å)*



	(1)†	(2)		(3)		(4)	Phenanthroline‡
		Molecule *A* (N31, N41)	Molecule *B* (N51, N61)	Molecule *A*† (N31)	Molecule *B* (N41, N51)		
a	1.353 (2)	1.361 (2)	1.350 (2)	1.357 (2)	1.352 (3)	1.350 (3)	1.359 (5)
b	1.406 (2)	1.406 (2)	1.406 (2)	1.411 (3)	1.412 (3)	1.406 (3)	1.406 (5)
c	1.398 (3)	1.405 (3)	1.396 (3)	1.401 (3)	1.405 (3)	1.405 (4)	1.417 (6)
d	1.349 (3)	1.359 (3)	1.352 (3)	1.350 (3)	1.349 (3)	1.350 (5)	1.356 (7)
e	1.391 (3)	1.390 (3)	1.385 (3)	1.392 (3)	1.392 (3)	1.387 (4)	1.396 (7)
f	1.330 (2)	1.314 (2)	1.322 (3)	1.325 (3)	1.317 (3)	1.313 (3)	1.313 (5)
g		1.358 (2)	1.351 (2)		1.354 (3)	1.350 (3)	
h		1.413 (2)	1.405 (2)		1.404 (3)	1.391 (3)	
i		1.401 (2)	1.390 (3)		1.399 (3)	1.399 (4)	
j		1.353 (3)	1.342 (3)		1.355 (3)	1.344 (4)	
k		1.386 (2)	1.394 (3)		1.395 (4)	1.373 (4)	
l		1.324 (2)	1.339 (3)		1.321 (3)	1.319 (3)	
m	1.444 (3)	1.441 (2)	1.445 (2)	1.448 (4)	1.446 (3)	1.438 (3)	1.454 (6)
n	1.430 (3)	1.424 (2)	1.416 (3)	1.431 (3)	1.426 (3)	1.426 (4)	1.426 (6)
o	1.335 (4)	1.342 (3)	1.340 (3)	1.337 (5)	1.340 (3)	1.326 (4)	1.331 (9)
p		1.427 (2)	1.424 (3)		1.431 (3)	1.429 (4)	

† Molecule lies across a twofold rotation axis, $a = g$ *etc.* ‡ Weighted average values (Nishigaki *et al.*, 1978).

which lie largely in the domain $0 < y < 0.5$ are mutually interwoven (Fig. 9), as are the two in the domain $0.5 < y < 1.0$; the weaving is thus of type {4, 2, 1} (Ferguson, Glidewell, Gregson & Meehan, 1998).

3.3. *Molecular conformations and dimensions*

3.3.1. *The phenol components*. In compound (1) the 4,4′-biphenol molecules lie across centres of inversion and the planes of the two aryl rings are thus parallel; these rings are not, however, necessarily coplanar and there is in fact a step of 0.169 (2) Å between their planes. The 4,4′-thiodiphenol molecules in compound (2), although potentially able to adopt a conformation having C_{2v} symmetry, or any subgroup of C_{2v}, do not in fact even approximate to C_2 or C_s symmetry, as judged from the C—S—C—C torsional angles defining the orientation of the aryl rings relative to the central CSC fragment (Table 3). By contrast, the 4,4′-sulfonyldiphenol molecules in compound (3) adopt almost exact C_2 symmetry; as frequently found for this bisphenol (Ferguson *et al.*, 1999), the conformation is dominated by the electrostatic interactions between the polar S═O bonds, polarized $S^{\delta+}$–$O^{\delta-}$, and the neighbouring aryl C—H bonds, polarized $C^{\delta-}$–$H^{\delta+}$, forming nearly planar *S*(5) ring motifs. The trisphenol component in compound (4) is very far from the optimum C_3 symmetry, as judged from the torsional angles between the aryl ring planes and the central molecular core planes.

3.3.2. *The 1,10-phenanthroline component*. The bond lengths in the phenanthroline components of compounds (1)–(4) are summarized in Table 4 along with weighted average values for 1,10-phenanthroline itself (space group *C*2, *Z* = 6; Nishigaki *et al.*, 1978). The pattern of these distances is extremely consistent over

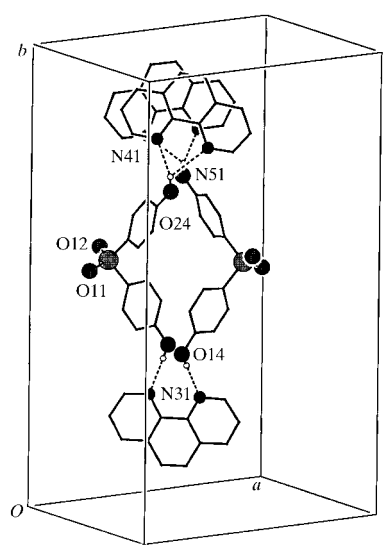


Fig. 7. The U-shaped hydrogen-bonded aggregate in compound (3). H atoms bonded to C are omitted for the sake of clarity.

