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# Crystal Engineering Using Bisphenols and Trisphenols. Complexes with Hexamethylenetetramine (HMTA): Strings, Multiple Helices and Chains-of-Rings in the Crystal Structures of the Adducts of HMTA with 4,4′-Thiodiphenol (1/1), 4,4′-Sulfonyldiphenol (1/1), 4,4′-Isopropylidenediphenol (1/1), 1,1,1-Tris(4-hydroxyphenyl)ethane (1/2) and 1,3,5-Trihydroxybenzene (2/3)

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## Abstract

The 4,4′-bisphenols (1), $X(C_6H_4OH)_2$ [*a*, $X$ = nil; *b*, $X$ = O; *c*, $X$ = S; *d*, $X = SO_2$; *e*, $X$ = CO; *f*, $X = CH_2$; *g*, $X = CMe_2$; *h*, $X = C(CF_3)_2$], when co-crystallized from alcoholic solutions with hexamethylenetetramine, $(CH_2)_6N_4$ (HMTA), form 1:1 adducts (4*a*)–(*h*). 4,4′-Thiodiphenol–hexamethylenetetramine (1/1), (4*c*), $C_{12}H_{10}O_2S.C_6H_{12}N_4$, and 4,4′-sulfonyldiphenol–hexamethylenetetramine (1/1), (4*d*), $C_{12}H_{10}O_4S.C_6H_{12}N_4$, are orthorhombic, $Pmn2_1$, (4*c*) $a$ = 15.029 (2), $b$ = 9.7954 (8), $c$ = 5.9817 (11) Å and (4*d*) $a$ = 14.779 (2), $b$ = 10.2558 (15), $c$ = 5.9817 (8) Å, with $Z$ = 2, and the structures consist of zigzag chains comprising strings of alternating bisphenol and HMTA units, each lying across mirror planes and linked by O—H···N hydrogen bonds. In addition, both (4*c*) and (4*d*) exhibit C—H···π(arene) hydrogen bonds with one $CH_2$ group of the HMTA unit acting as a donor to two different arene rings; (4*d*) also exhibits multiple C—H···O=S hydrogen bonds with three C—H bonds in each HMTA unit acting as donors towards a single sulfone O atom. 4,4′-Isopropylidenediphenol–hexamethylenetetramine (1/1), (4*g*), $C_{15}H_{16}O_2.C_6H_{12}N_4$, is monoclinic, $C2/c$, $a$ = 25.093 (6), $b$ = 7.1742 (13), $c$ = 23.612 (7) Å, $\beta$ = 110.42 (2)°, with $Z$ = 8, and again the structure is built from chains of alternating bisphenol and HMTA units linked by O—H···N hydrogen bonds, but these now form double helices around twofold rotation axes; the double helices are themselves linked into sheets by C—H···O hydrogen bonds. The trisphenol (2), $CH_3C(C_6H_4OH)_3$, forms three adducts (5*a*)–(*c*) with HMTA, having trisphenol:HMTA ratios of 1:2 (5*a*), 2:3 (5*b*) and 1:1 (5*c*). 1,1,1-Tris(4-hydroxyphenyl)ethane–hexamethylenetetramine (1/2), (5*a*), $C_{20}H_{18}O_3.(C_6H_{12}N_4)_2$, is orthorhombic, $P2_12_12_1$, $a$ = 6.9928 (10), $b$ = 14.0949 (15), $c$ = 30.999 (4) Å, with $Z$ = 4, and the trisphenol units and half the HMTA units form a triple helix around a $2_1$ axis, in which each strand consists of alternating phenol and HMTA units, linked as usual by O—H···N hydrogen bonds. The remaining HMTA units, which are external to the triple helix, are connected to it by O—H···N hydrogen bonds and are formed into externally buttressing stacks. The triol (3), $1,3,5\text{-}C_6H_3(OH)_3$, forms a 2:3 adduct (6) with HMTA. 1,3,5-Trihydroxybenzene–hexamethylenetetramine (2/3), (6), $C_6H_6O_3.(C_6H_{12}N_4)_{1.5}$, is monoclinic, $C2/c$, $a$ = 23.598 (2), $b$ = 7.136 (2), $c$ = 19.445 (3) Å, $\beta$ = 96.822 (11)°, with $Z$ = 8, and the dominant structural motif consists of centrosymmetric rings containing two molecules each of (3) and HMTA, connected by O—H···N hydrogen bonds; these rings are themselves linked into a chain-of-rings by further HMTA units lying on twofold rotation axes. The hydrogen-bonding patterns are codified using the graph-set approach.

## 1. Introduction

The O—H···N hydrogen bond is a robust and versatile synthon in crystal engineering (Fan, Vincent, Geib & Hamilton, 1994; Subramanian & Zaworotko, 1994; Desiraju, 1995). Since, in general, phenols are stronger acids than alcohols, the O—H···N hydrogen bonds formed between phenols and tertiary or aromatic amines are expected to be stronger than those formed between alcohols and amines. We have accordingly initiated a study of the use of bis- and trisphenols in crystal engineering and here we present results on the interaction of this type of phenol, acting as a hydrogen-bond donor, with hexamethylenetetramine, $(CH_2)_6N_4$ (HMTA), as a hydrogen-bond acceptor.

Simple mono-phenols usually crystallize with HMTA to form adducts having phenol:HMTA ratios of 1:1 or 2:1, in which the HMTA acts as either a mono-acceptor or a bis-acceptor of hydrogen bonds (Tse, Wong & Mak, 1977; Mak, Yu & Lam, 1978; Mahmoud & Wallwork, 1979); only in a single example (Jordan & Mak, 1970) has HMTA been found to act as a triple acceptor. Similarly, in the 1:2 adduct formed between

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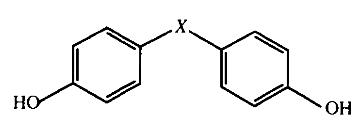
Table 1. *Analytical data*

| Compound | Analysis, Found C(%) | H(%) | N(%) | Ratio phenol:HMTA | Formula | Analysis, Calc. C(%) | H(%) | N(%) |
|---|---|---|---|---|---|---|---|---|
| (4*a*) | 66.3 | 6.7 | 17.3 | 1:1 | $C_{18}H_{22}N_4O_2$ | 66.2 | 6.8 | 17.2 |
| (4*b*) | 63.2 | 6.7 | 16.4 | 1:1 | $C_{18}H_{22}N_4O_3$ | 63.1 | 6.5 | 16.4 |
| (4*c*) | 60.2 | 6.0 | 15.7 | 1:1 | $C_{18}H_{22}N_4O_2S$ | 60.3 | 6.2 | 15.6 |
| (4*d*) | 55.1 | 5.6 | 14.3 | 1:1 | $C_{18}H_{22}N_4O_4S$ | 55.4 | 5.7 | 14.4 |
| (4*e*) | 64.1 | 6.1 | 15.9 | 1:1 | $C_{19}H_{22}N_4O_3$ | 64.4 | 6.3 | 15.8 |
| (4*f*) | 65.4 | 6.9 | 16.1 | 1:1 | $C_{19}H_{24}N_4O_2$ | 67.0 | 7.1 | 16.5 |
| (4*g*) | 68.5 | 7.7 | 15.0 | 1:1 | $C_{21}H_{28}N_4O_2$ | 68.5 | 7.7 | 15.2 |
| (4*h*) | 53.0 | 4.9 | 11.7 | 1:1 | $C_{21}H_{22}F_6N_4O_2$ | 52.9 | 4.7 | 11.8 |
| (4*i*) | 52.4 | 5.2 | 10.8 | 1:1[a] | $C_{22}H_{26}F_6N_4O_3$ | 52.0 | 5.2 | 11.0 |
| (5*a*) | 65.8 | 7.5 | 19.0 | 1:2[b] | $C_{32}H_{42}N_8O_3$ | 65.5 | 7.2 | 19.1 |
| (5*b*) | 67.3 | 7.0 | 16.8 | 2:3[c] | $C_{58}H_{72}N_{12}O_6$ | 67.4 | 7.0 | 16.3 |
| (5*c*) | 70.7 | 7.1 | 13.0 | 1:1[d] | $C_{26}H_{30}N_4O_3$ | 69.9 | 6.8 | 12.6 |
| (5*d*) | 68.6 | 8.1 | 11.1 | 1:1[e] | $C_{29}H_{38}N_4O_4$ | 68.8 | 7.6 | 11.1 |
| (6) | 53.8 | 7.5 | 25.0 | 2:3 | $C_{30}H_{48}N_{12}O_6$ | 53.6 | 7.2 | 25.0 |

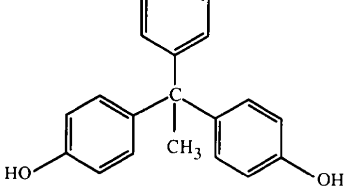
(*a*) Methanol solvate; (*b*) grown from ethanol, 1:1 input ratio; (*c*) grown from ethanol, 2:1 input ratio; (*d*) grown from propanol; (*e*) propanol solvate.

