Crystal Engineering Using Tris-phenols. Cross-Linked, Pairwise-Interwoven Two-Dimensional Nets in the 2:1 Adduct of 1,1,1-Tris(4-hydroxyphenyl)ethane with 1,2-Diaminoethane

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Abstract

In 1,1,1-tris(4-hydroxyphenyl)ethane–1,2-diaminoethane (2/1), $[CH_3C(C_6H_4OH)_3]_2.H_2NCH_2CH_2NH_2$ (1), triclinic, $P\bar{1}$, with $Z = 2$, $a = 10.9430\,(12)$, $b = 11.1075\,(12)$, $c = 15.249\,(2)$ Å, $\alpha = 98.672\,(15)$, $\beta = 96.312\,(10)$, $\gamma = 98.377\,(13)°$, the tris-phenol units form continuous two-dimensional nets, built from pseudo-hexagonal $R_4^4(38)$ rings, interwoven pairs of which are cross-linked by the 1,2-diaminoethane units. Each tris-phenol unit acts as a triple donor, forming two $O-H\cdots O$ and one $O-H\cdots N$ hydrogen bonds, and as a double acceptor in two $O-H\cdots O$ hydrogen bonds: the diamine unit, in which the CH_2 groups are disordered over two sets of sites with site-occupation factors of 0.740 (5) and 0.260 (5), respectively, acts as a double acceptor only and the $N-H$ bonds play no role in the hydrogen bonding. The $O\cdots O$ distances in the $O-H\cdots O$ hydrogen bonds are 2.642 (2), 2.690 (2), 2.810 (2) and 2.835 (2) Å, and the two independent $O\cdots N$ distances are both 2.665 (3) Å. Adjacent bilayers are connected into a continuous three-dimensional array by $C-H\cdots O$ hydrogen bonds, all having a $C\cdots O$ distance of 3.468 (4) Å.

1. Introduction

Although the interpenetrating chicken-wire structure of 1,3,5-benzenetricarboxylic acid was reported almost 30 years ago (Duchamp & Marsh, 1969), self-assembled structures consisting of interwoven sheets remain a rarity in supramolecular chemistry and the few subsequently reported examples are extremely diverse in nature. Thus, twofold interweaving occurs in an adduct of $[\{Re(CO)_3(\mu_3\text{-}OH)\}_4]$ with 4,4′-bipyridyl (Copp *et al.*, 1993), in a manganese(II) complex of *N,N′*-4-phenylenedimethylenebis(pyridin-4-one) (Goodgame *et al.*, 1995) and in 4,4′-sulfonyldiphenol (Glidewell & Ferguson, 1996), while threefold interwoven layers are observed in an adduct of 1,3,5-benzenetricarboxylic acid with 4,4′-bipyridyl (Sharma & Zaworotko, 1996). In view of the propensity of the tris-phenol 1,1,1-tris(4-hydroxyphenyl)ethane, $CH_3C(C_6H_4OH)_3$, to form interwoven three-dimensional structures (Ferguson *et al.*, 1997; Ferguson, Glidewell, Gregson & Meehan,

1998), we have embarked upon a systematic study of the properties of this tris-phenol as a supramolecular building block, with the aim of generating a family of interwoven architectures, by self-assembly from the tris-phenol and appropriately selected hydrogen-bond acceptors. Here we describe the interwoven structure formed by a 2:1 adduct with 1,2-diaminoethane, $[CH_3C(C_6H_4OH)_3]_2.H_2NCH_2CH_2NH_2$ (1).
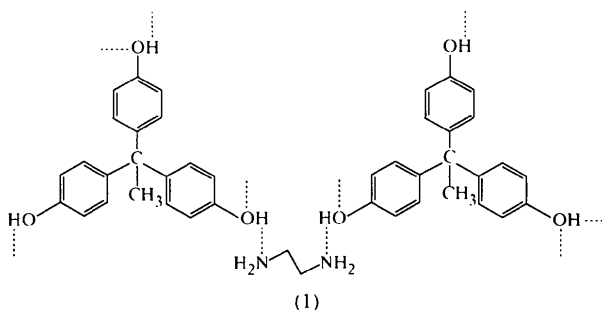
2. Experimental

2.1. Synthesis

Equimolar quantities (5 mmol of each) of 1,1,1-tris(4-hydroxyphenyl)ethane and 1,2-diaminoethane were separately dissolved in, or mixed with, methanol $(50\,cm^3)$. The solutions were mixed and set aside to crystallize, yielding analytically pure (1). Analysis: found C 75.0, H 6.6, N 4.2%; $C_{42}H_{44}N_2O_6$ requires C 75.0, H 6.6, N 4.2%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

2.2. Data collection, structure solution and refinement

Details of crystal data, data collection, and structure solution and refinement are summarized in Table 1. Compound (1) is triclinic; the space group $P\bar{1}$ was chosen and confirmed by successful structure solution and refinement.

(1)

In (1) it was clear from an early stage that the C atoms of the diamine component were disordered over two pairs of sites, with unequal occupancy. All H atoms,

Table 1. *Experimental details*

Table 1 (*cont.*)

Crystal data	
Chemical formula	$2(C_{20}H_{18}O_3).(C_2H_8N_2)$
Chemical formula weight	672.79
Cell setting	Triclinic
Space group	$P\bar{1}$
a (Å)	10.9430 (12)
b (Å)	11.1075 (12)
c (Å)	15.249 (2)
α (°)	98.672 (15)
β (°)	96.312 (10)
γ (°)	98.377 (13)
V (Å^3)	1796.2 (4)
Z	2
D_x (Mg m^{-3})	1.244
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.7107
No. of reflections for cell parameters	25
θ range (°)	10.35–18.50
μ (mm^{-1})	0.083
Temperature (K)	294 (1)
Crystal form	Block
Crystal size (mm)	0.42 × 0.41 × 0.40
Crystal colour	Colourless