the six independent phenanthroline units and shows clearly that the molecule must be regarded as two independent pyridine units, as in 2,2′-bipyridyl (Sørensen *et al.*, 1974; Lavender *et al.*, 1998*a*,*b*), connected by an isolated C═C double bond; there is no peripheral 14-π delocalization and hence in terms of the arithmetic of aromaticity $6 + 2 + 6 \neq 14$ (Glidewell & Lloyd, 1984, 1986), so that the phenanthroline components in compounds (1)–(4) are properly represented as in §1.

4. General comments

The structures of compounds (1)–(4) illustrate the great diversity of behaviour of 1,10-phenanthroline as a molecular building block: when hydrogen bonded it can act either as a chain builder, as in compounds (1) and (3), or as a chain terminator, as in compounds (2) and (3); in addition, its chain-building role can find it acting merely as a pendent group on other continuous two-dimensional, as in compound (4), or (at least in principle) three-dimensional networks. Moreover, while 1,10-phenanthroline acts primarily as a rigid acceptor of hydrogen bonds in all the compounds described here, it utilizes the π–π stacking interaction as a significant supramolecular motif in compounds (2) and (3).

It is also of interest to consider the roles of the phenolic components in compounds (1)–(4) in the context of their behaviour with other tertiary or heteroaromatic diamines. In 4,4′-biphenol, the lack of any angular spacer unit between the two aryl rings means that the location and orientation of one C—O bond necessarily fixes the position of the other; this bisphenol thus acts as a builder of simple chains, as found both in compound (1) and in the 1:1 adduct with 1,4-diazabicyclo[2.2.2]octane (DABCO) (Ferguson, Glidewell, Gregson, Meehan & Patterson, 1998). 4,4′-Thiodiphenol is similarly expected to act primarily as a chain builder, albeit of zigzag chains because of the angular spacer —S—, as in (2) and in the 1:1 adduct with hexamethylenetetramine (HMTA) (Coupar, Glidewell, & Ferguson, 1997); the reasons for the striking difference in the behaviour of the 1,10-phenanthroline components in compounds (1) and (2) are at present unclear. As well as acting as a builder of zigzag chains by acting as a double donor in O—H···*A* hydrogen bonds (Coupar, Glidewell & Ferguson, 1997), 4,4′-sulfonyldiphenol almost always acts also as a hydrogen-bond acceptor with one or both sulfone O atoms acting as acceptors, either from hard donors where these are available (Glidewell & Ferguson, 1996; Lavender *et al.*, 1998*b*; Ferguson *et al.*, 1999), or from soft donors such as aromatic C—H bonds, as in compound (3).

The pairwise-interwoven two-dimensional nets generated by the trisphenol component in compound (4) are entirely typical of the behaviour of this component. Thus, both the 1:1 adduct with HMTA (Coupar, Ferguson *et al.*, 1997) and the 2:1 adduct with 1,2-diaminoethane (Ferguson, Glidewell, Gregson & Meehan, 1998) contain pairwise-interwoven nets, while interwoven three-dimensional nets are found both in the

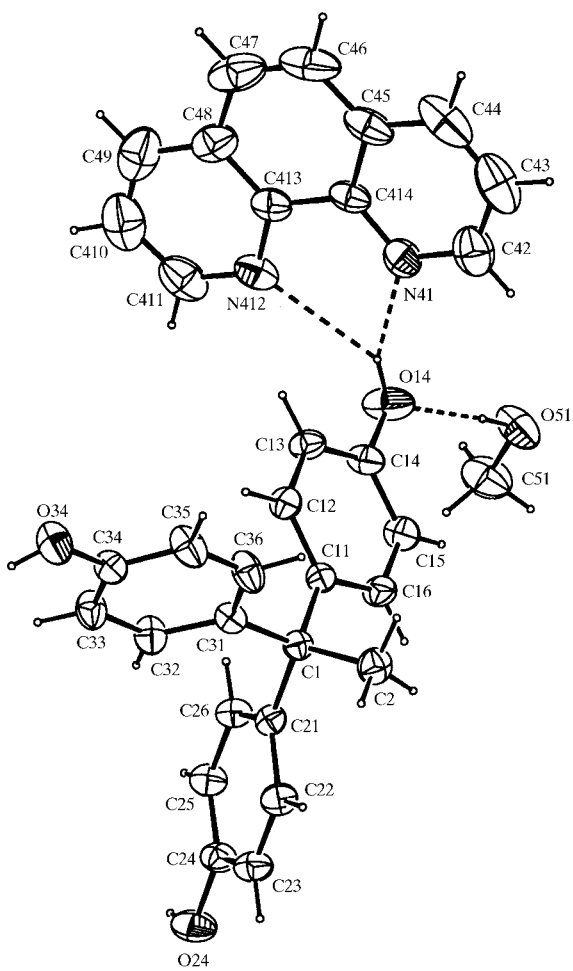


Fig. 8. The asymmetric unit of compound (4), showing the atom-labelling scheme. Atoms are depicted as in Fig. 1.