HMTA and ferrocene-1,1′-diylbis(diphenylmethanol), the HMTA acts as a bis-acceptor of hydrogen bonds (Ferguson, Glidewell, Lewis & Zakaria, 1995). With the dihydroxybenzenes hydroquinone and resorcinol, HMTA forms complexes of 1:1 stoichiometry in the solid state and the hydroquinone complex comprises chains of alternating hydrogen-bond donors and acceptors, in which the HMTA again acts as only a bis-acceptor: the structure of the resorcinol complex could not be solved explicitly, but it was thought to be similar to that of the hydroquinone complex (Mahmoud & Wallwork, 1979).

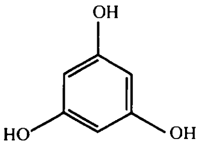
We have now studied the co-crystallization behaviour of HMTA with a range of 4,4′-bisphenols (1) and with two trihydroxy analogues (2) and (3). Of these, (1*a*) can adopt conformations in co-crystals having skeletal symmetry $D_{2h}$, or any of its subgroups, (1*b*)–(*h*) can adopt $C_{2v}$ skeletal symmetry, or any of its subgroups, while (2) and (3) can adopt $C_{3v}$ or $D_{3h}$, or any subgroup symmetry, respectively. For (1) and (2) the expected intramolecular O···O distances all lie around 9.5 Å, while in (3) the O···O distance is *ca* 4.8 Å. In HMTA the hydrogen-bond acceptor orbitals are tetrahedrally disposed around the cage with an N···N distance of *ca* 2.4 Å. Binary combinations of these phenols with HMTA can therefore be expected to give rise to a wide variety of structural types in co-crystals. We have now isolated crystalline adducts (4*a*)–(*h*), of 1:1 stoichiometry, formed by co-crystallizing (1*a*)–(*h*) with HMTA; adducts (5*a*)–(*c*), having phenol:HMTA ratios of 1:2, 2:3 and 1:1, respectively, all formed from HMTA and (2); a 2:3 adduct (6) formed from HMTA and (3). We report here the crystal structures of (4*c*), (4*d*), (4*g*), (5*a*) and (6); adducts (4*c*) and (4*d*) prove to have rather simple crystal structures, albeit exhibiting some uncommon intermolecular interactions, namely C—H···O=S and C—H···π(arene) hydrogen bonds, while the crystal structures of (4*g*), (5*a*) and (6) become progressively more complex.



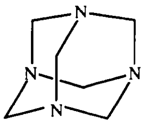
(1*a*) $X$ = nil
(*b*) $X$ = O
(*c*) $X$ = S
(*d*) $X$ = $SO_2$
(*e*) $X$ = CO
(*f*) $X$ = $CH_2$
(*g*) $X$ = $CMe_2$
(*h*) $X$ = $C(CF_3)_2$



(2)



(3)



HMTA

## 2. Experimental

### 2.1. *Preparation of the complexes*

The two components were separately dissolved in methanol, ethanol or propanol and the solutions were then mixed to give phenol:HMTA stoichiometric ratios of 1:1, 2:1 or 4:1 and set aside to crystallize. The resulting colourless crystals were isolated by filtration and were dried briefly over calcium chloride. In general, materials isolated in this way were analytically pure with a small integer ratio of the two components (Table 1); crystals suitable for single-crystal X-ray diffraction were selected directly from these preparations.

Table 2. *Experimental details*

| | (4*c*) | (4*d*) | (4*g*) | (5*a*) | (6) |
|---|---|---|---|---|---|
| Crystal data | | | | | |
| Chemical formula | $C_{12}H_{10}O_2S.C_6H_{12}N_4$ | $C_{12}H_{10}O_4S.C_6H_{12}N_4$ | $C_{21}H_{28}N_4O_2$ | $C_{20}H_{18}O_3.(C_6H_{12}N_4)_2$ | $C_6H_6O_3.(C_6H_{12}N_4)_{1.5}$ |
| Chemical formula weight | 358.46 | 390.46 | 368.47 | 586.74 | 336.40 |
| Cell setting | Orthorhombic | Orthorhombic | Monoclinic | Orthorhombic | Monoclinic |
| Space group | $Pmn2_1$ | $Pmn2_1$ | $C2/c$ | $P2_12_12_1$ | $C2/c$ |
| $a$ (Å) | 15.029 (2) | 14.779 (2) | 25.093 (6) | 6.9928 (10) | 23.598 (2) |
| $b$ (Å) | 9.7954 (8) | 10.2558 (15) | 7.1742 (13) | 14.0949 (15) | 7.136 (2) |
| $c$ (Å) | 5.9817 (11) | 5.9817 (8) | 23.612 (7) | 30.999 (4) | 19.445 (3) |
| $\beta$ (°) | | | 110.42 (2) | | 96.822 (11) |
| $V$ (Å$^3$) | 880.6 (2) | 906.7 (2) | 3983.6 (18) | 3055.4 (7) | 3251.2 (11) |
| $Z$ | 2 | 2 | 8 | 4 | 8 |
| $D_x$ (Mg m$^{-3}$) | 1.352 | 1.430 | 1.229 | 1.276 | 1.375 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ |
| Wavelength (Å) | 0.7107 | 0.7107 | 0.7107 | 0.7107 | 0.7107 |
| No. of reflections for cell parameters | 25 | 25 | 25 | 25 | 25 |
| $\theta$ range (°) | 8.95–21.60 | 9.98–18.86 | 7.22–15.73 | 6.16–10.59 | 10.44–18.01 |
| $\mu$ (mm$^{-1}$) | 0.204 | 0.212 | 0.081 | 0.085 | 0.099 |
| Temperature (K) | 294 (1) | 294 (1) | 294 (1) | 294 (1) | 294 (1) |
| Crystal form | Plate | Plate | Plate | Needle | Plate |
| Crystal size (mm) | 0.42 × 0.35 × 0.12 | 0.42 × 0.29 × 0.14 | 0.38 × 0.30 × 0.15 | 0.41 × 0.20 × 0.20 | 0.42 × 0.35 × 0.21 |
| Crystal colour | Colourless | Colourless | Colourless | Colourless | Colourless |
| Data collection | | | | | |
| Diffractometer | Enraf–Nonius CAD-4 | 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 | $\theta/2\theta$ scans |
| Absorption correction | None | None | None | None | None |
| No. of measured reflections | 1096 | 1138 | 2496 | 3085 | 3619 |
| No. of independent reflections | 1096 | 1138 | 2441 | 3085 | 3521 |
| No. of observed reflections | 818 | 834 | 1109 | 1415 | 1516 |
| Criterion for observed reflections | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ |
| $R_{\rm int}$ | – | – | 0.037 | – | 0.019 |
| $\theta_{\rm max}$ (°) | 26.91 | 27 | 22 | 25 | 27 |
| Range of $h, k, l$ | $0 \rightarrow h \rightarrow 19$<br>$0 \rightarrow k \rightarrow 12$<br>$0 \rightarrow l \rightarrow 7$ | $0 \rightarrow h \rightarrow 18$<br>$0 \rightarrow k \rightarrow 13$<br>$0 \rightarrow l \rightarrow 7$ | $-26 \rightarrow h \rightarrow 24$<br>$0 \rightarrow k \rightarrow 7$<br>$0 \rightarrow l \rightarrow 24$ | $0 \rightarrow h \rightarrow 8$<br>$0 \rightarrow k \rightarrow 16$<br>$0 \rightarrow l \rightarrow 36$ | $-30 \rightarrow h \rightarrow 29$<br>$0 \rightarrow k \rightarrow 9$<br>$0 \rightarrow l \rightarrow 24$ |
| No. of standard reflections | 3 | 3 | 3 | 3 | 3 |
| Frequency of standard reflections (min) | 120 | 60 | 60 | 60 | 120 |
| Intensity decay (%) | 2.7, allowed for by scaling | No decay, variation 1.2 | 2.5 corrected for by scaling | 2.0 | 2.2 |
| Refinement | | | | | |
| Refinement on | $F^2$ | $F^2$ | $F^2$ | $F^2$ | $F^2$ |
| $R[F^2 > 2\sigma(F^2)]$ | 0.0323 | 0.0421 | 0.0401 | 0.0636 | 0.0628 |
| $wR(F^2)$ | 0.0863 | 0.0947 | 0.1027 | 0.1022 | 0.1392 |
| $S$ | 1.100 | 1.034 | 0.913 | 0.938 | 0.923 |
| No. of reflections used in refinement | 1096 | 1138 | 2441 | 3085 | 3521 |
| No. of parameters used | 122 | 135 | 247 | 392 | 221 |
| H-atom treatment | Riding [*SHELXL*93 (Sheldrick, 1993) defaults, C—H 0.93–0.97, O—H 0.82 Å] | Riding (C—H 0.93–0.97, O—H 0.82 Å) | Riding [*SHELXL*93 (Sheldrick, 1993) defaults, C—H 0.93–0.97, O—H 0.82 Å] | Riding [*SHELXL*93 (Sheldrick, 1993) defaults, C—H 0.93–0.96, O—H 0.82 Å] | Riding (C—H 0.93–0.97, O—H 0.82 Å) |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0420P)^2 + 0.0837P]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0448P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0444P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0235P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0478P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$ |
| $(\Delta/\sigma)_{\rm max}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $\Delta\rho_{\rm max}$ (e Å$^{-3}$) | 0.213 | 0.252 | 0.163 | 0.161 | 0.184 |
| $\Delta\rho_{\rm min}$ (e Å$^{-3}$) | −0.170 | −0.238 | −0.133 | −0.177 | −0.176 |
| Extinction method | None | None | *SHELXL*93 (Sheldrick, 1993) | *SHELXL* (Sheldrick, 1993) | None |
| Extinction coefficient | – | – | 0.0024 (2) | 0.0042 (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) | *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4) |