Data collection	
Diffractometer	Enraf–Nonius CAD-4
Data collection method	$\theta/2\theta$ scans
Absorption correction	None
No. of measured reflections	8179
No. of independent reflections	8179
No. of observed reflections	4624
Criterion for observed reflections	$I > 2\sigma(I)$
θ_{max} (°)	27.37
Range of h, k, l	$-14 \rightarrow h \rightarrow 13$
	$0 \rightarrow k \rightarrow 14$
	$-19 \rightarrow l \rightarrow 19$
No. of standard reflections	3
Frequency of standard reflections (min)	120
Intensity decay (%)	No decay, variation 1.0

Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0517
$wR(F^2)$	0.1203
S	1.252
No. of reflections used in refinement	8179
No. of parameters used	467
H-atom treatment	H atoms constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0630P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.000
$\Delta\rho_{max}$ (e Å^{-3})	0.194
$\Delta\rho_{min}$ (e Å^{-3})	-0.156
Extinction method	SHELXL93 (Sheldrick, 1993)
Extinction coefficient	0.0196 (16)
Source of atomic scattering factors	International Tables for Crystallography (1992, Vol. C)

Computer programs	
Data collection	CAD-4 (Enraf–Nonius, 1992)
Cell refinement	SET4 and CELDIM (Enraf–Nonius, 1992)
Data reduction	DATRD2 in NRCVAX96 (Gabe et al., 1989)
Structure solution	SOLVER in NRCVAX96
Structure refinement	NRCVAX96 and SHELXL93 (Sheldrick, 1993)
Preparation of material for publication	NRCVAX96, SHELXL93 and WordPerfect macro PRPCIF97 (Ferguson, 1997)

except those bonded to N in the minor conformer of the diamine component, were clearly located from difference maps; those bonded to C or O were included in the refinements as riding atoms in idealized positions, with C—H distances in the range 0.93–0.96 Å and O—H distances of 0.82 Å. The disorder of the diamine component was modelled as follows: the site-occupation factors for the two pairs of C atoms were refined to values of 0.740 (5) and 0.260 (5). The H atoms bonded to N were included in the refinements as riding atoms, with an N—H distance of 0.89 Å, at the sites corresponding to the major conformer only. The values for D_x, μ and the chemical formula weight in Table 1 correspond to full occupancy of one set of diamine sites, *i.e.* strict 2:1 trisphenol:amine stoichiometry. All non-H atoms were allowed anisotropic displacement parameters, with the exception of the minor components of the diamine C atoms which were allowed individual isotropic displacement parameters. Analysis of the refined structure using PLATON (Spek, 1996a) showed that there were no solvent-accessible voids. The diagrams were prepared with the aid of ORTEPII (Johnson, 1976) and PLUTON (Spek, 1996b). Final fractional coordinates are given in Table 2 and selected dimensions in Table 3.† Fig. 1 shows the asymmetric unit with the atom-numbering scheme and Figs. 2–6 show aspects of the crystal structure.

3. Results and discussion

3.1. *Crystal structure and molecular packing*

The crystal structure analysis of (1) confirms both the unusual 2:1 molar ratio of tris-phenol to diamine and the unusual 3:1 ratio of hydroxyl to amino groups, and shows that while both N atoms of the diamine act as hydrogen-bond acceptors, neither acts as a donor. Hence, the diamine, with its usual *trans* and almost planar conformation, acts as a fairly rigid bis-acceptor unit, somewhat analogous to 1,4-diazabicyclo[2.2.2]octane (DABCO) or 4,4′-bipyridyl. Each of the six hydroxy groups in the asymmetric unit (Fig. 1) acts as a hydrogen-bond donor, two of them (O11 and O21) to N atoms and the remainder to other O atoms;

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† Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference AB0389). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* $(\mathring{A}^2)$

