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Crystal Engineering Using Trisphenols. Three-Dimensional Hydrogen-Bonding Networks in 1,1,1-Tris(4-hydroxyphenyl)ethane, its Hydrated Adduct with 1,4-Diazabicyclo[2.2.2]octane (1/1/1) and its Adduct with Piperazine (4/3)

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Abstract

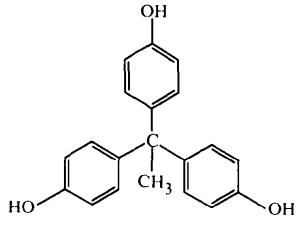
In 1,1,1-tris(4-hydroxyphenyl)ethane, $C_{20}H_{18}O_3$ (1), monoclinic *Ia*, a = 7.9781 (10), b = 18.558 (3), c = 11.1995 (13) Å, β = 101.668 (9)°, with Z = 4, each of the hydroxyl groups acts as both a donor and an acceptor of hydrogen bonds of the type O—H···O. The molecules are thus connected into square nets, graph set $R_4^4(38)$, pairs of which are then interwoven; the nets are themselves interconnected by further hydrogen bonds to give a continuous three-dimensional network. In 1,1,1-tris(4-hydroxyphenyl)ethane–1,4-diazabicyclo[2.2.2]octane–water (1/1/1), $C_{20}H_{18}O_3.C_6H_{12}N_2.H_2O$ (2), triclinic $P\bar{1}$, a = 10.421 (2), b = 10.734 (2), c = 10.9756 (13) Å, α = 76.645 (12), β = 74.513 (11), γ = 89.305 (13)°, with Z = 2, the water molecules are linked to the trisphenol and the diamine units by O—H···O and O—H···N hydrogen bonds, respectively, to form a linear aggregate. These aggregates are linked into chains by the formation of O—H···N hydrogen bonds between the trisphenol and the neighbouring diamine; however, alongside hydrogen-bond formation between the trisphenol and the diamine, there is also partial transfer of a proton, so that the intra-chain links between trisphenol and diamine units are in fact a mixture of O—H···N and N—H···O hydrogen bonds. These chains in the [101] direction are cross-linked by further O—H···O hydrogen bonds, involving only trisphenol O atoms, which form chains in both the [010] and [001] directions, thus generating a continuous three-dimensional network. Adduct (3), 1,1,1-tris(4-hydroxyphenyl)ethane–piperazine (4/3), $(C_{20}H_{18}O_3)_4.(C_4H_{10}N_2)_3$, triclinic $P\bar{1}$, a = 12.5049 (11), b = 12.7046 (10), c = 14.6226 (9) Å, α = 113.738 (6), β = 100.839 (6), γ = 102.438 (7)°, with Z = 1, has two independent trisphenol molecules in general positions and three independent piperazine molecules lying about centres of inversion. The five independent components of the asymmetric unit are linked together by means of three O—H···N and one O—H···O hydrogen bonds to form an open aggregate containing no hydrogen-bonded rings. These aggregates are connected into three sets of interlinked chains in the [010], [001] and [$\bar{1}$10] directions: the [010] and [$\bar{1}$10] chains employ only O—H···O hydrogen bonds, while the [001] chains employ both O—H···N and N—H···O hydrogen bonds. Additionally, the inversion symmetry at each piperazine unit gives rise to further interlinks.

1. Introduction

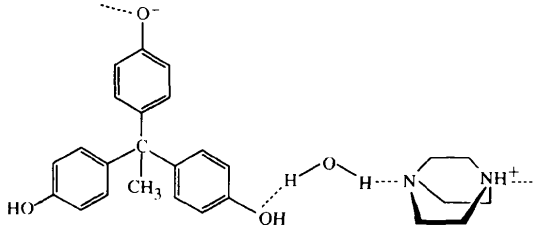
Simple unfunctionalized bisphenols such as 4,4′-diphenol, HOC_6H_4–C_6H_4OH, and 4,4′-isopropylidenediphenol, $Me_2C(C_6H_4OH)_2$, adopt crystal structures in which each hydroxyl group acts as both a donor and an acceptor of hydrogen bonds (Jackisck, Fronczek, Geiger, Hale, Daly & Butler, 1990; Goldberg, Stein, Tanaka & Toda, 1991). In this way each molecule is hydrogen bonded to four others and in both structures this leads to the formation of sheets. In the structure of the triol 1,3,5-trihydroxybenzene again each hydroxyl group acts as both a donor and an acceptor of hydrogen bonds, so that each molecule is hydrogen bonded to six others in a very compact molecular array (Maartmann-Moe, 1965). The two bisphenols 4,4′-diphenol and 4,4′-isopropylidenediphenol both form adducts with diamines such as 1,4-diazabicyclo[2.2.2]octane, $N(CH_2CH_2)_3N$ (DABCO), or piperazine, $HN(CH_2CH_2)_2NH$, in each case having 1:1 bisphenol:diamine stoichiometry. In the DABCO adduct with 4,4′-isopropylidenediphenol, the bisphenol and diamine units are linked by O—H···N hydrogen bonds into continuous chains of alternating bis-donors and bis-acceptors of hydrogen bonds (Ferguson, Coupar & Glidewell, 1997). The stoichiometries of the other adducts formed by these bisphenols with DABCO or piperazine are certainly consistent with, in each case, the bisphenol acting solely as a donor of hydrogen bonds and the diamine acting as a bis-acceptor; simple chain structures consisting of alternating bisphenols and diamines are the simplest structural type for such adducts.

In seeking routes to self-assembled microporous organic solids we have turned our attention to

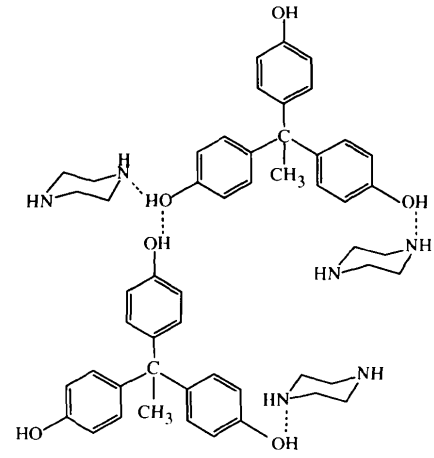
the trigonally symmetric trisphenol 1,1,1-tris(4-hydroxyphenyl)ethane, $CH_3C(C_6H_4OH)_3$ (1); in this molecule the hydroxyl O atoms are expected to be *ca* 9.5 Å apart (*cf. ca* 4.8 Å in 1,3,5-trihydroxybenzene) and if all these hydroxyl groups act either as both a donor and an acceptor of hydrogen bonds or as donors only to diamines, it may be expected that solid-state structures of some complexity will result. We have previously shown (Coupar, Glidewell & Ferguson, 1997) that the trisphenol (1) forms several adducts with hexamethylenetetramine, $(CH_2)_6N_4$, in which the trisphenol:tetramine ratios are 1:1, 2:3 and 1:2, and we have shown further that the structure of the 1:2 adduct consists of parallel stacks, each stack consisting of a triple helix with individual strands containing alternating tetramine and trisphenol units. We have now found that with DABCO the trisphenol (1) forms a hydrated adduct (2) of stoichiometry (1).DABCO.H_2O and with piperazine it forms an adduct (3) of stoichiometry $(1)_4$.$(piperazine)_3$. Here we describe the crystal structures of (1) itself and the two adducts (2) and (3); not only do these structure analyses confirm and elucidate the unusual stoichiometries of (2) and (3), but they establish that (1)–(3) all contain continuous three-dimensional hydrogen-bonded networks. These structures, taken together with those of adducts of bisphenols with DABCO (Mak, Yip & Book, 1984; Ferguson, Coupar & Glidewell, 1997) and piperazine (Coupar, Ferguson & Glidewell, 1996*a*,*b*), provide a further illustration of the enormous versatility of the O—H···N and O—H···O synthons in crystal engineering (Subramanian & Zaworotko, 1994; Desiraju, 1995).