Table 2 (*cont.*)

| | (4*c*) | (4*d*) | (4*g*) | (5*a*) | (6) |
|---|---|---|---|---|---|
| Computer programs | | | | | |
| Data collection | *CAD*-4 (Enraf–Nonius, 1989) | *CAD*-4 (Enraf–Nonius, 1989) | *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) | *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) | *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) | *SOLVER* in *NRCVAX*94 | *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) | *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 | *NRCVAX*94, *SHELXL*93 and *WordPerfect* macro PREPCIF | *NRCVAX*94, *SHELXL*93 and *WordPerfect* macro PREPCIF |

### 2.2. *Powder X-ray diffraction*

Powder diffractograms were recorded using a Stoe STADI/P diffractometer, with Cu $K\alpha$ radiation ($\lambda$ = 1.5418 Å). For the adducts (4*a*)–(*e*), (4*g*) and (4*h*) the diffractograms showed that the same polymorph of the 1:1 adducts was formed, irrespective of the initial reaction stoichiometry and of the alcohol employed as solvent. Similarly, the same polymorph of (6) was found, independent of the stoichiometry and solvent used.

### 2.3. *Single-crystal X-ray diffraction*

Details of the X-ray experimental conditions, unit-cell data, data collection and refinements are summarized in Table 2. Adducts (4*c*) and (4*d*) both crystallized in the orthorhombic system, with space groups $Pmn2_1$, $P2_1nm$ and $Pmnm$ all possible from the systematic absences: the $E$ statistics indicated a non-centrosymmetric system. Structure solutions were attempted in all three space groups, but for both (4*c*) and (4*d*) were successful only for $Pmn2_1$ (number 31). In both (4*c*) and (4*d*) each component lies across a crystallographic mirror plane. Adduct (4*g*) crystallized in the monoclinic system, with space groups $C2/c$ and $Cc$ possible from the systematic absences: space group $C2/c$ was chosen and confirmed by the analysis. Data collection for (4*g*) was terminated at $2\theta$ = 44°, as it became obvious that no further 'observed' data were being measured. Compound (5*a*) crystallized in the orthorhombic system and the space group $P2_12_12_1$ was established uniquely from the systematic absences. The crystals did not diffract well and only 46% of the data from the crystal chosen for intensity measurements were labelled as 'observed'. Adduct (6) crystallized in the monoclinic system with space groups $C2/c$ and $Cc$ possible from the systematic absences. Space group $C2/c$ was chosen and confirmed by the analysis: the triol and one HMTA unit were found in general positions with a second HMTA unit lying on a twofold rotation axis, consistent with the phenol:HMTA ratio of 2:3 deduced from the elemental analysis. A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed to reduce statistical bias (Wilson, 1976). Analysis of all the refined structures using *PLATON* (Spek, 1995*a*) showed that there were no solvent-accessible voids in any of the structures. The figures were prepared with the aid of *ORTEP*II (Johnson, 1976) and *PLUTON* (Spek, 1995*b*). Refined atomic coordinates are in Table 3 and details of the hydrogen-bonding are given in Table 4.* Figs. 1, 3, 5, 7 and 10 show perspective views of the structural components with the atom-numbering schemes and Figs. 2, 4, 6, 9 and 11 show the crystal structures.

## 3. Results and discussion

### 3.1. *Co-crystallization behaviour*

When co-crystallized with HMTA from alcoholic solvents, the bisphenols $X(C_6H_4OH)_2$ (1*a*)–(*h*) yield the corresponding complexes (4*a*)–(*h*) of 1:1 phenol:HMTA stoichiometry. For the majority of spacer groups $X$ studied in this work the composition of the adduct is independent both of the phenol:HMTA molar ratio in the initial solution (in the range 1:1–4:1) and of the solvent (methanol, ethanol or propanol) employed. Where, for a given bisphenol (1), analytically identical materials were isolated either using different starting ratios of the components or using different solvents, powder X-ray diffraction showed that these were all the same polymorph. The only exceptions observed were for (1*f*), $X = CH_2$, where no homogeneous crystalline material was isolated from either methanol or ethanol solutions, but where the use of propanol instead gave the 1:1 adduct (4*f*); for (1*h*), where in addition to the usual 1:1 complex (4*h*) a methanol solvate (4*i*) of composition (1*h*).HMTA.MeOH was also isolated; for $X$ = 1,3-adamantanediyl, $C_{10}H_{14}$, where no homogeneous material crystallized under any conditions studied.