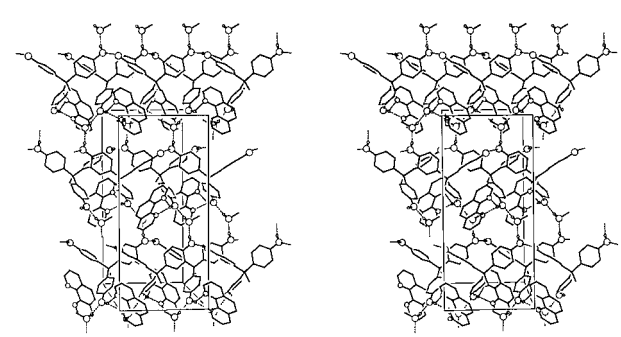


Fig. 9. Stereoview of part of the structure of compound (4), showing the pairwise-interwoven (010) nets in the domain $0 < y < 0.5$. H atoms bonded to C are omitted for the sake of clarity.

pure compound and in its adducts with DABCO and piperazine (Ferguson *et al.*, 1997).

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.

References

Bényei, A. C., Coupar, P. I., Ferguson, G., Glidewell, C., Lough, A. J. & Meehan, P. R. (1998). *Acta Cryst.* C**54**, 1515–1519.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Braga, D., Grepioni, F., Biradha, K., Pedireddi, V. R. & Desiraju, G. R. (1995). *J. Am. Chem. Soc.* **117**, 3156–3166.

Brock, C. P. & Dunitz, J. D. (1994). *Chem. Mater.* **6**, 1118–1127.

Coupar, P. I., Ferguson, G. & Glidewell, C. (1996). *Acta Cryst.* C**52**, 2524–2528.

Coupar, P. I., Ferguson, G., Glidewell, C. & Meehan, P. R. (1997). *Acta Cryst.* C**53**, 1978–1980.

Coupar, P. I., Glidewell, C. & Ferguson, G. (1997). *Acta Cryst.* B**53**, 521–533.

Enraf–Nonius (1992). *CAD*-4-*PC Software.* Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Ferguson, G. (1997). *PRPCIF*97 – *a WordPerfect*-5.1 *Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL*93 *Programs.* University of Guelph, Canada.

Ferguson, G., Bell, W., Coupar, P. I. & Glidewell, C. (1997). *Acta Cryst.* B**53**, 534–543.

Ferguson, G., Glidewell, C., Gregson, R. M. & Lavender, E. S. (1999). *Acta Cryst.* B**55**, 573–590.

Ferguson, G., Glidewell, C., Gregson, R. M. & Meehan, P. R. (1998). *Acta Cryst.* B**54**, 330–338.

Ferguson, G., Glidewell, C., Gregson, R. M., Meehan, P. R. & Patterson, I. L. J. (1998). *Acta Cryst.* B**54**, 151–161.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Glidewell, C. & Ferguson, G. (1996). *Acta Cryst.* C**52**, 2528–2530.

Glidewell, C. & Lloyd, D. (1984). *Tetrahedron*, **40**, 4455–4472.

Glidewell, C. & Lloyd, D. (1986). *J. Chem. Educ.* **63**, 306–309.

Jeffrey, G. A. & Saenger, W. (1991). *Hydrogen Bonding in Biological Structures.* Berlin: Springer-Verlag.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lavender, E. S., Glidewell, C. & Ferguson, G. (1998*a*). *Acta Cryst.* C**54**, 1637–1639.

Lavender, E. S., Glidewell, C. & Ferguson, G. (1998*b*). *Acta Cryst.* C**54**, 1639–1642.

Nishigaki, S., Yoshioka, H. & Nakatsu, K. (1978). *Acta Cryst.* B**34**, 875–879.

Sharma, C. V. K. & Zaworotko, M. J. (1996). *Chem. Commun.* pp. 2655–2656.

Sheldrick, G. M. (1997*a*). *SHELXS*97. *Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXL*97. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sørensen, G. O., Mahler, L. & Rastrup-Andersen, N. (1974). *J. Mol. Struct.* **20**, 119–126.

Spek, A. L. (1998). *PLATON. Molecular Geometry Program.* March 1998 version. University of Utrecht, The Netherlands.

Wilson, A. J. C. (1976). *Acta Cryst.* A**32**, 994–996.