(1)



(2)



(3)

2. Experimental

2.1. *Synthesis*

Compound (1) was obtained from Aldrich: crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in methanol. Compounds (2) and (3) were obtained by co-crystallization of equimolar quantities of (1) and DABCO or piperazine, respectively, from methanol solutions exposed to air. Analysis: (2) found: C 72.0, H 7.3, N 6.4%; $C_{26}H_{32}N_2O_4$ requires: C 71.5, H 7.4, N 6.4%; (3) found: C 75.1, H 7.0, N 5.7%; $C_{92}H_{102}N_6O_{12}$ requires: C 74.5, H 6.9, N 5.7%. Samples of adducts (2) and (3) suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

2.2. *Data collection, structure solution and refinement*

Details of cell data, data collection and refinement are summarized in Table 1. For compound (1) the systematic absences (*hkl* absent if $h + k + l = 2n + 1$, *h*0*l* absent if $h = 2n + 1$) permitted the space group to be *I*2/*a* or *Ia*; *Ia* (*Cc*, number 9) was chosen on the basis of the expected density for $Z = 4$ and confirmed by successful analysis. Compounds (2) and (3) are both triclinic; in each case space group $P\bar{1}$ was chosen and confirmed by the analysis. All structures were solved by direct methods (Gabe, Le Page, Charland, Lee & White, 1989). A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed to reduce statistical bias (Wilson, 1976). H atoms bonded to carbon or nitrogen were positioned on geometric grounds (C—H 0.93–0.97, N—H 0.90 Å) and coordinates for hydroxyl H atoms were originally obtained from difference maps. For compound (2) it was clear from an early stage that one of the hydroxyl H atoms, that on O3, was in fact disordered with partial transfer to a neighbouring N atom; the site occupation factors for the two alternative sites refined to 0.63 (5) and 0.37 (5). All H atoms were included in the refinements

Table 1. *Experimental details*

	(1)	(2)	(3)
Crystal data			
Chemical formula	$C_{20}H_{18}O_3$	$C_{20}H_{18}O_3.C_6H_{12}N_2.H_2O$	$4(C_{20}H_{18}O_3).3(C_4H_{10}N_2)$
Chemical formula weight	306.34	436.54	1483.80
Cell setting	Monoclinic	Triclinic	Triclinic
Space group	*Ia*	$P\bar{1}$	$P\bar{1}$
a (Å)	7.9781 (10)	10.421 (2)	12.5049 (11)
b (Å)	18.558 (3)	10.734 (2)	12.7046 (10)
c (Å)	11.1995 (13)	10.9756 (13)	14.6226 (9)
α (°)		76.645 (12)	113.738 (6)
β (°)	101.668 (9)	74.513 (11)	100.839 (6)
γ (°)		89.305 (13)	102.438 (7)
V (Å^3)	1623.9 (4)	1149.5 (3)	1976.1 (3)
Z	4	2	1
D_x (Mg m^{-3})	1.253	1.261	1.247
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
θ range (°)	10.22–17.43	9.6–16.4	9.3–17.3
μ (mm^{-1})	0.083	0.085	0.082
Temperature (K)	294 (1)	294 (1)	294 (1)
Crystal form	Plate	Block	Plate
Crystal size (mm)	0.43 × 0.35 × 0.07	0.42 × 0.38 × 0.26	0.41 × 0.41 × 0.25
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	None	None	None
No. of measured reflections	2786	4984	6910
No. of independent reflections	1499	4984	6910
No. of observed reflections	919	2195	2455
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.030	–	–
θ_{max} (°)	25	27	25
Range of h, k, l	$0 \rightarrow h \rightarrow 9$ $-21 \rightarrow k \rightarrow 22$ $-13 \rightarrow l \rightarrow 12$	$-13 \rightarrow h \rightarrow 13$ $0 \rightarrow k \rightarrow 13$ $-13 \rightarrow l \rightarrow 13$	$-14 \rightarrow h \rightarrow 14$ $0 \rightarrow k \rightarrow 15$ $-17 \rightarrow l \rightarrow 15$
No. of standard reflections	3	3	3
Frequency of standard reflections (min)	120	120	60
Intensity decay (%)	No decay, variation 1.2	No decay, variation 1.1	5.2
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0447	0.0629	0.0542
$wR(F^2)$	0.0917	0.1618	0.1311
S	0.968	0.932	0.866
No. of reflections used in refinement	1499	4984	6910
No. of parameters used	212	299	503
H-atom treatment	Riding (C—H 0.93–0.96, O—H 0.82 Å)	Riding (C—H 0.93–0.97, N—H 0.91, O—H 0.82 Å)	Riding (C—H 0.93–0.97, N—H 0.90, O—H 0.82 Å)
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0399P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0681P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0480P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.002	0.000	0.026
$\Delta\rho_{max}$ (e Å^{-3})	0.166	0.223	0.262
$\Delta\rho_{min}$ (e Å^{-3})	−0.148	−0.285	−0.185
Extinction method	*SHELXL*93 (Sheldrick, 1993)	None	None
Extinction coefficient	0.0112 (14)	–	–
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)
Computer programs			
Data collection	*CAD*-4 (Enraf–Nonius, 1989)	*CAD*-4 (Enraf–Nonius, 1989)	*CAD*-4 (Enraf–Nonius, 1989)
Cell refinement	*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*94 (Gabe, Le Page, Charland, Lee & White, 1989)	*DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989)	*DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989)
Structure solution	*SHELXS*86 (Sheldrick, 1985)	*SHELXS*86 (Sheldrick, 1985)	*SHELXS*86 (Sheldrick, 1985)
Structure refinement	*NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993)	*NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993)	*NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993)
Preparation of material for publication	*NRCVAX*94, *SHELXL*93 and *WordPerfect* macro PREPCIF	*NRCVAX*94, *SHELXL*93 and *WordPerfect* macro PREPCIF	*NRCVAX*94, *SHELXL*93 and *WordPerfect* macro PREPCIF