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* Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: AB0361). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

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

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| (4*c*) | | | | |
| S1 | 0 | 0.55486 (10) | 0.0000 (2) | 0.0438 (3) |
| O1 | 0.30569 (14) | 0.2224 (3) | 0.3064 (4) | 0.0625 (7) |
| C11 | 0.0914 (2) | 0.4535 (3) | 0.0913 (5) | 0.0338 (6) |
| C12 | 0.1296 (2) | 0.3595 (3) | −0.0521 (5) | 0.0376 (7) |
| C13 | 0.2020 (2) | 0.2821 (3) | 0.0150 (6) | 0.0400 (7) |
| C14 | 0.2364 (2) | 0.2978 (3) | 0.2270 (5) | 0.0387 (7) |
| C15 | 0.1990 (2) | 0.3915 (3) | 0.3717 (5) | 0.0402 (7) |
| C16 | 0.1270 (2) | 0.4684 (3) | 0.3052 (5) | 0.0376 (7) |
| N1 | 0.41862 (14) | 0.0862 (2) | 0.0276 (5) | 0.0374 (6) |
| C2 | 0.4208 (2) | 0.0782 (3) | −0.2193 (6) | 0.0479 (8) |
| N3 | 1/2 | 0.0065 (4) | −0.2996 (6) | 0.0442 (9) |
| C4 | 1/2 | −0.1320 (4) | −0.2015 (9) | 0.0487 (12) |
| N5 | 1/2 | −0.1285 (3) | 0.0415 (7) | 0.0417 (9) |
| C6 | 0.4215 (2) | −0.0554 (3) | 0.1160 (5) | 0.0436 (8) |
| C7 | 1/2 | 0.1557 (4) | 0.1022 (8) | 0.0419 (10) |
| (4*d*) | | | | |
| S1 | 0 | 0.53271 (12) | 0.0000 (2) | 0.0326 (3) |
| O11 | 0 | 0.5360 (4) | 0.2403 (6) | 0.0415 (10) |
| O12 | 0 | 0.6531 (3) | −0.1234 (7) | 0.0446 (10) |
| C11 | 0.0941 (2) | 0.4415 (3) | −0.0876 (6) | 0.0295 (8) |
| C12 | 0.1291 (2) | 0.4601 (3) | −0.3008 (6) | 0.0338 (9) |
| C13 | 0.2024 (2) | 0.3860 (4) | −0.3690 (7) | 0.0381 (9) |
| C14 | 0.2393 (2) | 0.2925 (4) | −0.2292 (7) | 0.0354 (9) |
| O1 | 0.3069 (2) | 0.2193 (3) | −0.3128 (5) | 0.0581 (9) |
| C15 | 0.2039 (2) | 0.2761 (3) | −0.0166 (7) | 0.0383 (9) |
| C16 | 0.1315 (2) | 0.3499 (3) | 0.0538 (6) | 0.0348 (9) |
| N1 | 0.4171 (2) | 0.0762 (3) | −0.0452 (5) | 0.0327 (8) |
| C2 | 0.4202 (2) | −0.0558 (3) | −0.1451 (7) | 0.0395 (9) |
| N3 | 1/2 | −0.1291 (4) | −0.0759 (8) | 0.0399 (12) |
| C4 | 1/2 | −0.1379 (6) | 0.1691 (9) | 0.043 (2) |
| N5 | 1/2 | −0.0098 (4) | 0.2774 (7) | 0.0367 (11) |
| C6 | 0.4200 (3) | 0.0612 (4) | 0.2010 (7) | 0.0401 (10) |
| C7 | 1/2 | 0.1442 (5) | −0.1127 (10) | 0.0352 (13) |
| (4*g*) | | | | |
| O1 | −0.04876 (10) | −0.0950 (3) | 0.04983 (10) | 0.0623 (8) |
| O2 | 0.22618 (11) | −0.4460 (4) | 0.43906 (12) | 0.0693 (8) |
| C11 | 0.08189 (14) | 0.0615 (5) | 0.20871 (14) | 0.0457 (9) |
| C12 | 0.05202 (14) | −0.1023 (5) | 0.20450 (14) | 0.0519 (10) |
| C13 | 0.00836 (14) | −0.1524 (5) | 0.15179 (15) | 0.0522 (10) |
| C14 | −0.00589 (14) | −0.0407 (6) | 0.1018 (2) | 0.0470 (10) |
| C15 | 0.02396 (14) | 0.1229 (5) | 0.10500 (14) | 0.0540 (11) |
| C16 | 0.06696 (14) | 0.1725 (5) | 0.1577 (2) | 0.0582 (11) |
| C21 | 0.15080 (15) | −0.0314 (5) | 0.31179 (15) | 0.0472 (10) |
| C22 | 0.1878 (2) | −0.1635 (6) | 0.3036 (2) | 0.0575 (11) |
| C23 | 0.21209 (14) | −0.3022 (5) | 0.3455 (2) | 0.0529 (10) |
| C24 | 0.19943 (14) | −0.3125 (5) | 0.3976 (2) | 0.0463 (9) |
| C25 | 0.16157 (14) | −0.1882 (5) | 0.40633 (15) | 0.0492 (10) |
| C26 | 0.13783 (13) | −0.0498 (5) | 0.36396 (15) | 0.0501 (10) |
| C3 | 0.1277 (2) | 0.1290 (5) | 0.26752 (15) | 0.0611 (11) |
| C31 | 0.1778 (2) | 0.2192 (6) | 0.2535 (2) | 0.114 (2) |
| C32 | 0.1000 (2) | 0.2801 (6) | 0.2941 (2) | 0.112 (2) |
| N1 | −0.10450 (11) | 0.2092 (4) | −0.01872 (12) | 0.0482 (8) |
| N3 | −0.18874 (12) | 0.2484 (4) | −0.10879 (12) | 0.0494 (8) |
| N5 | −0.11403 (14) | 0.4844 (4) | −0.08227 (15) | 0.0626 (9) |
| N10 | −0.17417 (11) | 0.4506 (4) | −0.02115 (11) | 0.0456 (8) |
| C2 | −0.14826 (14) | 0.1172 (5) | −0.06996 (14) | 0.0524 (10) |
| C4 | −0.1572 (2) | 0.3843 (6) | −0.1312 (2) | 0.0715 (12) |
| C6 | −0.0753 (2) | 0.3471 (6) | −0.0439 (2) | 0.0670 (12) |
| C7 | −0.13371 (15) | 0.3126 (5) | 0.01511 (14) | 0.0564 (10) |
| C8 | −0.21553 (14) | 0.3509 (5) | −0.07254 (15) | 0.0521 (10) |
| C9 | −0.1427 (2) | 0.5806 (5) | −0.0465 (2) | 0.0628 (11) |
| (5*a*) | | | | |
| O1 | 0.6185 (7) | 0.1687 (3) | 0.55506 (13) | 0.0693 (15) |
| O2 | −0.1951 (8) | 0.5524 (3) | 0.70787 (15) | 0.082 (2) |
| O3 | −0.0460 (7) | 0.6408 (3) | 0.41385 (13) | 0.0690 (15) |
| C1 | 0.3450 (8) | 0.5479 (4) | 0.5703 (2) | 0.0368 (14) |
| C2 | 0.5056 (8) | 0.6201 (4) | 0.5807 (2) | 0.050 (2) |
| C11 | 0.4304 (9) | 0.4489 (4) | 0.5632 (2) | 0.040 (2) |
| C12 | 0.5952 (9) | 0.4202 (4) | 0.5838 (2) | 0.055 (2) |
| C13 | 0.6629 (10) | 0.3285 (4) | 0.5813 (2) | 0.062 (2) |
| C14 | 0.5654 (11) | 0.2627 (5) | 0.5580 (2) | 0.053 (2) |
| C15 | 0.4036 (10) | 0.2879 (4) | 0.5365 (2) | 0.066 (2) |
| C16 | 0.3380 (10) | 0.3814 (4) | 0.5393 (2) | 0.060 (2) |
| C21 | 0.2065 (8) | 0.5500 (4) | 0.6085 (2) | 0.041 (2) |
| C22 | 0.0965 (9) | 0.6289 (4) | 0.6162 (2) | 0.044 (2) |
| C23 | −0.0371 (9) | 0.6316 (4) | 0.6496 (2) | 0.048 (2) |
| C24 | −0.0629 (9) | 0.5552 (5) | 0.6756 (2) | 0.050 (2) |
| C25 | 0.0489 (11) | 0.4767 (5) | 0.6694 (2) | 0.077 (3) |
| C26 | 0.1795 (10) | 0.4746 (4) | 0.6357 (2) | 0.064 (2) |
| C31 | 0.2386 (8) | 0.5815 (4) | 0.5291 (2) | 0.0350 (15) |
| C32 | 0.3153 (9) | 0.6396 (4) | 0.4978 (2) | 0.045 (2) |
| C33 | 0.2189 (9) | 0.6605 (4) | 0.4602 (2) | 0.047 (2) |
| C34 | 0.0390 (10) | 0.6220 (4) | 0.4524 (2) | 0.046 (2) |
| C35 | −0.0439 (9) | 0.5678 (4) | 0.4838 (2) | 0.049 (2) |
| C36 | 0.0528 (9) | 0.5477 (4) | 0.5216 (2) | 0.049 (2) |
| N1*A* | 0.9156 (8) | 0.1076 (4) | 0.6066 (2) | 0.0543 (15) |
| N3*A* | 1.1576 (7) | −0.0176 (3) | 0.60833 (15) | 0.0442 (14) |
| N5*A* | 0.9070 (9) | −0.0127 (4) | 0.6634 (2) | 0.061 (2) |
| N10*A* | 1.1545 (8) | 0.1080 (4) | 0.6638 (2) | 0.060 (2) |
| N1*B* | −0.4111 (8) | 0.7075 (3) | 0.7240 (2) | 0.0507 (14) |
| N3*B* | −0.6264 (9) | 0.8395 (4) | 0.7127 (2) | 0.062 (2) |
| N5*B* | −0.3937 (9) | 0.8457 (5) | 0.7699 (2) | 0.072 (2) |
| N10*B* | −0.6643 (9) | 0.7414 (4) | 0.7765 (2) | 0.063 (2) |
| C2*A* | 1.0393 (9) | 0.0445 (4) | 0.5815 (2) | 0.059 (2) |
| C4*A* | 1.0275 (10) | −0.0716 (4) | 0.6363 (2) | 0.060 (2) |
| C6*A* | 0.7942 (9) | 0.0481 (5) | 0.6344 (2) | 0.066 (2) |
| C7*A* | 1.0374 (11) | 0.1652 (4) | 0.6354 (2) | 0.068 (2) |
| C8*A* | 1.2713 (9) | 0.0441 (5) | 0.6367 (2) | 0.061 (2) |
| C9*A* | 1.0285 (10) | 0.0481 (5) | 0.6897 (2) | 0.071 (2) |
| C2*B* | −0.5180 (10) | 0.7645 (5) | 0.6928 (2) | 0.070 (2) |
| C4*B* | −0.4953 (12) | 0.8992 (4) | 0.7375 (3) | 0.080 (3) |
| C6*B* | −0.2905 (10) | 0.7710 (5) | 0.7486 (2) | 0.070 (2) |
| C7*B* | −0.5550 (11) | 0.6686 (4) | 0.7549 (2) | 0.072 (2) |
| C8*B* | −0.7605 (9) | 0.7966 (5) | 0.7430 (2) | 0.072 (2) |
| C9*B* | −0.5307 (12) | 0.8032 (5) | 0.7990 (2) | 0.076 (3) |
| (6) | | | | |
| O1 | 0.08055 (9) | −0.0337 (3) | 0.51823 (13) | 0.0664 (8) |
| O3 | 0.21032 (8) | 0.3343 (3) | 0.40077 (13) | 0.0531 (7) |
| O5 | 0.01941 (8) | 0.5283 (3) | 0.41161 (12) | 0.0568 (7) |
| C1 | 0.09416 (12) | 0.1180 (4) | 0.48081 (14) | 0.0385 (8) |
| C2 | 0.14745 (12) | 0.1411 (4) | 0.45930 (14) | 0.0369 (7) |
| C3 | 0.15785 (12) | 0.2978 (4) | 0.42123 (14) | 0.0344 (7) |
| C4 | 0.11563 (12) | 0.4286 (4) | 0.40377 (14) | 0.0361 (7) |
| C5 | 0.06260 (12) | 0.4041 (4) | 0.42639 (14) | 0.0340 (7) |
| C6 | 0.05156 (12) | 0.2481 (4) | 0.46468 (14) | 0.0391 (8) |
| N11 | 0.15670 (10) | −0.2708 (3) | 0.59019 (12) | 0.0390 (6) |
| C12 | 0.19623 (12) | −0.4015 (5) | 0.56327 (14) | 0.0457 (8) |
| N13 | 0.22300 (10) | −0.5286 (3) | 0.61708 (12) | 0.0385 (6) |
| C14 | 0.17706 (12) | −0.6313 (4) | 0.6464 (2) | 0.0436 (8) |
| N15 | 0.13696 (10) | −0.5070 (3) | 0.67538 (12) | 0.0390 (6) |
| C16 | 0.11240 (12) | −0.3817 (4) | 0.6199 (2) | 0.0447 (8) |
| C17 | 0.18796 (14) | −0.1633 (4) | 0.6470 (2) | 0.0522 (9) |
| C18 | 0.25283 (12) | −0.4129 (5) | 0.6731 (2) | 0.0518 (9) |
| C19 | 0.16913 (14) | −0.3929 (5) | 0.7291 (2) | 0.0529 (9) |
| N10 | 0.21466 (11) | −0.2838 (4) | 0.70277 (13) | 0.0473 (7) |
| N21 | 0.02194 (10) | 0.7951 (3) | 0.31046 (12) | 0.0390 (6) |
| C22 | −0.02502 (13) | 0.9154 (5) | 0.32753 (15) | 0.0469 (9) |
| N23 | −0.04728 (11) | 1.0347 (4) | 0.26962 (13) | 0.0508 (8) |
| C24 | 0 | 1.1475 (7) | 1/4 | 0.064 (2) |
| C25 | 0 | 0.6807 (6) | 1/4 | 0.0438 (12) |
| C26 | −0.06744 (13) | 0.9155 (5) | 0.2106 (2) | 0.0532 (9) |