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq}
O11	0.5207 (2)	0.21985 (14)	0.31182 (10)	0.0695 (5)
O12	0.94916 (15)	−0.1690 (2)	−0.07229 (13)	0.0783 (5)
O13	0.06146 (12)	−0.36818 (13)	−0.14679 (9)	0.0540 (4)
C11	0.5125 (2)	−0.2513 (2)	0.09903 (12)	0.0386 (4)
C12	0.5232 (2)	−0.3529 (2)	0.15744 (13)	0.0531 (5)
C111	0.5027 (2)	−0.1299 (2)	0.16003 (11)	0.0387 (4)
C112	0.5903 (2)	−0.0851 (2)	0.23512 (13)	0.0512 (5)
C113	0.5941 (2)	0.0293 (2)	0.28552 (13)	0.0577 (6)
C114	0.5094 (2)	0.1031 (2)	0.26282 (13)	0.0493 (5)
C115	0.4183 (2)	0.0590 (2)	0.19129 (13)	0.0512 (5)
C116	0.4157 (2)	−0.0559 (2)	0.14032 (13)	0.0470 (5)
C121	0.6303 (2)	−0.2305 (2)	0.05267 (11)	0.0384 (4)
C122	0.6872 (2)	−0.3284 (2)	0.01947 (13)	0.0487 (5)
C123	0.7924 (2)	−0.3104 (2)	−0.02306 (14)	0.0544 (5)
C124	0.8440 (2)	−0.1932 (2)	−0.03231 (13)	0.0502 (5)
C125	0.7891 (2)	−0.0943 (2)	−0.00087 (13)	0.0485 (5)
C126	0.6834 (2)	−0.1138 (2)	0.04030 (12)	0.0437 (5)
C131	0.3954 (2)	−0.2908 (2)	0.02907 (11)	0.0368 (4)
C132	0.2817 (2)	−0.3391 (2)	0.05412 (13)	0.0469 (5)
C133	0.1729 (2)	−0.3652 (2)	−0.00511 (13)	0.0493 (5)
C134	0.1737 (2)	−0.3449 (2)	−0.09184 (13)	0.0423 (4)
C135	0.2845 (2)	−0.2997 (2)	−0.11907 (13)	0.0474 (5)
C136	0.3931 (2)	−0.2729 (2)	−0.05890 (12)	0.0464 (5)
O21	−0.04722 (13)	0.29115 (13)	0.30605 (10)	0.0593 (4)
O22	0.46334 (12)	−0.2537 (2)	0.51177 (9)	0.0599 (4)
O23	−0.42196 (14)	−0.44068 (14)	0.42606 (12)	0.0713 (5)
C21	0.0122 (2)	−0.2129 (2)	0.29919 (12)	0.0431 (4)
C22	0.0137 (2)	−0.2790 (2)	0.20169 (13)	0.0574 (6)
C211	0.0060 (2)	−0.0758 (2)	0.29892 (12)	0.0425 (4)
C212	−0.0741 (2)	−0.0403 (2)	0.23408 (14)	0.0541 (5)
C213	−0.0905 (2)	0.0803 (2)	0.23644 (14)	0.0554 (6)
C214	−0.0272 (2)	0.1708 (2)	0.30454 (13)	0.0460 (5)
C215	0.0535 (2)	0.1388 (2)	0.36942 (13)	0.0522 (5)
C216	0.0701 (2)	0.0174 (2)	0.36597 (13)	0.0497 (5)
C221	0.1318 (2)	−0.2259 (2)	0.35797 (12)	0.0412 (4)
C222	0.2465 (2)	−0.2110 (2)	0.32645 (14)	0.0574 (6)
C223	0.3550 (2)	−0.2186 (2)	0.37844 (14)	0.0597 (6)
C224	0.3523 (2)	−0.2412 (2)	0.46452 (12)	0.0440 (5)
C225	0.2410 (2)	−0.2536 (2)	0.49894 (12)	0.0437 (4)
C226	0.1324 (2)	−0.2451 (2)	0.44546 (12)	0.0426 (4)
C231	−0.1041 (2)	−0.2721 (2)	0.33473 (12)	0.0400 (4)
C232	−0.1427 (2)	−0.3996 (2)	0.31817 (15)	0.0547 (5)
C233	−0.2470 (2)	−0.4543 (2)	0.3495 (2)	0.0589 (6)
C234	−0.3172 (2)	−0.3826 (2)	0.39839 (13)	0.0480 (5)
C235	−0.2795 (2)	−0.2566 (2)	0.41816 (13)	0.0458 (5)
C236	−0.1746 (2)	−0.2031 (2)	0.38606 (12)	0.0425 (4)
N1	0.3904 (2)	0.3775 (2)	0.2444 (2)	0.0777 (6)
C1	0.2661 (3)	0.3981 (4)	0.2679 (3)	0.0769 (12)
C2	0.2718 (3)	0.4110 (3)	0.3683 (2)	0.0698 (12)
N2	0.1524 (2)	0.4458 (2)	0.3945 (2)	0.0811 (6)
C1A	0.2926 (9)	0.3574 (9)	0.3038 (7)	0.074 (3)
C2A	0.2273 (9)	0.4675 (9)	0.3208 (6)	0.087 (4)

in addition, four of the O atoms (O11, O13, O21 and O22) also act as acceptors in O—H⋯O hydrogen bonds. The complementarity of hydrogen-bond donor and acceptor capacities between amino groups and hydroxyl groups, postulated as a mechanism for molecular recognition among alcohols and amines (Ermer & Eling, 1994), is clearly not manifest in (1); indeed, it is

noteworthy that while two of the O atoms (O12 and O23) do not act as acceptors in O—H⋯O hydrogen bonds, neither do they so act in N—H⋯O hydrogen bonds, despite the plenitude of free N—H bonds in the structure. Indeed, even the shortest (N)—H⋯O distance in the structure is, at 2.666 (3) Å, only marginally less than the corresponding sum of van der Waals radii, 2.72 Å. Careful study of difference maps showed that there was no transfer of protons from the tris-phenol to the diamine: this may be contrasted with the partial transfer of one proton per tris-phenol to DABCO (Ferguson *et al.*, 1997) and with the complete
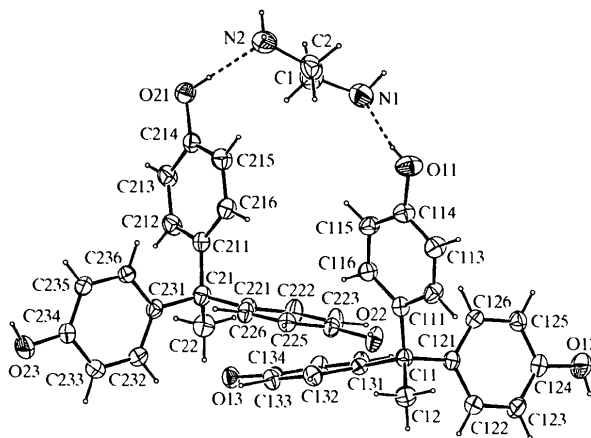

Fig. 1. The asymmetric unit in (1), showing the atom-numbering scheme. Anisotropic displacement ellipsoids are drawn at the 30% probability level: H atoms are drawn as small spheres of arbitrary radius.
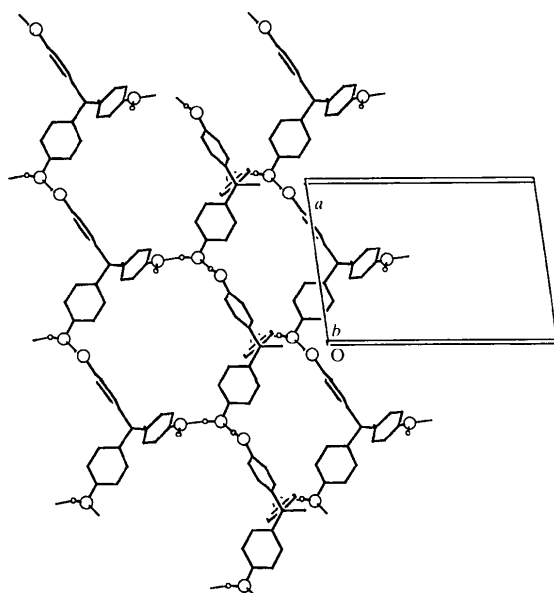

Fig. 2. View of one of the two-dimensional nets of $R_4^4(38)$ rings built from tris-phenol molecules: H atoms bonded to carbon are omitted for the sake of clarity.