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
(1)				
O1	−0.4520 (5)	0.3902 (2)	0.3383 (3)	0.0618 (10)
O2	0.2624 (5)	0.1039 (2)	−0.0559 (3)	0.0565 (10)
O3	−0.3512 (5)	0.4798 (2)	−0.4711 (3)	0.0561 (10)
C1	0.0000 (6)	0.3855 (2)	0.0000 (4)	0.0409 (13)
C2	0.1576 (6)	0.4327 (2)	0.0475 (4)	0.0490 (14)
C11	−0.1211 (6)	0.3877 (2)	0.0902 (4)	0.0368 (12)
C12	−0.0773 (6)	0.4212 (2)	0.2027 (4)	0.0464 (13)
C13	−0.1846 (7)	0.4222 (3)	0.2865 (4)	0.0472 (13)
C14	−0.3424 (6)	0.3899 (2)	0.2571 (4)	0.0448 (13)
C15	−0.3917 (6)	0.3559 (3)	0.1474 (4)	0.0486 (13)
C16	−0.2826 (6)	0.3555 (2)	0.0651 (4)	0.0470 (13)
C21	0.0676 (6)	0.3087 (3)	−0.0121 (4)	0.0396 (12)
C22	0.1683 (6)	0.2961 (2)	−0.0966 (5)	0.0529 (15)
C23	0.2346 (7)	0.2293 (3)	−0.1125 (4)	0.0517 (14)
C24	0.2020 (6)	0.1728 (2)	−0.0418 (4)	0.0432 (13)
C25	0.1029 (6)	0.1827 (3)	0.0436 (4)	0.0498 (14)
C26	0.0372 (7)	0.2508 (3)	0.0585 (4)	0.0462 (13)
C31	−0.0939 (6)	0.4115 (2)	−0.1257 (4)	0.0376 (11)
C32	−0.0806 (6)	0.4820 (2)	−0.1644 (4)	0.0385 (12)
C33	−0.1640 (6)	0.5062 (3)	−0.2779 (4)	0.0438 (13)
C34	−0.2646 (6)	0.4591 (3)	−0.3562 (4)	0.0404 (12)
C35	−0.2810 (6)	0.3890 (3)	−0.3220 (4)	0.0490 (13)
C36	−0.1950 (7)	0.3655 (2)	−0.2077 (4)	0.0456 (13)
(2)				
O1	0.2334 (2)	0.3294 (2)	0.7246 (2)	0.0453 (5)
O2	0.0813 (2)	−0.4856 (2)	0.6297 (2)	0.0639 (7)
O3	0.0842 (2)	0.2453 (2)	−0.0508 (2)	0.0528 (6)
O4	0.4315 (4)	0.4874 (3)	0.7708 (4)	0.1144 (12)
N1	0.8502 (3)	0.3227 (2)	0.9525 (2)	0.0442 (6)
N2	0.6398 (3)	0.4008 (3)	0.8936 (3)	0.0521 (7)
C1	0.3182 (3)	0.0137 (3)	0.3579 (3)	0.0324 (7)
C2	0.4703 (3)	0.0093 (3)	0.3048 (3)	0.0450 (8)
C11	0.2912 (3)	0.0954 (3)	0.4602 (3)	0.0301 (6)
C12	0.3443 (3)	0.2210 (3)	0.4254 (3)	0.0407 (8)
C13	0.3254 (3)	0.2969 (3)	0.5135 (3)	0.0423 (8)
C14	0.2496 (3)	0.2489 (3)	0.6419 (3)	0.0359 (7)
C15	0.1944 (3)	0.1265 (3)	0.6778 (3)	0.0370 (7)
C16	0.2145 (3)	0.0514 (3)	0.5877 (3)	0.0350 (7)
C21	0.2576 (3)	−0.1238 (3)	0.4236 (3)	0.0322 (7)
C22	0.3257 (3)	−0.2133 (3)	0.4928 (3)	0.0451 (8)
C23	0.2702 (3)	−0.3333 (3)	0.5606 (3)	0.0505 (9)
C24	0.1430 (3)	−0.3684 (3)	0.5620 (3)	0.0421 (8)
C25	0.0727 (3)	−0.2835 (3)	0.4935 (3)	0.0409 (7)
C26	0.1298 (3)	−0.1626 (3)	0.4259 (3)	0.0373 (7)
C31	0.2562 (3)	0.0748 (3)	0.2471 (3)	0.0309 (6)
C32	0.3114 (3)	0.0674 (3)	0.1193 (3)	0.0394 (7)
C33	0.2534 (3)	0.1225 (3)	0.0208 (3)	0.0430 (8)
C34	0.1370 (3)	0.1881 (3)	0.0464 (3)	0.0376 (7)
C35	0.0799 (3)	0.1932 (3)	0.1744 (3)	0.0375 (7)
C36	0.1392 (3)	0.1391 (3)	0.2705 (3)	0.0385 (7)
C41	0.8430 (3)	0.2843 (3)	0.8328 (3)	0.0562 (9)
C42	0.8503 (3)	0.4643 (3)	0.9303 (3)	0.0578 (9)
C43	0.7332 (3)	0.2646 (4)	1.0596 (3)	0.0664 (11)
C51	0.7152 (4)	0.3326 (4)	0.7992 (4)	0.0832 (13)
C52	0.7231 (3)	0.5091 (3)	0.8927 (4)	0.0678 (11)
C53	0.6066 (3)	0.3151 (4)	1.0228 (4)	0.0724 (11)
(3)				
O1	0.1611 (2)	0.0938 (2)	0.2901 (2)	0.0600 (8)
O2	0.1312 (2)	0.7820 (2)	0.2845 (2)	0.0516 (7)
O3	0.0805 (3)	0.6982 (3)	0.9016 (2)	0.0546 (7)
C1	0.2798 (3)	0.5983 (3)	0.5676 (3)	0.0355 (9)
C2	0.4119 (3)	0.6590 (3)	0.6184 (3)	0.0487 (10)
C11	0.2520 (3)	0.4610 (3)	0.5014 (3)	0.0352 (9)
C12	0.3125 (3)	0.4169 (3)	0.4330 (3)	0.0451 (10)
C13	0.2822 (3)	0.2951 (3)	0.3643 (3)	0.0475 (10)
C14	0.1891 (3)	0.2131 (3)	0.3628 (3)	0.0376 (9)
C15	0.1282 (3)	0.2526 (3)	0.4303 (3)	0.0425 (10)
C16	0.1593 (3)	0.3755 (3)	0.4989 (3)	0.0412 (10)
C21	0.2379 (3)	0.6499 (3)	0.4933 (3)	0.0333 (9)
C22	0.2848 (3)	0.7696 (3)	0.5151 (3)	0.0514 (11)
C23	0.2483 (3)	0.8132 (3)	0.4469 (3)	0.0525 (11)
C24	0.1622 (3)	0.7371 (3)	0.3535 (3)	0.0408 (10)
C25	0.1103 (3)	0.6204 (3)	0.3322 (3)	0.0490 (11)
C26	0.1492 (3)	0.5775 (3)	0.4008 (3)	0.0429 (10)
C31	0.2240 (3)	0.6261 (3)	0.6558 (3)	0.0322 (9)
C32	0.2540 (3)	0.5919 (3)	0.7330 (3)	0.0412 (10)
C33	0.2064 (3)	0.6156 (3)	0.8138 (3)	0.0394 (9)
C34	0.1265 (3)	0.6754 (3)	0.8204 (3)	0.0373 (9)
C35	0.0925 (3)	0.7073 (3)	0.7434 (3)	0.0413 (10)
C36	0.1412 (3)	0.6837 (3)	0.6623 (3)	0.0416 (10)
O4	0.0052 (2)	0.9201 (2)	0.2931 (3)	0.0740 (9)
O5	−0.7377 (2)	0.9719 (3)	0.1493 (2)	0.0641 (8)
O6	−0.6843 (2)	0.2305 (2)	0.0682 (3)	0.0847 (10)
C3	−0.4530 (3)	0.7429 (3)	0.2988 (3)	0.0389 (9)
C4	−0.4369 (3)	0.7783 (3)	0.4166 (3)	0.0543 (11)
C41	−0.3320 (3)	0.7865 (3)	0.2907 (3)	0.0423 (10)
C42	−0.2987 (4)	0.8767 (4)	0.2633 (3)	0.0674 (13)
C43	−0.1868 (4)	0.9215 (4)	0.2645 (4)	0.0762 (15)
C44	−0.1053 (3)	0.8740 (3)	0.2919 (3)	0.0527 (11)
C45	−0.1358 (3)	0.7835 (4)	0.3203 (3)	0.0594 (12)
C46	−0.2474 (3)	0.7410 (3)	0.3187 (3)	0.0590 (12)
C51	−0.5312 (3)	0.8053 (3)	0.2621 (3)	0.0353 (9)
C52	−0.5912 (3)	0.7578 (3)	0.1569 (3)	0.0426 (10)
C53	−0.6598 (3)	0.8137 (3)	0.1201 (3)	0.0414 (10)
C54	−0.6692 (3)	0.9203 (3)	0.1894 (3)	0.0417 (10)
C55	−0.6082 (3)	0.9717 (3)	0.2931 (3)	0.0502 (11)
C56	−0.5412 (3)	0.9140 (3)	0.3280 (3)	0.0490 (11)
C61	−0.5112 (3)	0.6044 (3)	0.2336 (3)	0.0388 (9)
C62	−0.6107 (3)	0.5496 (4)	0.2482 (3)	0.0526 (11)
C63	−0.6677 (3)	0.4261 (4)	0.1915 (3)	0.0533 (11)
C64	−0.6271 (3)	0.3527 (4)	0.1192 (3)	0.0527 (11)
C65	−0.5308 (4)	0.4048 (4)	0.0999 (3)	0.0600 (12)
C66	−0.4743 (3)	0.5295 (3)	0.1563 (3)	0.0508 (11)
N71	0.0641 (3)	0.6229 (3)	0.0854 (2)	0.0516 (9)
C72	0.1121 (3)	0.5218 (4)	0.0612 (3)	0.0619 (12)
C73	−0.0616 (3)	0.5750 (4)	0.0517 (3)	0.0577 (12)
N81	−0.0157 (3)	0.8746 (3)	0.9292 (3)	0.0670 (10)
C82	−0.0374 (4)	0.9063 (3)	1.0278 (3)	0.0568 (11)
C83	0.0673 (4)	0.9777 (3)	0.9314 (3)	0.0628 (12)
N91	−0.5499 (3)	0.0906 (3)	−0.0081 (3)	0.0756 (11)
C92	−0.6072 (4)	−0.0372 (4)	−0.0763 (3)	0.0722 (14)
C93	−0.4723 (4)	0.1124 (4)	0.0888 (3)	0.0689 (13)