Similarly, 1,3,5-trihydroxybenzene (3) gave the same 2:3 adduct from methanol, ethanol and propanol solutions with HMTA; again, powder X-ray diffraction showed that these materials were all the same polymorph (6) of composition (3)$_2$.(HMTA)$_3$.

By contrast, the behaviour of the trisphenol $CH_3C(C_6H_4OH)_3$ (2) is far more complex. By variation of the initial molar ratio of phenol:HMTA

Table 4. *Hydrogen-bonding parameters (Å, °)*

| *D*—H···*A* | H—*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|
| (4*c*) | | | |
| O1—H1···N1 | 1.94 | 2.728 (3) | 162 |
| C4—H4*A*···C11$^{\rm i}$ | 2.89 | | |
| C4—H4*A*···C12$^{\rm i}$ | 2.76 | | |
| C4—H4*A*···C13$^{\rm i}$ | 2.82 | | |
| C4—H4*A*···C14$^{\rm i}$ | 3.00 | | |
| C4—H4*A*···C16$^{\rm i}$ | 3.05 | | |
| (4*d*) | | | |
| O4—H4···N1 | 1.94 | 2.715 (4) | 159 |
| C6—H6*A*···O12$^{\rm ii}$ | 2.46 | 3.330 (5) | 150 |
| C4—H4*A*···C11$^{\rm iii}$ | 2.93 | | |
| C4—H4*A*···C12$^{\rm iii}$ | 3.03 | | |
| C4—H4*A*···C13$^{\rm iii}$ | 3.06 | | |
| C4—H4*A*···C14$^{\rm iii}$ | 2.98 | | |
| C4—H4*A*···C15$^{\rm iii}$ | 2.89 | | |
| C4—H4*A*···C16$^{\rm iii}$ | 2.87 | | |
| (4*g*) | | | |
| O1—H1···N1 | 1.98 | 2.785 (4) | 166 |
| O2—H2···N10$^{\rm iv}$ | 1.99 | 2.789 (3) | 165 |
| C8—H8*A*···O2$^{\rm v}$ | 2.45 | 3.306 (5) | 146 |
| C9—H9*B*···O1$^{\rm vi}$ | 2.58 | 3.522 (5) | 163 |
| (5*a*) | | | |
| O1—H1···N1*A* | 1.98 | 2.758 (6) | 158 |
| O2—H2···N1*B* | 1.91 | 2.704 (6) | 163 |
| O3—H3···N3*A*$^{\rm vii}$ | 2.02 | 2.790 (6) | 157 |
| C2—H23···O3$^{\rm viii}$ | 2.50 | 3.394 (7) | 155 |
| C4*B*—H42*B*···O2$^{\rm ix}$ | 2.54 | 3.495 (7) | 167 |
| (6) | | | |
| O1—H1···N11 | 1.97 | 2.727 (4) | 153 |
| O3—H3···N13$^{\rm x}$ | 1.94 | 2.737 (4) | 166 |
| O5—H5···N21 | 1.97 | 2.740 (4) | 156 |

Symmetry codes: (i) $\frac{1}{2} - x, -y, z - \frac{1}{2}$; (ii) $\frac{1}{2} + x, 1 - y, \frac{1}{2} + z$; (iii) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (iv) $-x, y - 1, \frac{1}{2} - z$; (v) $x - \frac{1}{2}, -\frac{1}{2} - y, z - \frac{1}{2}$; (vi) $x, 1 + y, z$; (vii) $x - \frac{3}{2}, \frac{1}{2} - y, 1 - z$; (viii) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$; (ix) $-1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (x) $\frac{1}{2} - x, -\frac{1}{2} - y, 1 - z$.