Table 3. *Selected molecular dimensions* $(\text{Å}, °)$

O11—C114	1.377 (2)	O21—C214	1.383 (2)
O12—C124	1.372 (2)	O22—C224	1.379 (2)
O13—C134	1.376 (2)	O23—C234	1.372 (2)
N1—C1	1.485 (4)	N2—C2	1.494 (4)
C1—C2	1.508 (5)		
C112—C111—C11—C12	52.1 (2)	C212—C211—C21—C22	43.7 (2)
C122—C121—C11—C12	38.7 (2)	C222—C221—C21—C22	42.2 (2)
C132—C131—C11—C12	46.0 (2)	C232—C231—C21—C22	41.5 (2)
N1—C1—C2—N2	173.8 (3)	N1—C1A—C2A—N2	−168.7 (6)
O11···N1	2.665 (3)	O11—H11···N1	168
O12···O13[i]	2.835 (2)	O12—H12···O13[i]	166
O13···O21[ii]	2.690 (2)	O13—H13···O21[ii]	163
O21···N2	2.665 (3)	O21—H21···N2	177
O22···O11[iii]	2.642 (2)	O22—H22···O11[iii]	167
O23···O22[iv]	2.810 (2)	O23—H23···O22[iv]	169
C2···O23[v]	3.468 (4)	C2—H2E···O23[v]	151
C235···O22[iv]	3.294 (3)	C235—H235···O22[iv]	133

Symmetry codes: (i) $1 + x, y, z$; (ii) $-x, -y, -z$; (iii) $1 - x, -y, 1 - z$; (iv) $-1 + x, y, z$; (v) $1 + x, 1 + y, z$.

transfer of one proton per tris-phenol to 1,4,8,11-tetraazacyclododecane [cyclam (Ferguson, Glidewell, Gregson & Meehan, 1998)]. As in the adducts of 1,2-diaminoethane with 4,4'-biphenol (Ferguson, Glidewell, Gregson, Meehan & Patterson, 1998), there are no N—H···N hydrogen bonds in the crystal structure of (1); such bonds occur, however, in the pure crystalline diamine, with N···N distances of 3.22 (1) Å (Jamet-Delcroix, 1973).

The supramolecular architecture is best regarded as built from pairwise-interwoven nets generated by the tris-phenol units only and cross-linked by the diamines, and the hydrogen bonding will be described and discussed in terms of these cross-linked nets. Within the tris-phenol networks, each of the two types of tris-phenol molecule, denoted 1 and 2 (Fig. 1), acts a donor in two O—H···O hydrogen bonds. Atom O12 in the tris-phenol (molecule 1) at (x, y, z) acts as a donor to O13 i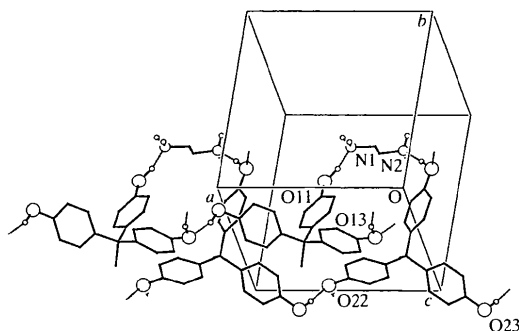n the tris-phenol at $(1 + x, y, z)$, thus generating a chain running parallel to **a**. Atom O13 in the unit at (x, y, z) acts as a donor to O21 in the tris-phenol of type 2 at $(-x, -y, -z)$: O23 in this unit at $(-x, -y, -z)$ acts as a donor to O22 in the tris-phenol at $(1 - x, -y, -z)$, thus generating a second chain running parallel to **a**, and O22 at $(-x, -y, -z)$ acts as a donor to O11 in the tris-phenol of type 1 at $(-1 + x, y, -1 + z)$, thus giving rise to a chain running parallel to the [101] direction.
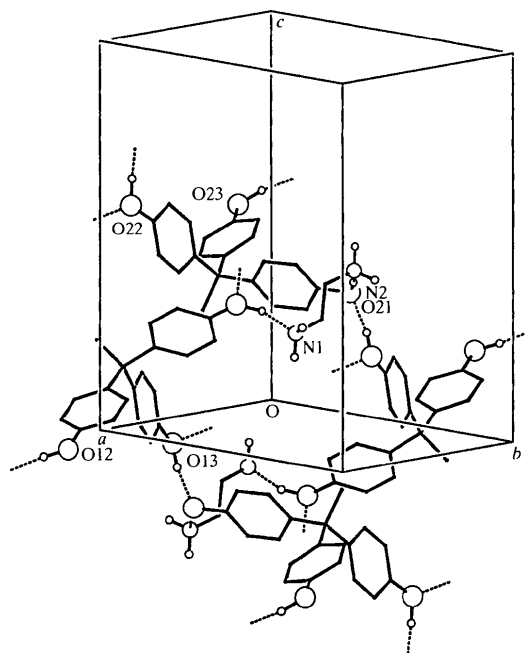

Fig. 3. The $R_6^6(58)$ figure-of-eight motif generated by the asymmetric units at (x, y, z) and $(1 + x, y, z)$: H atoms bonded to carbon are omitted for the sake of clarity.

Fig. 4. The centrosymmetric $R_6^6(38)$ motif generated by the asymmetric units at (x, y, z) and $(-x, -y, -z)$: H atoms bonded to carbon are omitted for the sake of clarity.