as riding atoms. The diagrams were prepared using *ORTEP*II (Johnson, 1976). Final fractional coordinates are presented in Table 2 and selected dimensions in Table 3.*

3. Results and discussion

3.1. *Structures and molecular packing*

3.1.1. *Compound (1).* In the structure of the trisphenol (1) each of the hydroxyl groups acts as both a donor and an acceptor of hydrogen bonds, so that each molecule is linked to six others, *via* hydrogen bonds of the O—H···O type. O1 (Fig. 1) in the molecule at (x, y, z) acts as a hydrogen-bond donor to O3 in the molecule at (x, y, 1 + z), thus generating chains of molecules running in the [001] direction (Fig. 2), where

* Lists of atomic coordinates, anisotropic displacement parameters and structure factors, and a difference map for (2) have been deposited with the IUCr (Reference: AB0362). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected molecular dimensions (Å, °)*

(1)			
C1—C11	1.533 (6)	O1—C14	1.383 (5)
C1—C21	1.539 (6)	O2—C24	1.386 (5)
C1—C31	1.533 (6)	O3—C34	1.387 (5)
C1—C2	1.536 (6)		
C2—C1—C11—C12	−7.0 (6)		
C2—C1—C21—C22	−65.4 (5)		
C2—C1—C31—C32	−24.2 (6)		
O1···O3^{i}	2.697 (5)	O1—H1···O3^{i}	173
O2···O1^{ii}	2.775 (4)	O2—H2···O1^{ii}	169
O3···O2^{iii}	2.715 (5)	O3—H3···O2^{iii}	162
(2)			
C1—C11	1.546 (4)	O1—C14	1.370 (3)
C1—C21	1.544 (4)	O2—C24	1.372 (3)
C1—C31	1.539 (4)	O3—C34	1.350 (3)
C1—C2	1.540 (4)		
N1—C41	1.485 (4)	N2—C51	1.459 (4)
N1—C42	1.482 (4)	N2—C52	1.456 (4)
N1—C43	1.473 (4)	N2—C53	1.456 (4)
C41—C51	1.528 (5)	C42—C52	1.531 (4)
C43—C53	1.537 (5)		
C2—C1—C11—C12	56.9 (3)	N1—C41—C51—N2	0.0 (4)
C2—C1—C21—C22	36.2 (3)	N1—C42—C52—N2	1.5 (4)
C2—C1—C31—C32	29.0 (4)	N1—C43—C53—N2	1.7 (4)
O1···O3^{i}	2.504 (3)	O1—H1···O3^{i}	169
O2···O1^{iv}	2.718 (3)	O2—H2···O1^{iv}	167
O3···N1^{v}	2.560 (3)	O3—H3···N1^{v}	148
O4···O1	2.905 (4)	O4—H4*A*···O1	162
O4···N2	2.886 (4)	O4—H4*B*···N2	172
N1···O3^{vi}	2.560 (3)	N1—H1*A*···O3^{vi}	158
(3)			
C1—C11	1.534 (4)	C3—C41	1.539 (5)
C1—C21	1.546 (4)	C3—C51	1.533 (4)
C1—C31	1.535 (4)	C3—C61	1.540 (5)
C1—C2	1.550 (4)	C3—C4	1.555 (4)
O1—C14	1.372 (4)	O4—C44	1.373 (4)
O2—C24	1.380 (4)	O5—C54	1.367 (4)
O3—C34	1.370 (4)	O6—C64	1.366 (4)
N71—C72	1.477 (4)	N71—C73	1.462 (4)
C72—C73^{vii}	1.508 (5)	C73—C72^{vii}	1.508 (5)
N81—C82	1.429 (4)	N81—C83	1.470 (4)
C82—C83^{viii}	1.509 (5)	C83—C82^{viii}	1.509 (5)
N91—C92	1.438 (5)	N91—C93	1.441 (5)
C92—C93^{ix}	1.507 (5)	C93—C92^{ix}	1.507 (5)
C2—C1—C11—C12	−46.6 (4)	C4—C3—C41—C42	−114.1 (4)
C2—C1—C21—C22	−36.2 (4)	C4—C3—C51—C52	−156.8 (3)
C2—C1—C31—C32	−58.1 (4)	C4—C3—C61—C62	50.8 (4)
O1···O4^{iv}	2.633 (3)	O1—H1···O4^{iv}	162
O2···N71	2.623 (4)	O2—H2···N71	169
O3···N81	2.693 (4)	O3—H3···N81	177
O4···O2	2.582 (3)	O4—H4···O2	166
O5···O1^{x}	2.739 (4)	O5—H5···O1^{x}	158
O6···N91	2.761 (4)	O6—H6···N91	167
N71···O3^{xi}	3.220 (4)	N71—H71···O3^{xi}	154
C82···O6^{xii}	3.270 (5)	C82—H82*B*···O6^{xii}	132