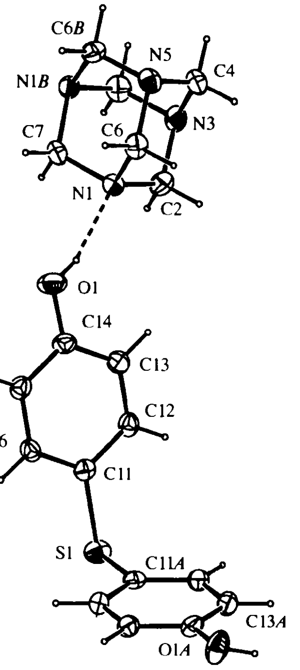

Fig. 1. Perspective view of the molecular aggregate in (4*c*), showing the atom-numbering scheme; atoms whose labels end in '*A*' or '*B*' are in the equivalent positions (–*x*, *y*, *z*) and (1 – *x*, *y*, *z*), respectively. Thermal ellipsoids are drawn at the 30% probability level.

within the range 1:1–4:1 and by the use of either ethanol or propanol as solvent, three distinct solvent-free complexes with stoichiometric ratios 1:2 (5*a*), 2:3 (5*b*) and 1:1 (5*c*) were isolated (Table 1): in addition, a propanol solvate (5*d*) of composition (2).HMTA.propanol was also isolated. For both (4*i*) and (5*d*) the presence of 1 mol of solvent per phenol–HMTA unit was confirmed by thermogravimetric analysis.

### 3.2. *Crystal and molecular structures of adducts (4c), (4d), (4g), (5a) and (6)*

3.2.1. *4,4′-Thiodiphenol–HMTA (1/1) adduct (4c) and 4,4′-sulfonyldiphenol–HMTA (1/1) adduct (4d).* In each of the two 1:1 adducts (4*c*) and (4*d*) there is a surfeit of conventional hydrogen-bond acceptors over donors. While there are only two O—H donors per bisphenol/HMTA aggregate, each of the four N atoms in the HMTA component, as well as the two O atoms of the bisphenol component, could act as acceptors; in addition, the sulfide linkage in (4*c*) and, more plausibly, the O atoms of the sulfone linkage in (4*d*) are all potential hydrogen-bond acceptors. For each complex, structure

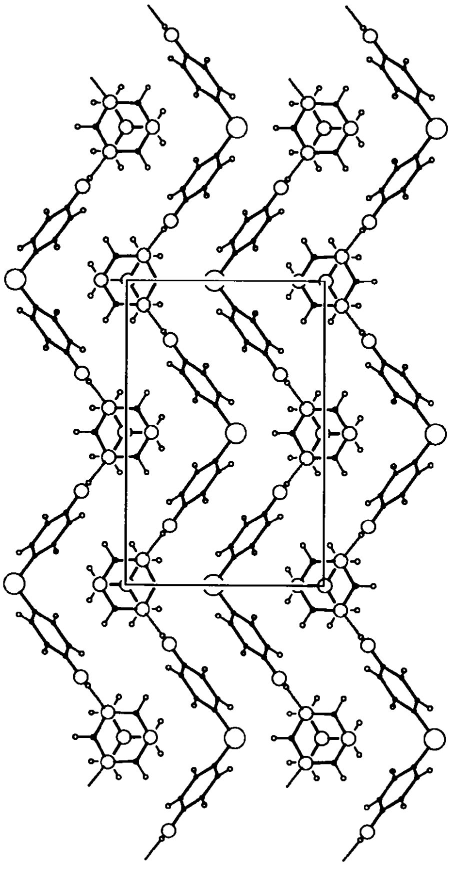

Fig. 2. View of the crystal structure of (4*c*), viewed down the *c* axis, with the *b* axis horizontal and the origin at the lower right.

analysis shows that the hydroxyl groups of the bisphenol act as hydrogen-bond donors to two of the four N atoms of the HMTA (Figs. 1 and 3). This hydrogen bonding leads to simple chains in the [100] direction consisting of alternating bisphenol and HMTA units, having a particularly simple zigzag conformation (Figs. 2 and 4). Complexes (4*c*) and (4*d*) not only have very similar structures in the same space group, but also very similar cell dimensions (Table 2), except that the *b* dimension of (4*d*) is significantly longer than that of (4*c*), in order to accommodate the sulfone O atoms in (4*d*). Choosing the correct chiral direction, as indicated by the Flack parameter refinement (Flack, 1983), shows that we have, by chance, selected crystals of (4*c*) and (4*d*) which have opposite hand; thus, the direction of the unique O—H group is pointing approximately along $[00\bar{1}]$ in (4*c*) and along [001] in (4*d*); plots of the individual chains in (4*c*) and (4*d*) are very similar in projection (Figs. 2 and 4).

As well as the O—H···N hydrogen bonds which generate the chains, there are further hydrogen-bonding interactions between the chains. In (4*d*) there are short C—H···O hydrogen bonds (Table 4) in which the two symmetry-related H atoms H6*A* of the HMTA unit at $(x, y, z)$ act as donors to the sulfone O12 atom in the bisphenol unit at $(\frac{1}{2} + x, 1 - y, \frac{1}{2} + z)$; the corresponding HMTA H atoms in the unit at $(\frac{1}{2} + x, 1 - y, \frac{1}{2} + z)$ act in turn as hydrogen-bond donors to the sulfone O12 atom in the bisphenol at $(1 + x, y, 1 + z)$. These interactions generate a spiral parallel to the [001] direction around the $2_1$ axis at $(\frac{1}{4}, \frac{1}{2}, z)$, with a similar spiral of opposite hand around the $2_1$ axis at $(\frac{3}{4}, \frac{1}{2}, z)$.

In addition, in both (4*c*) and (4*d*) the symmetry-related H4*A* and H4*B* atoms on C4 of the HMTA unit at $(x, y, z)$ are directed towards the arene rings of the bisphenol unit at $(\frac{1}{2} - x, -y, \frac{1}{2} + z)$, although offset from the ring centres in each case (see Table 4): the H4*A* and H4*B* atoms of the HMTA unit at $(\frac{1}{2} - x, -y, \frac{1}{2} + z)$ are in turn directed towards the arene rings at $(x, y, 1 + z)$. These C—H···π(arene) interactions thus form a spiral about the $2_1$ axis at $(\frac{1}{4}, 0, z)$, with a similar spiral of opposite hand around the $2_1$ axis at $(\frac{3}{4}, 0, z)$. In (4*c*) there are intermolecular C···H contacts from H4*A* to C11, C12, C13 and C14, all of which are less than 3.00 Å (Table 3), whereas in (4*d*), atoms H4*A* and H4*B* are almost equidistant from all six atoms of the adjacent arene rings, with H···C distances ranging from 2.87 to 3.06 Å. These C—H···π(arene) interactions thus serve in (4*c*) to link the chains parallel to the [100] direction into puckered two-ply sheets normal to the [010] direction, while in (4*d*) the two types of spiral generated by the C—H···O=S and C—H···π(arene)

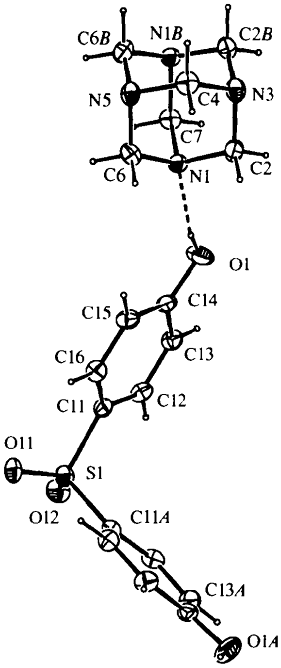

Fig. 3. Perspective view of the molecular aggregate in (4*d*), showing the atom-numbering scheme; atoms whose labels end in '*A*' or '*B*' are in the equivalent positions $(-x, y, z)$ and $(1 - x, y, z)$, respectively. Atoms are depicted as in Fig. 1.