The combination of these three chain motifs generates a puckered two-dimensional net (Fig. 2), built of pseudo-hexagonal rings containing seven O atoms, but only four O—H···O hydrogen bonds. Each ring contains contributions from only four molecular fragments, but the vertices of the reticulation are alternately the central C atoms (C11 or C21) of the trisphenol and O atoms from the tris-phenols (Fig. 2). The formation of such a net utilizes only two of the four tris-phenol molecules in the unit cell: molecule 1 at (x, y, z) and molecule 2 at $(-x, -y, -z)$. There is an entirely equivalent net, related to the first by the action of the inversion centres, built from tris-phenol molecules of type 1 at $(-x, -y, -z)$ and type 2 at (x, y, z). The approximate internal dimensions of the cavities at the ring centres in these nets are 8.5 × 8.0 Å, as judged from the atomic coordinates and allowing for the van der Waals radii of the atoms. Although there are no O—H···O hydrogen bonds between the two independent nets, they are in fact interwoven in pairs to form two-dimensional bilayers and tris-phenol molecules of type 1 in either net lie close to the ring centres of the other net: these nets are stacked parallel to the ac plane.

The formation of these pairs of nets accounts for all the O—H···O hydrogen bonds in the structure (Table 3), but still leaves unused the donor capacity of two O atoms, O11 and O21. Within the asymmetric unit O11 and O21 act as donors to N1 and N2, respectively (Fig. 1): although O11 and O21 are in different tris-phenol nets of an interwoven pair, the O—H···N hydrogen bonds cross-link these two interwoven nets and two such cross-links per unit cell join the entire bilayer into a tightly connected whole. The presence of the diamine units generates further hydrogen-bonded ring motifs. The three-component aggregates (Fig. 1) at (x, y, z) and $(1 + x, y, z)$ together generate a figure-of-eight motif

(Fig. 3), while the corresponding aggregates at (x, y, z) and $(-x, -y, -z)$ generate a simple centrosymmetric ring (Fig. 4): each of these motifs contains two O—H···O and four O—H···N hydrogen bonds.

Within these interwoven bilayers, neither O12 nor O23 acts as an acceptor of O—H···O hydrogen bonds, so that the hydrogen-bonding potential is not yet exhausted. There are, in fact, two types of C—H···O hydrogen bond, one each involving O22 and O23, although not O12. The C235 atom (Fig. 1) in the tris-

(a)

(b)
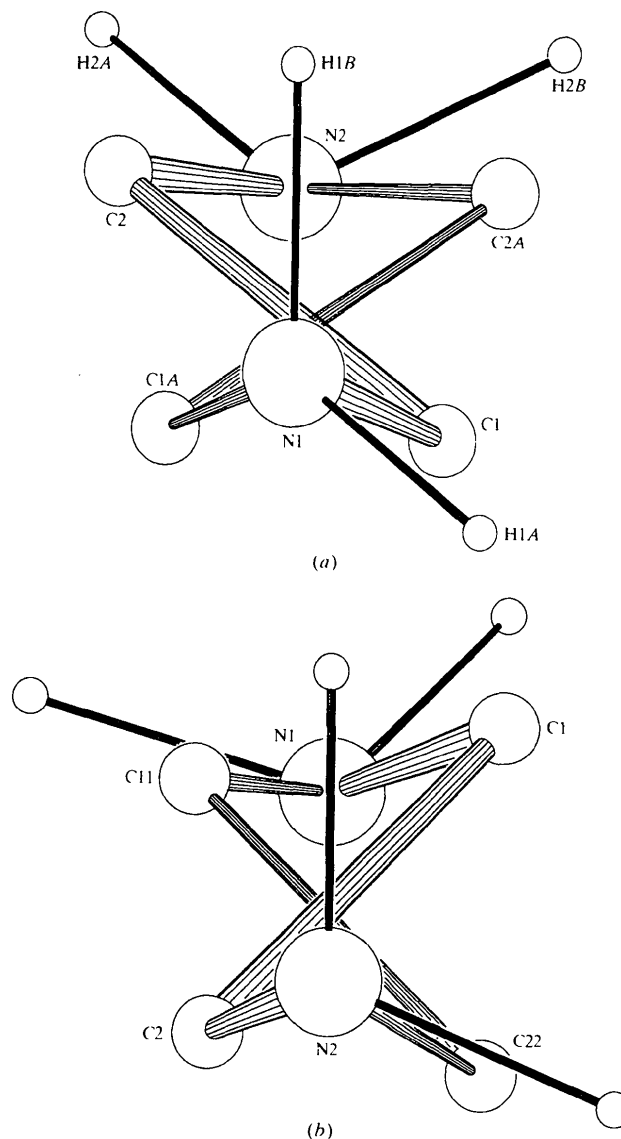
Fig. 6. The disordered 1,2-diaminoethane components in (a) (1) and (b) 4,4'-biphenol-1,2-diaminoethane-methanol (2/1/1), with the original atom labelling in (b). In each figure the N—H bonds are shown as thin lines, the C—N and C—C bonds in the major orientation are shown as thick lines, and the C—N and C—C bonds in the minor orientation as lines of intermediate thickness: C—H bonds are omitted for the sake of clarity.

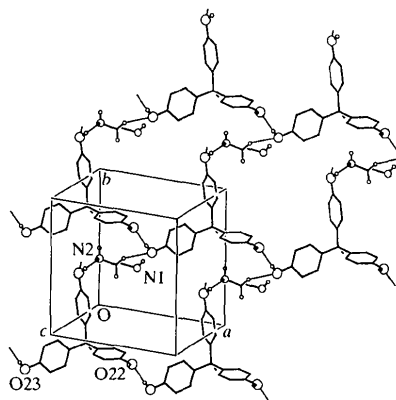

Fig. 5. The $C_3^3(17)$ spirals along the [010] direction, generated by a combination of C—H···O, O—H···O and O—H···N hydrogen bonds; the $C_2^2(15)$ chains along the [110] direction, generated by a combination of C—H···O and O—H···N hydrogen bonds; the resulting $R_6^6(44)$ motif. Except for the CH$_2$ group involved in hydrogen bonding, H atoms bonded to carbon are omitted.

phenol of type 2 at (x, y, z) acts as a donor in a C—H$\cdots$O bond to O22 in the corresponding unit at $(-1 + x, y, z)$, Table 3: the effect of this is simply to reinforce the chain-forming O23—H$\cdots$O22 interaction. The second type of C—H$\cdots$O interaction involves only the major orientation of the diamine, but provides links between adjacent interwoven bilayers, hence connecting the entire structure into a three-dimensional continuum. Atom C2 in the diamine at (x, y, z) acts, via H2E, as a donor to O23 in the tris-phenol at $(1 + x, 1 + y, z)$, thus generating a chain in the [110] direction: since the individual bilayers lie parallel to the (010) plane, C—H$\cdots$O hydrogen bonds of this type have the effect of connecting neighbouring bilayers. The diamine at (x, y, z) forms a connection to the adjacent bilayer in the [010] direction, while that at $(-x, -y, -z)$ forms a link to the adjacent bilayer in the [0$\bar{1}$0] direction, thus connecting each bilayer to its two immediate neighbours.