Symmetry codes: (i) $x, y, 1+z$; (ii) $1+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (iii) $-\frac{1}{2}+x, \frac{1}{2}+y, -\frac{1}{2}+z$; (iv) $x, -1+y, z$; (v) $-1+x, y, -1+z$; (vi) $1+x, y, 1+z$; (vii) $-x, 1-y, -z$; (viii) $-x, 2-y, 2-z$; (ix) $-1-x, -y, -z$; (x) $-1+x, 1+y, z$; (xi) $x, y, -1+z$; (xii) $-1-x, 1-y, 1-z$.

the hydrogen-bonding motif has graph-set $C(12)$ (Etter, 1990; Etter, MacDonald & Bernstein, 1990; Bernstein, Davis, Shimoni & Chang, 1995). O1 at (x, y, z) acts as an acceptor from O2 at $(x-1, \frac{1}{2}-y, \frac{1}{2}+z)$ to give, upon repetition, a further $C(12)$ chain running parallel to the [102] direction. The interaction of these two $C(12)$ motifs produces square nets (Fig. 3) characterized by the graph set $R_4^4(38)$, somewhat similar to the square $R_4^4(32)$ nets observed in the structure of 4,4′-sulfonyldiphenol, $O_2S(C_6H_4OH)_2$ (Glidewell & Ferguson, 1996). In (1) there are two such independent nets, related to one another by a unit translation along the [100] direction. Nets based on very large reticulations encircle large void spaces and, as a consequence of this, the two independent nets are interwoven to form an interpenetrating structure (Fig. 4), again similar to that found in 4,4′-sulfonyldiphenol. Within these interwoven nets O1 is acting as both a donor and an acceptor of hydrogen bonds (Table 3), O2 as a donor only and O3 as an acceptor only, so that the hydrogen-bonding potential is not yet exhausted. Thus, finally, O3 at (x, y, z) acts as a donor to O2 in the molecule at $(x-\frac{1}{2}, \frac{1}{2}+y, z-\frac{1}{2})$ to give a third $C(12)$ chain running parallel to the $[\bar{1}1\bar{1}]$ direction (Fig. 2). This third $C(12)$ chain motif, as well as generating a continuous three-dimensional network,

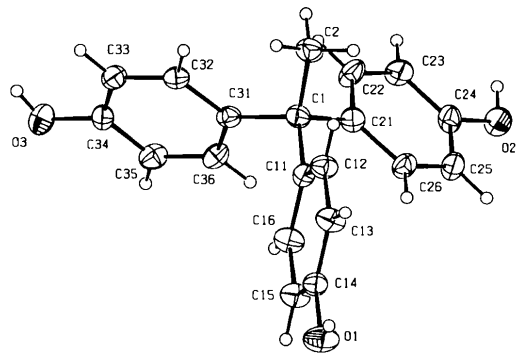


Fig. 1. View of the molecule of (1), showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

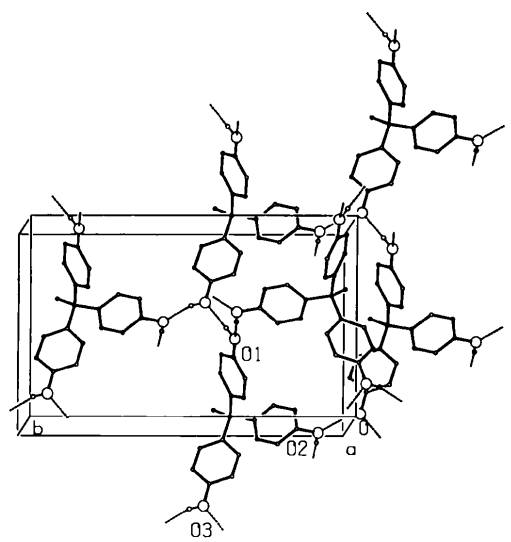


Fig. 2. Packing diagram of the crystal structure of (1), viewed approximately along the a axis, showing the formation of the $C(12)$ chains along [001] and the $C_3^3(6)$ chains along [100].

also gives rise to a $C_3^3(6)$ chain of O—H···O hydrogen bonds running in zigzag fashion in the [100] direction (Fig. 2). O1 at (x, y, z) acts as a donor to O3 at (x, y, $1 + z$) and this O3 atom acts as a donor to O2 at ($x - \frac{1}{2}$, $\frac{1}{2} + y$, $z - \frac{1}{2}$), which in turn acts as a donor to O1 at ($x - \frac{1}{2}$, $-y$, z). Repetition of this sequence brings the hydrogen bonding to O1 in the molecule at ($1 + x$, y, z), acting as an acceptor, and so generates the [100] chain.

3.1.2. *Compound (2).* The asymmetric unit (Fig. 5) comprises one molecule each of the trisphenol, DABCO and water, in which the water molecule acts as a hydrogen-bond donor to N2 of the DABCO molecule and to O1 of the trisphenol; these units are then linked into chains in the [101] direction by means of hydrogen bonds between O3 of the trisphenol at (x, y, z) and N1 in the DABCO molecule at ($x - 1$, y, $z - 1$). This simple description of the asymmetric unit is, however, complicated by the partial transfer of the hydroxyl H atom from O3 of the trisphenol to the neighbouring N1 atom in the next DABCO unit along the chain. A difference map calculated in the plane C34, O3, N1^{v} [symmetry code: (v) $x - 1$, y, $-1 + z$, Table 3] shows clearly the two occupied sites for the H atom, whose site occupation factors refined to 0.63 (5) (adjacent to N1) and 0.37 (5) (adjacent to O3). There is thus a partial transfer of the hydrogen from oxygen (site H3) to nitrogen (site H1*A*) and the chain-forming links between trisphenol and DABCO units are a mixture of N—H···O (major occupancy) and O—H···N (minor occupancy) hydrogen bonds. This chain-forming motif thus employs both N atoms of the DABCO molecule as hydrogen-bond acceptors and both O—H bonds of the water molecule together with one of the hydroxyl groups of the trisphenol as hydrogen-bond donors. There thus remain two potential hydrogen-bond donors within each asymmetric unit, atoms O1 and O2.