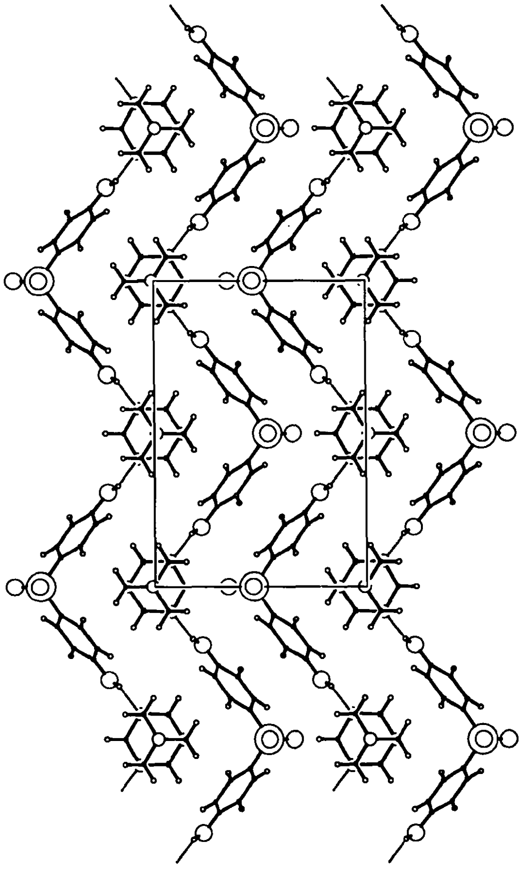

Fig. 4. View of the crystal structure of (4*d*), viewed down the *c* axis, with the *b* axis horizontal and the origin at the lower right.

hydrogen bonds link all the units into a continuous three-dimensional array. In space groups containing mirror planes, the special positions on these planes are always occupied (Brock & Dunitz, 1994): this is because unoccupied mirror planes would lead to unfavourable like–like interactions between neighbouring molecules. Although $Pmn2_1$ is a rather uncommon space group, most examples have $Z' = 0.5$, as found here.

The basic chain structure of adducts (4*c*) and (4*d*), with folding into a zigzag pattern consequent upon the disposition of the N atoms in the HMTA component, is amongst the simplest arrangements that can be envisaged for a binary system in which each component provides either two donors or two acceptors. The simplicity of the basic structure also owes something to the C—H···π(arene) and C—H···O=S interactions which serve to prevent the main O—H···N hydrogen-bonded chain from folding or twisting. Similar double-donor plus double-acceptor chains are also formed in the adducts (4*g*) and (5*a*), but in these the folding of the chains is more elaborate, forming multiple helices rather than simple zigzag arrangements.

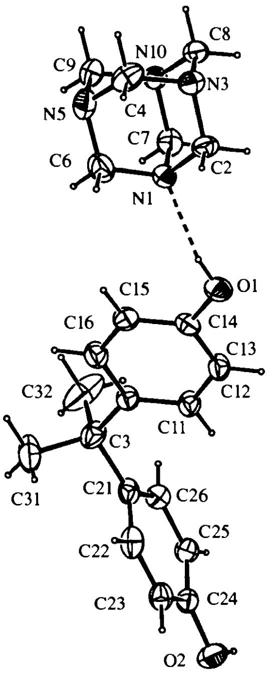

Fig. 5. Perspective view of the molecular aggregate in (4*g*), showing the atom-numbering scheme. Atoms are depicted as in Fig. 1.

3.2.2. *4,4'-Isopropylidenediphenol–HMTA (1/1) adduct (4g).* In adduct (4*g*) the mismatch between the numbers of hydrogen-bond donors and acceptors is much less marked than in the adducts (4*c*) and (4*d*). Again, in (4*g*) each hydroxyl group of the bisphenol acts as a donor and just two of the four N atoms in HMTA act as acceptors, giving again a chain of alternating bisphenol and HMTA units linked by O—H···N hydrogen bonds. However, by contrast with the zigzag chains in (4*c*) and (4*d*), which are generated by the repeated action of mirror planes normal to the [100] direction, the crystal structure of (4*g*) is dominated by the action of a twofold rotation axis. The asymmetric units (Fig. 5) are arranged in pairs about the twofold rotation axis and within the asymmetric unit O1 acts as a hydrogen-bond donor to N1. The other O atom, O2, acts as a donor to N10 in the unit at $(-x, y-1, \frac{1}{2}-z)$, while O2 in this unit acts as a donor to N10 in the unit at $(x, -2+y, z)$. Hence, the hydrogen bonding generates two independent symmetry-related helices parallel to the [010] direction, each of which mimics the action of a $2_1$ screw axis (*cf.* the Staff of Aesculepius). Four such double helices run through the unit cell, two of each hand.

In addition to the O—H···N hydrogen bonding within each double helix, there are also C—H···O hydrogen bonds between helices (Table 4). C9 in the HMTA unit

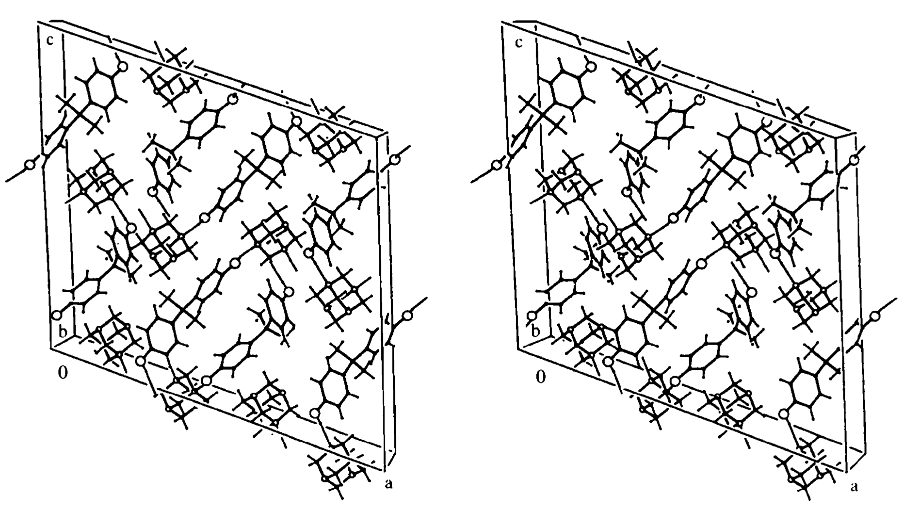

Fig. 6. Stereoview of the crystal structure of (4*g*), viewed approximately down the *b* axis.

at (*x*, *y*, *z*) acts as a hydrogen-bond donor, *via* H9*B*, to O1 in the bisphenol unit at (*x*, 1 + *y*, *z*), that is, the bisphenol immediately adjacent in the [010] direction, but in the other strand of the helix; this interaction thus serves to link the two strands of the double helix. Secondly, C8 in the HMTA unit at (*x*, *y*, *z*) acts as a hydrogen-bond donor, *via* H8*A*, to O2 in the bisphenol unit at $(x - \frac{1}{2}, -\frac{1}{2} - y, z - \frac{1}{2})$; this interaction links the double helix around the twofold axis at $(0, y, \frac{1}{4})$ to that around $(-\frac{1}{2}, y, -\frac{1}{4})$ and, by symmetry, to that around $(\frac{1}{2}, y, \frac{3}{4})$, so connecting individual double helices and joining them into sheets parallel to the $[\bar{1}01]$ direction.

The complexity of the structure of (4*g*) may be compared and contrasted with the almost stark simplicity of the crystal structure of the closely analogous adduct 4,4′-isopropylidenediphenol–1,4-diazabicyclo[2.2.2]octane (Ferguson, Coupar & Glidewell, 1997), where the components form simple, essentially linear chains with no interactions between the chains.