As well as forming chains in the [110] direction the inter-layer C—H$\cdots$O hydrogen bonds generate spirals parallel to **b** (Fig. 5). Atom C2 in the diamine at (x, y, z) is a donor to O23 at $(1 + x, 1 + y, z)$, which in turn is a donor to O22 at $(x, 1 + y, z)$; O21 in the same tris-phenol at $(x, 1 + y, z)$ acts as a donor to N2 of the diamine at $(x, 1 + y, z)$, shifted one cell along **b** from the initial diamine and again tying together the adjacent layers. These spirals contain sequences of three types of hydrogen bond: C—H$\cdots$O, O—H$\cdots$O and O—H$\cdots$N.

3.2. Hydrogen-bonding motifs and molecular weaving

The tris-phenol component in (1) acts as a triple donor of hydrogen bonds, but there is no evidence for proton transfer from the tris-phenol to the diamine component: this differs from the behaviour of the related DABCO (see above) adduct, in which there is partial transfer of one proton from each tris-phenol molecule to a DABCO molecule (Ferguson *et al.*, 1997).

The chains running parallel to **a** in (1) contain a single type of O—H$\cdots$O hydrogen bond and have graph set $C(12)$ (Etter, 1990; Bernstein *et al.*, 1995), while the [101] chains (Fig. 2) contain two types of hydrogen bond, O13—H$\cdots$O21 and O22—H$\cdots$O11, so that these chains have $N_1 = DD$, $N_2 = C_2^2(24)$. The pseudo-hexagonal rings generated by the intersection of these two types of chain contain four O—H$\cdots$O hydrogen bonds, of three types: O12—H$\cdots$O13, O23—H$\cdots$O22 and two occurrences of either O13—H$\cdots$O21 or O22—H$\cdots$O11. The corresponding graph sets are thus $N_1 = DDD$, $N_2 = R_4^4(38)$. There are two other types of ring in (1) involving both O—H$\cdots$O and O—H$\cdots$N hydrogen bonds. The figure-of-eight motif (Fig. 3) generated by translation of the entire asymmetric unit along **a** contains six hydrogen bonds of four types so that $N_1 = DDDD$ and $N_2 = R_6^6(58)$; the other centrosymmetric ring (Fig. 4) contains three different types of

hydrogen bond and is characterized by $N_1 = DDD$, $N_2 = R_6^6(38)$. The C—H$\cdots$O hydrogen bond involving C2 and O23 generates two further chain motifs: the chains running parallel to the [110] direction have $N_1 = DD$, $N_2 = C_2^2(15)$, and the spiral around **b** (Fig. 5) containing three different types of hydrogen bond, C—H$\cdots$O, O—H$\cdots$O and O—H$\cdots$N, has $N_1 = DDD$, $N_2 = C_3^3(17)$. The combination of these $C_2^2(15)$ and $C_3^3(17)$ motifs with the $C(12)$ O—H$\cdots$O motif running parallel to **a** (Figs. 2 and 5) generates a further motif, of $R_6^6(44)$ type (Fig. 5).

For hydrogen-bonded adducts built from simple aromatic carriers of hydrogen-bond donors and acceptors, which are not otherwise encumbered by sterically demanding substituents, the extent and complexity of the molecular weaving of two-dimensional nets depends to a large degree on the ring size characteristic of the nets. Thus, in (1) reported here and in 4,4'-sulfonyldiphenol, $O_2S(C_6H_4OH)_2$ (Glidewell & Ferguson, 1996), the network structures are built from $R_4^4(38)$ and $R_4^4(32)$ rings, respectively, and the internal dimensions of such rings, containing no aromatic groups other than unsubstituted –C_6H_4– fragments, allow just a single strand of similar type to pass through, giving a twofold interwoven bilayer. Similarly, the $R_6^6(48)$ rings in the 1:1 adduct of 1,1,1-tris(4-hydroxyphenyl)ethane with hexamethylenetetramine (HMTA), $(CH_2)_6N_4$, allow just one similar strand to pass through (Coupar, Ferguson *et al.*, 1997), while in 1,3,5-benzenetricarboxylic acid (Duchamp & Marsh, 1969) a network built from $R_6^6(48)$ rings allows three strands to pass through each ring. Possibly the difference arises from the fundamentally two-dimensional nature of all the building units in the carboxylic acid, compared with the three-dimensional fragments in 1,1,1-tris(4-hydroxyphenyl)ethane/HMTA: in any event the $R_6^6(48)$ rings are much more puckered in 1,1,1-tris(4-hydroxyphenyl)ethane/HMTA than in 1,3,5-benzenetricarboxylic acid. In contrast to these finitely interwoven systems, in 1,1'-bis(4-hydroxybenzoyl)ferrocene, $[Fe(C_5H_4COC_6H_4OH)_2]$, there are two symmetry-related stacks of nets built from $R_4^4(40)$ rings and inclined at ~56° to one another, which are continuously interwoven; at the centre of each ring, in either stack of nets, lies a ferrocenediphenol molecule belonging to a net in the other stack (Bényei *et al.*, 1997).