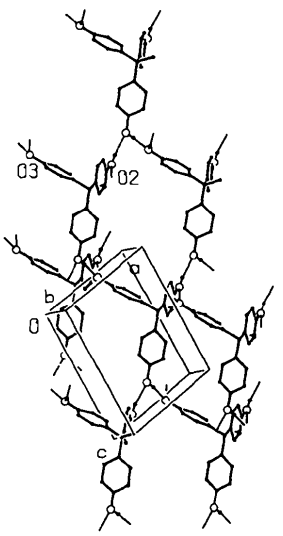


Fig. 3. View of part of the structure of (1), approximately along the *b* axis, showing the formation of the $R_4^4(38)$ net arising from the [001] and [20$\bar{1}$] chains.

Atom O1 in the asymmetric unit at (x, y, z) acts as a hydrogen-bond donor to O3 in the unit at (x, y, $1 + z$), while O2 at (x, y, z) acts as a donor to O1 at (x, $y - 1$, z). In this manner the original tripartite chains are cross-linked by O—H···O hydrogen bonds in both the [001] and [010] directions, thereby generating a continuous three-dimensional hydrogen-bonded network (Fig. 6).

For the dominant distribution of the disordered H atom, therefore, N1 and N2 act within this scheme as hydrogen-bond donor and acceptor, respectively, O1 as a donor and as a double acceptor, O2 as a donor only,

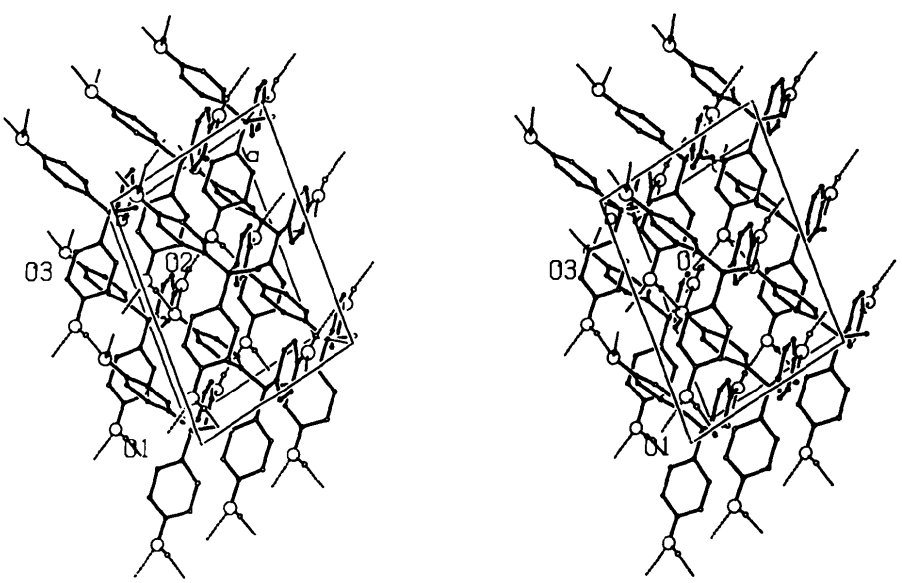


Fig. 4. Stereoview of the crystal structure of (1), viewed along the *b* axis, showing the interpenetration of the $R_4^4(38)$ nets.

O3 as a double acceptor and O4 as a double donor of hydrogen bonds. In addition to these strong interactions of N—H···O, O—H···N and O—H···O types O2 and O4 both act as acceptors in weak hydrogen bonds of the C—H···O type. O2 in the trisphenol at (x, y, z) acts as an acceptor in two C—H···O hydrogen bonds, where the donors are a pair of roughly parallel C—H bonds, C41—H41*B* and C42—H42*A*, in the same DABCO molecule, that at ($x-1$, $y-1$, z); on the other hand, the O atom of the water molecule, O4, acts as an acceptor from an aryl C—H bond, C23—H23, in the trisphenol at (x, $1+y$, z) and from a DABCO C—H bond, C53—H53*B*, in the DABCO unit at ($1-x$, $1-y$, $2-z$). In this manner, of the nine oxygen lone pairs in the dominant disorder form of the asymmetric unit (two each on O1, O2 and O4, and three on O3) all but one on O3 are utilized as hydrogen-bond acceptors.

3.1.3. *Compound (3).* This adduct crystallizes in space group $P\bar{1}$ with two independent molecules of the trisphenol component lying in general positions and three independent piperazine molecules lying about the centres of inversion at (0, 0, 0), ($\frac{1}{2}$, 0, 0) and (0, $\frac{1}{2}$, 0). The total unit-cell contents, therefore, comprise four trisphenol molecules and three piperazine molecules, entirely consistent with the composition of (3) deduced from elemental analysis. So far as the piperazine units alone are concerned, a Z' value of 1.5 is highly unusual, and a recent survey (Brock & Dunitz, 1994) found that only *ca* 0.3% of $P\bar{1}$ structures had this value of Z'. Moreover, it was also pointed out that in $P\bar{1}$ structures there are almost always seven, and usually eight, unoccupied inversion centres: in (3) there are only five.

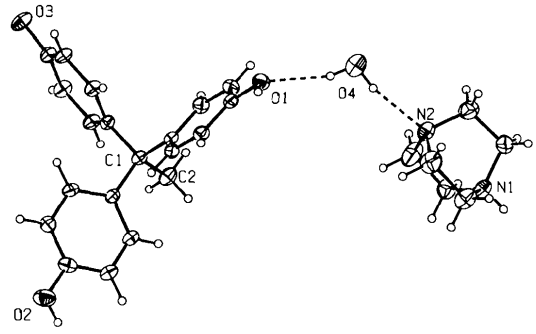


Fig. 5. View of the asymmetric unit of (2), showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

It is convenient, although not essential, to discuss the hydrogen bonding first in terms of the interactions within the asymmetric unit (Fig. 7), bearing in mind the symmetry-generated interactions involving the centrosymmetric piperazine units, and secondly in terms of the interactions between such aggregates. Within the asymmetric unit there are six independent hydroxyl groups, all of which may be expected to act as donors of hydrogen bonds and any or all of which could in addition act as acceptors. There are also three independent NH groups within the asymmetric unit, each of which may be expected to act as hydrogen-bond acceptors and any or all of which could also act as donors. If all the hydroxyl groups act as hydrogen-bond donors, then at least half must act as acceptors of O—H···O hydrogen bonds as there are only six N atoms per unit cell to act as possible hydrogen-bond acceptors.

Within the asymmetric unit O2, O3, O4 and O6 act as hydrogen-bond donors to N71, N81, O2 and N91, respectively: these interactions tie together all the components of the asymmetric unit into an open aggregate without the formation of any hydrogen-bonded rings (Fig. 7). This aggregate is attached by means of O—H···O, O—H···N, N—H···O and C—H···O hydrogen bonds to seven other such aggregates: O1 acts as a donor to O4 in the aggregate at (x, $y-1$, z), giving rise to chain formation parallel to the [010] direction; N71 acts as a donor to O3 in the aggregate at (x, y, $z-1$), giving rise to chains parallel to the [001] direction; O5 acts as a donor to O1 in the aggregate at ($x-1$, $1+y$, z), giving rise to chains in the direction [$\bar{1}$10] (Fig. 8).

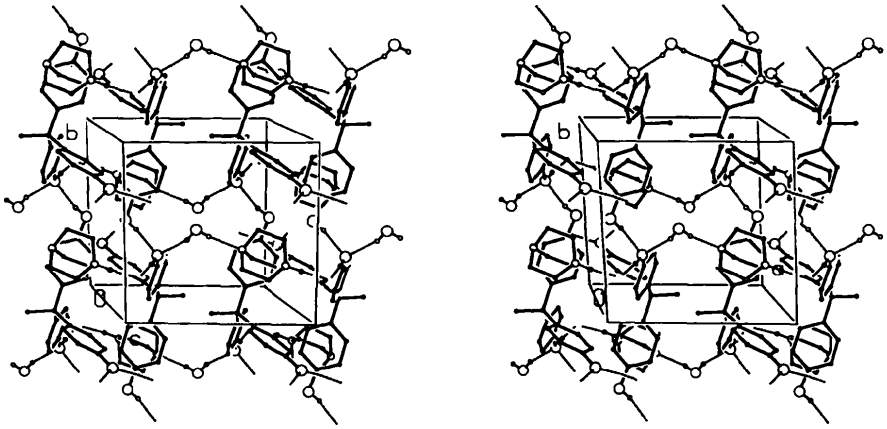


Fig. 6. Stereoview of the crystal structure of (2), showing the chains running in the [010], [001] and [101] directions.

In addition, the centrosymmetric piperazine rings form links, with N71*A* as an acceptor from O2 at (–*x*, 1 – *y*, –*z*), N81*A* as an acceptor from O3 at (–*x*, 2 – *y*, 2 – *z*) and N91*A* as an acceptor from O6 at (–1 – *x*, –*y*, –*z*). Finally, O6 acts as an acceptor from a piperazine C—H bond, C82—H82*B*, in the unit at (–1 – *x*, 1 – *y*, 1 – *z*). In this manner N71, O1, O2, O3, O4 and O6 all act as both donors and acceptors of hydrogen bonds. O5, uniquely in this structure, acts only as a donor and N81 and N91 act as only acceptors; the overall effect of these multiple hydrogen bonds is, as in (2), the generation of a continuous three-dimensional network of hydrogen bonds.

3.2. *Molecular conformations and dimensions*

In none of (1)–(3) does the trisphenol molecule adopt a conformation which reflects its potential threefold rotational symmetry: the torsional angles C2—C1—C*n*1—C*n*2 (*n* = 1–3) in (1)–(3) and the angles C4—C3—C*n*1—C*n*2 (*n* = 4–6) in (3) (Table 3) indicate wide divergence from threefold symmetry. The closest approach to threefold symmetry is made in one of the trisphenol molecules in (3), that centred on C1. The DABCO component in (2) shows no evidence of any twist about the N···N vector away from the optimum D_{3h} symmetry. In (3) the piperazine units are all centrosymmetric and, therefore, adopt the chair conformation and in each the N atoms have the N—H bonds in the axial sites and the lone pairs in the equatorial sites. In free piperazine there is only a very low (*ca* 1.5 kJ mol^{-1}) preference for equatorial N—H sites over axial N—H sites (Jones, Katritzky, Richards, Wyatt, Bishop & Sutton, 1970); hydrogen-bond energies exceed by several-fold this site preference energy difference (Aakeröy & Seddon, 1993).

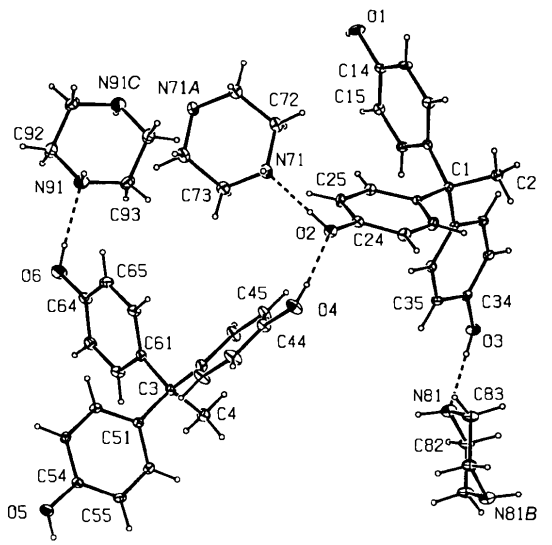


Fig. 7. View of the two independent trisphenol molecules and the three complete centrosymmetric piperazine molecules in (3), showing the atom-numbering scheme. For the sake of clarity, thermal ellipsoids are drawn at the 10% probability level.

In (1) the bond lengths to the central C atom are typical of their types (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), but the C—O distances, although virtually identical (Table 3), are all above the upper quartile value, 1.373 Å, for such bonds in phenols. On the other hand, in (2), where partial proton transfer from O3 to N1 has occurred, the O3—C34 bond is significantly shorter than the other two O—C bonds in this system. At the same time, within the partially protonated DABCO component, the N—C bonds to N1 are significantly longer than those to N2 [mean values 1.480 (4) and 1.457 (4) Å]; these values fall on either side of the value reported for pure crystalline DABCO, 1.470 (7) Å (Nimmo & Lucas, 1976), although the C—C distances found here are rather larger than the 1.513 (5) Å reported for DABCO itself (Nimmo & Lucas, 1976). The C—N bond lengths in the piperazine components of (3) range from 1.429 (4) to 1.477 (4) Å, with the mean value 1.453 Å, whereas the C—C bond lengths are identical within experimental error (Table 3). For isolated piperazine molecules, forming no hydrogen bonds and having both N—H bonds equatorial (rather than axial, as found here), the C—N and C—C bond lengths are 1.467 (4) and 1.540 (8) Å, respectively (Yokozeki & Kuchitsu, 1971).

3.3. *Hydrogen-bonding motifs and dimensions*

The three intersecting chains in (1) which all have graph set *C*(12) have already been described. All of the

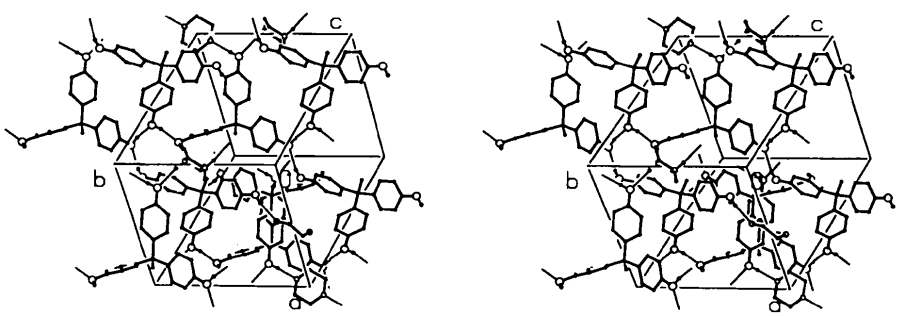


Fig. 8. Stereoview of the crystal structure of (3), showing the chain formation in the [010], [001] and [1̄10] directions.

individual O—H···O hydrogen bonds in these systems have O···O distances similar to those found in bisphenols (Jackisck, Fronczek, Geiger, Hale, Daly & Butler, 1990; Goldberg, Stein, Tanaka & Toda, 1991; Ferguson & Glidewell, 1996; Glidewell & Ferguson, 1996).