Very large rings, such as the $R_{12}^{12}(102)$ rings in 1,3,5-benzenetricarboxylic acid–4,4'-bipyridyl (2/3) (Sharma & Zaworotko, 1996) and the $R_{12}^{12}(126)$ rings in 1,1,1-tris(4-hydroxyphenyl)ethane/4,4'-bipyridyl (2/3) (Bényei *et al.*, 1998), allow multiple interweaving and it seems clear that, in large measure, the extent of molecular weaving can be pre-designed by the construction of appropriately sized initial networks. There is no reason to suppose that rings substantially larger than those observed in 1,1,1-tris(4-hydroxyphenyl)ethane/ 4,4'-bipyridyl cannot be readily produced by self-

assembly from appropriately designed building blocks, using supramolecular synthons (Desiraju, 1995) no more complex than $O-H\cdots O$, $O-H\cdots N$ and $N-H\cdots O$. For the successful construction of finite interwoven structures, it is usually necessary to have some degree of puckering of the individual sheets. The tris-phenol 1,1,1-tris(4-hydroxyphenyl)ethane is thus ideal for the construction of such structures because of the tetrahedral nature of the central molecular core. Although interwoven structures can be formed using 1,3,5-benzenetricarboxylic acid as the hydrogen-bond donor (Duchamp & Marsh, 1969; Sharma & Zaworotko, 1996), the puckering here is facultative rather than obligate: in the 1:1 adduct of this acid with DABCO (Meehan et al., 1997) the $R_6^6(38)$ nets lie on mirror planes, so that no twofold or similar interweaving is possible.

For interwoven structures built from hydrogen-bonded sheets there are a number of parameters in addition to the graph-set descriptor which are necessary for a complete description of the structure. These are: p, the number of independent nets required to generate the entire contents of the unit cell; q, the number of such nets which are interwoven; r, the number of strands of other nets passing through the reticulations (assumed identical) of any given net. Thus, in the structure of 4,4'-sulfonyldiphenol, built from nets of $R_4^4(32)$ rings (Glidewell & Ferguson, 1996), the values of p, q and r are, respectively, 4, 2 and 1, so that the interweaving mode can be described by the shorthand notation {4,2,1}. Similarly, the interweaving in both (1) and the 1:1 adduct of 1,1,1-tris(4-hydroxyphenyl)ethane with hexamethylenetetramine (Coupar, Ferguson et al., 1997) can also be described as {4,2,1}; for 1,3,5-benzenetricarboxylic acid–4,4'-bipyridyl (2/3) (Sharma & Zaworotko, 1996) and 1,1,1-tris(4-hydroxyphenyl)ethane/4,4'-bipyridyl (2/3) (Bényei et al., 1998) the interweaving can be described as {18,3,2} and {10,10,9}, respectively. Where the interweaving is, in fact, continuous as with two inclined stacks of near-planar nets, then $q = \infty$ regardless of the value of p; thus, for 1,1'-bis-(4-hydroxybenzoyl)ferrocene (Bényei et al., 1997) the interweaving can be described as {2, ∞, 1}.

3.3. Molecular conformations and dimensions

The tris-phenol component could, in principle, adopt molecular symmetry as high as C_{3v} (3m): while in crystalline compounds the skeletal symmetry of this component never approaches C_{3v}, it is sometimes close to C_3, as found in molecule 2, judged by the torsional angles describing the orientation of the aryl groups relative to the central $H_3C-C[-C(ar)]_3$ core of the molecule (Table 3).

The 1,2-diaminoethane component exhibits orientational disorder: the two C atoms occupy two sets of

sites, whose site-occupation factors (s.o.f.'s) refined to values of 0.740 (5) and 0.260 (5), respectively, although the N atoms were not disordered. For the major conformer only, the H atoms of the NH_2 groups were located from difference maps and these were included in the refinement as riding atoms. In each orientation the $N-C-C-N$ fragment is trans and essentially planar (Table 3); this conformation is similar to those in adducts of the diamine with phenol (Loehlin et al., 1994) and with 4,4'-biphenol (Ferguson, Glidewell, Gregson, Meehan & Patterson, 1998) and in the diamine itself, where the molecules lie across centres of inversion with no reported disorder at 213 K (Jamet-Delcroix, 1973). However, an electron-diffraction study of 1,2-diaminoethane in the gas phase, i.e. as isolated molecules, showed that at least 95% of the molecules had the gauche conformation with an $N-C-C-N$ torsional angle of 64 (4)° (Yokozeki & Kuchitsu, 1971): hence, the conformations close to trans observed in the solid state must be determined by the sum of all the intermolecular forces, of which the hydrogen bonds are probably the dominant contributor. The dihedral angle between the best planes described by the $N-C-C-N$ fragments of the two orientations is 60.1 (11)° (Fig. 6a).

The orientational disorder in (1) may be compared with that in 4,4'-biphenol–1,2-diaminoethane–methanol (2/1/1) (Ferguson, Glidewell, Gregson, Meehan & Patterson, 1998): in this compound the C atoms of the diamine again occupy two sets of sites with refined s.o.f.'s of 0.874 (4) and 0.126 (4), with a dihedral angle between the two almost planar $N-C-C-N$ fragments of 81.4 (9)° (Fig. 6b). In (1) each NH_2 group has one $N-H$ bond trans to the $C-C$ bond of the major orientation (Fig. 6a), whereas in the 4,4'-biphenol adduct this is so only for N1; N2 has a lone pair trans to the $C-C$ bond of the major orientation (Fig. 6b). In the 1:1 adduct of 4,4'-biphenol and 1,2-diaminoethane, where there is no orientational disorder of the diamine, one $N-H$ bond of each NH_2 group is again trans to the $C-C$ bond. In (1), 4,4'-biphenol–1,2-diaminoethane–methanol (2/1/1) and 4,4'-biphenol–1,2-diaminoethane (1/1) the N atoms all act as hydrogen-bond acceptors, but as donors of zero, one and two hydrogen bonds, respectively: hence, the orientation of the NH_2 groups relative to the NCCN frameworks is likely to be dominated by the hydrogen-bond acceptor requirements of the diamine rather than by its donor behaviour. It may be noted that when the disordered diamine components in (1) and 4,4'-biphenol–1,2-diaminoethane–methanol (2/1/1) are oriented similarly (so that the $N-H$ bonds are in similar positions), the sites occupied by the C atoms in the major orientation in either compound correspond to those occupied in the minor orientation in the other (Fig. 6).