In (2) there are three chain-forming motifs: that in the [101] direction (Fig. 6) is characterized by three different types of hydrogen bond and the descriptor for its binary-level graph set (Bernstein, Davis, Shimoni & Chang, 1995) is $C_3^3(19)$, while those in the [010] and [001] directions (Fig. 6) are both characterized by a single type of hydrogen bond and both have graph set $C(12)$. Interaction of the [001] and [101] chains yields $R_8^7(42)$ rings, while interaction of the [010] and [101] chains yields $R_8^7(52)$ rings: the difference between the numbers of donors and acceptors in these descriptors arises from the fact that within these rings atoms O3 and O1, respectively, act as double acceptors of hydrogen bonds, while no acceptor acts as a double donor. The O—H···O hydrogen bonds which involve only neutral O atoms have typical O···O distances (Table 3), *cf.* (1) above. However, the O—H···O hydrogen bond involving the partially deprotonated O3 atom as an acceptor has a very much shorter O···O distance and may therefore be presumed to be much stronger. Although the O···O distance is some 0.50 Å less than the sum of the van der Waals radii (Bondi, 1964), so that this hydrogen bond can readily be classified as strong (Emsley, 1980), a difference map showed clearly that the H atom is adjacent to O1, rather than being symmetrically disposed, or nearly so, between the two O atoms, as commonly found with such O···O distances. Similarly, the N···O distance involving the disordered hydrogen sites, which encompass ionic N^+—H···O^- as well as neutral O—H···N hydrogen bonds, is very short. These data support the view that hydrogen bonds involving ionic components are generally significantly stronger than those involving only neutral species (Aakeröy & Seddon, 1993; Gilli, Bertolasi, Ferretti & Gilli, 1994).

In (3) the chains formed in the [010] and [001] directions each contain two types of hydrogen bond. In the [010] chains these are both of the O—H···O type, with O1 and O4 acting as donors to O2 and $O4^{iv}$ [(iv) $x, -1 + y, z$; Table 3], respectively, and the binary-level graph set is $C_2^2(14)$; in the [001] direction, both O—H···N and N—H···O hydrogen bonds occur with O2 and N71 acting as donors to N71 and $O3^{xi}$ [(xi) $x, y, z - 1$], respectively, with again the binary-level graph set $C_2^2(14)$. In the [$\bar{1}$10] direction the chain-forming motif contains two types of O—H···O hydrogen bond, with O4 and O5 acting as donors to O2 and $O1^x$ [(x) $x - 1, 1 + y, z$]; the binary-level graph set is $C_2^2(24)$.

These hydrogen bonds all generate chains by means of translations and none of the interaggregate connections so far described are between aggregates of opposite chirality. There are actually two interpenetrating networks of opposite hand which have common nodes at the centrosymmetric piperazine molecules. If the piperazine N atoms were disconnected rather than being components of a diamine, there would in fact be no hydrogen-bonded connections between the two interpenetrating networks of opposite hand.

The O···O and O···N distances in (3) for hydrogen bonds of the types O—H···O and O—H···N are generally typical of those in bisphenols and their simple adducts, although the O···O distance in the O4—H···O2 hydrogen bond is rather short (Table 3). As in (2), examination of difference maps showed clearly that, despite the short O···O distance, the hydrogen is clearly adjacent to O4, rather than being approximately centred between the oxygens. On the other hand, the sole N—H···O hydrogen bond in (3) is barely shorter than the C—H···O interaction (Table 3).

4. General comments and conclusions

From the results presented here, and in previous papers (Coupar, Ferguson & Glidewell, 1996*a*,*b*; Coupar, Glidewell & Ferguson, 1997; Ferguson, Coupar & Glidewell, 1997), some generalizations can be drawn about the co-crystallization behaviour of bis- and trisphenols with simple cyclic and cage aza-compounds. While HMTA can act as a mono-, a bis- or, in one recorded example (Jordan & Mak, 1970), as a tris-acceptor of hydrogen bonds, DABCO and piperazine appear always to act as double acceptors, while piperazine can also act as a hydrogen-bond donor, forming both N—H···O and N—H···π(arene) hydrogen bonds (Coupar, Ferguson & Glidewell, 1996*a*). The phenol components always employ all the available hydroxy groups as hydrogen-bond donors and in systems where there are insufficient other acceptors these hydroxy groups will act as acceptors as well as donors.

The principal difference, in structural terms, between the effects of DABCO and those of HMTA, arises from the relative disposition of the hydrogen-bond acceptor lone pairs, which in the case of HMTA introduces bends into any chain containing HMTA. It is the additional flexibility conferred by this chain-bending which gives rise to the double and triple helical structures formed by HMTA with 4,4′-isopropylidenediphenol and 1,1,1-tris(4-hydroxyphenyl)ethane, respectively (Coupar, Glidewell & Ferguson, 1997). This observation leads to a much more general point, of considerable significance in crystal engineering terms. While the behaviour of the individual supramolecular synthons (Desiraju, 1995) employed here, particularly the hard (Braga, Grepioni, Biradha, Pedireddi & Desiraju, 1995) hydrogen bonds such as O—H···O, O—H···N and N—H···O, is reasonably well understood, it is the existence of conformational flexibility (as in the phenolic components

employed here, although not in the amine components) modulated, if not controlled, by the cooperative action of weak soft hydrogen bonds such as C—H···O and C—H···π(arene), which leads to the very wide range of structural types observed. A key deduction from these structural studies is that, even in chemically simple but conformationally flexible systems, the soft hydrogen bonds are of major importance, but if the conformational flexibility is restricted the soft hydrogen bonds are of little structural significance. Conformational flexibility is rather easily controlled by the appropriate molecular design, but the control of soft hydrogen bonds is extremely problematical.

It is noteworthy that the successful design and construction of specific structures in continuous one-, two- or three-dimensional molecular solids (as opposed to finite aggregates) has largely been limited, so far, to systems using molecular building blocks with few, if any, degrees of conformational freedom (Zaworotko, 1994; Fan, Vicent, Geib & Hamilton, 1994; Subramanian & Zaworotko, 1994; Desiraju, 1995; Russell & Ward, 1996). Based upon the knowledge gained from the present study our own future work will be focussed, on the one hand, on the use of designed molecular components with specific dispositions of donor and acceptor sites, aimed at the production of microporous molecular materials, and on the other, on the use of components, particularly polyphenols, with limited conformational flexibility.

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