The $C-C$ and $C-N$ bond lengths for the major conformer of the diamine component of (1) (Table 3) are fairly similar to those reported (at 213 K) for the

pure crystalline diamine, C—C 1.51 (2) and C—N 1.47 (1) Å (Jamet-Delcroix, 1973), but they differ significantly from the values reported for the gaseous diamine, C—C 1.548 (8) and C—N 1.469 (4) Å (Yoko-zeki & Kuchitsu, 1971). Indeed, the values of these bond lengths seem to be rather variable in adducts with phenols: the C—C distance ranges from 1.499 (4) Å in $(C_6H_5OH)_2.C_2H_8N_2$ (Loehlin *et al.*, 1994) to 1.448 (4) Å in HOC_6H_4C $1_4OH.C_2H_8N_2$ (Ferguson, Glidewell, Gregson, Meehan & Patterson, 1998), while the C—N distance varies from 1.494 (4) Å in (1) to 1.466 (4) Å in $(C_6H_5OH)_2.C_2H_8N_2$.

Several points stand out from the data on the O—H···O and O—H···N hydrogen bonds (Table 3). In (1) the O···N distances are comparable to the shortest of the O···O distances, while the O···O distances span a rather wide range, 2.642 (2)–2.835 (2) Å: the longest O···O distances are those associated not only with the simple chain-forming motifs, but in the case of $O23···O22^{iv}$ (Table 3) with reinforcement by a C—H···O hydrogen bond to the same atom, O22. Although the O—H···O hydrogen bonds in (1) cannot be regarded as short or strong, the O—H···N bonds are undoubtedly short. Similarly, the C—H···O hydrogen bonds are all fairly short in comparison with the values now accepted as indicative of C—H···O hydrogen bonds (Taylor & Kennard, 1982; Desiraju, 1991; Braga *et al.*, 1995), so that the cross-linking interactions should all be regarded as fairly strong for their type. As usual, however, it is not the strength of particular individual hydrogen bonds which accounts for the coherence of the crystal architectures in compounds of this type, but rather the collective and cooperative action of all the hydrogen bonds, both hard and soft (Braga *et al.*, 1995).

4. General comments and conclusions

The structure of (1) reported here and those of other adducts reported elsewhere (Coupar, Glidewell & Ferguson, 1997; Ferguson *et al.*, 1997; Coupar, Ferguson *et al.*, 1997; Ferguson, Glidewell, Gregson & Meehan, 1998) illustrate the versatility of 1,1,1-tris(4-hydro-xyphenyl)ethane as a building block for self-assembled supramolecular systems. In the pure compound (Ferguson *et al.*, 1997) each of the hydroxy groups acts as both a donor and an acceptor of hydrogen bonds, and only hard hydrogen bonds of the type O—H···O are present in the structure, which consists of twofold interwoven $R_4^4(38)$ nets cross-connected into a contin-uous three-dimensional network.

In both the 1:1 adduct with HMTA (Coupar, Ferguson *et al.*, 1997) and the analogous 1:2 adduct (Coupar, Glidewell & Ferguson, 1997) the tris-phenol again acts as a triple donor in O—H···N hydrogen bonds, but there is a striking structural contrast between the 1:1 and 1:2 adducts: the 1:1 adduct forms

pairwise-interwoven $R_6^6(48)$ nets and the 1:2 adduct forms triple helices. In each compound one of the O atoms in each tris-phenol acts as an acceptor in a C—H···O hydrogen bond for which the donor is a C—H bond in an HMTA unit. On the other hand, there is no evidence for hydrogen bonds other than those of the O—H···N type in the 4,4'-bipyridyl adduct (Bényei *et al.*, 1998), even though the C—H bonds of this heteroaromatic amine might be expected to be rather better than the CH_2 groups in HMTA as donors to oxygen. The adducts with the bis-secondary amine piperazine (Ferguson *et al.*, 1997) and the bis-primary amine 1,2-diaminoethane, compound (1), both contain O—H···N as well as O—H···O hydrogen bonds, but the piperazine adduct also exhibits many different N—H···O interactions, while (1) contains none of these. While 1,1,1-tris(4-hydroxyphenyl)ethane thus exhibits very versatile behaviour in its hydrogen-bonded adducts with simple amines, the systematics of this behaviour are as yet unclear.

The hydrogen-bonding behaviour of 1,2-diami-noethane in adducts with molecular hydroxy compounds is extremely variable. In (1), as well as in $[\{Mn(CO)_3(\mu_3\text{-}OH)\}_4].H_2NCH_2CH_2NH_2$ (Copp *et al.*, 1992), the diamine acts solely as a bis-acceptor of O—H···N hydrogen bonds; in the 2:1 adduct with phenol, $(C_6H_5OH)_2.H_2NCH_2CH_2NH_2$ (Loehlin *et al.*, 1994), and in the methanol-solvated 2:1 adduct with 4,4'-biphenol, $(HOC_6H_4C_6H_4OH)_2.H_2NCH_2CH_2NH_2.MeOH$ (Fergu-son, Glidewell, Gregson, Meehan & Patterson, 1998), each nitrogen is both an acceptor and a single donor, while in the 1:1 adduct with 4,4'-biphenol each N atom of the diamine acts as a single donor and double acceptor of hydrogen bonds in a continuous three-dimensional diamondoid network (Ferguson, Glidewell, Gregson, Meehan & Patterson, 1998). Only in the 1:1 adduct with 4,4'-biphenol is the idealized comple-mentarity (Ermer & Eling, 1994) of NH_2 groups (as double donors and single acceptors of hydrogen bonds) and OH groups (as single donors and double acceptors) apparent. In all these adducts the diamine adopts a *trans* conformation, which is nearly, or precisely, planar. Despite the variety of donor–acceptor behaviour available, in each of the adducts the two independent amino groups of the diamine behave similarly, although there is no obvious necessity for this. The systematics of the hydrogen-bonding behaviour of 1,2-diaminoethane will clearly repay further study.

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