Almost certainly, the key factor underlying the structural differences between the DABCO and HMTA adducts of 4,4′-isopropylidenediphenol is the angle between the two hydrogen-bond acceptor lone pairs on the amine molecules, 180° in DABCO and *ca* 109.5° in HMTA. The chains formed in the DABCO adduct are therefore essentially linear at the amine components, while in the HMTA adduct the chains are bent at the amine component. It is these bends in the chains which permit the chains to coil, in the absence of any significant interactions to prevent it [as in (4*c*) and (4*d*)].

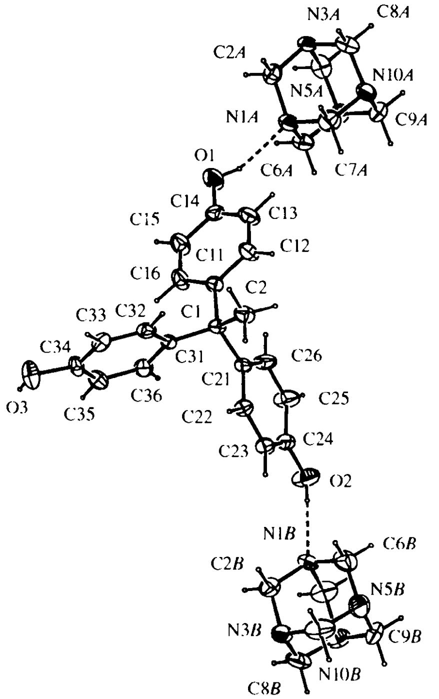

Fig. 7. Perspective view of the molecular aggregate in (5*a*), showing the atom-numbering scheme. Atoms are depicted as in Fig. 1.

3.2.3. *1,1,1-Tris(4-hydroxyphenyl)ethane–HMTA (1/2) adduct (5a).* In this adduct the trisphenol acts as a triple donor of hydrogen bonds: one half of the molecules of HMTA act as double acceptors and the other half as only single acceptors of hydrogen bonds. The asymmetric unit of the structure consists of one molecule of the trisphenol hydrogen-bonded *via* O atoms O1 and O2 to two HMTA units, each acting as an acceptor (Fig. 7). O3 in the unit at (*x*, *y*, *z*) acts as a hydrogen-bond donor to N3*A* in the unit at $(x - \frac{3}{2}, \frac{1}{2} - y, 1 - z)$, while O3 in this latter unit acts as a donor to N3*A* in the unit at (*x* − 3, *y*, *z*), generating a helix around

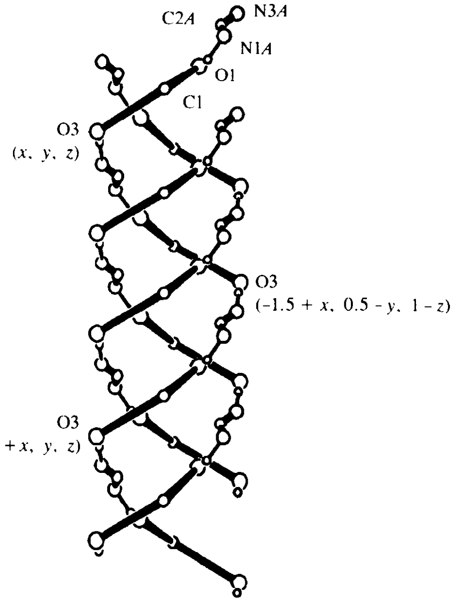

Fig. 8. Schematic view of the triple helix in (5*a*), viewed normal to the *a* direction; phenyl rings C1*n* and C3*n* (*n* = 1–6) are represented by bold lines and the only other atoms shown are those in the $C_2^2(16)$ motifs, see text.

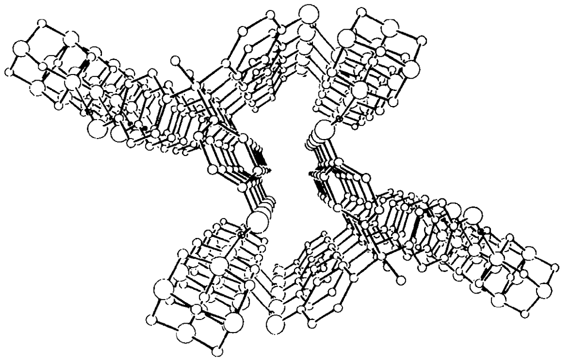

Fig. 9. Perspective view of the structure of (5*a*), viewed along the *a* direction; non-hydroxyl H atoms are omitted for the sake of clarity.

the $2_1$ axis parallel to the [100] direction. However, one turn of this helix is associated with a three-cell shift along the [100] direction and consequently there are three independent parallel helices generated by the action of the $2_1$ axis on the units at $(x, y, z)$, $(1 + x, y, z)$ and $(2 + x, y, z)$ (Fig. 8); there are no covalent or hydrogen-bonding interactions between the independent helices.

At each half turn of each helix there is a pendent HMTA unit, hydrogen bonded *via* O2. The pendent units therefore form two stacks, parallel to the [100] direction and exterior to the triple-helical structure and acting towards it as buttresses (Fig. 9). Within the buttressing stacks of HMTA units there are close contacts at van der Waals' distances (Bondi, 1964) between neighbouring units: the closest contacts between different triple helices occur between an exterior HMTA stack of one and an internal HMTA stack of another. There are also some C—H···O hydrogen bonds in this triple-helical structure (Table 4). C2 in the trisphenol at $(x, y, z)$ acts as a hydrogen-bond donor, *via* H23, to O3 in the trisphenol at $(\frac{1}{2} + x, \frac{3}{2} - y, 1 - z)$; this interaction has the effect of linking the triple helix generated by the asymmetric unit at $(x, y, z)$ with that generated by the unit at $(x, 1 + y, z)$. C4*B* in the HMTA unit at $(x, y, z)$ acts as a donor, *via* H42*B*, to O2 in the bisphenol at $(-1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, which lies in the triple helix related to that generated from $(x, y, z)$ by the action of the $2_1$ axis at $(-\frac{1}{2}, y, \frac{3}{4})$. Hence, all the triple helices are interlinked, although there are no hydrogen-bonding interactions between the individual strands within a triple helix. Although both components are achiral, their interaction produces helices and in space group $P2_12_12_1$ all the helices in a given crystal are of the same hand; the formation of this chiral structure may be regarded as an example of conglomerate crystallization (Bernal, Cetrullo, Cai & Massoud, 1995). The one-dimensional structure found here, with three identical but unconnected intertwined helices, has some resemblance to the three-dimensional structures found for methanetetraacetic acid (Ermer & Eling, 1988), adamantane tetracarboxylic acid (Ermer, 1988) and trimesic acid (Duchamp & Marsh, 1969), where there are three, five and six independent interpenetrating networks, respectively. In every case structures consisting of just a single network would lead to materials of very low density containing a high proportion of voids.

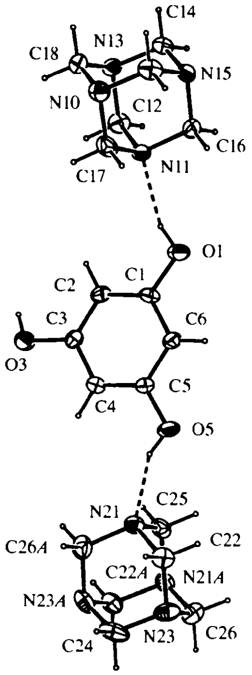

Fig. 10. Perspective view of the molecular aggregate in (6), showing the atom-numbering scheme. A twofold axis runs through atoms C24 and C25 of one HMTA molecule; atoms whose labels end in '*A*' are in the equivalent position $(-x, y, \frac{1}{2} - z)$. Atoms are depicted as in Fig. 1.

It is noteworthy that although both (4*g*) and (5*a*) contain chains of alternating HMTA molecules and $(HOC_6H_4)_2C(R)Me$ units [where $R = CH_3$ in (4*g*) and $C_6H_4OH$ in (5*a*)], with almost identical O···O distances in the two different phenols, the coiling of the chains (itself dependent on the chain-bending at the HMTA units) gives a double helix in (4*g*) and a triple helix in (5*a*). Similarly, whereas (4*g*) crystallizes in a centrosymmetric space group, (5*a*)

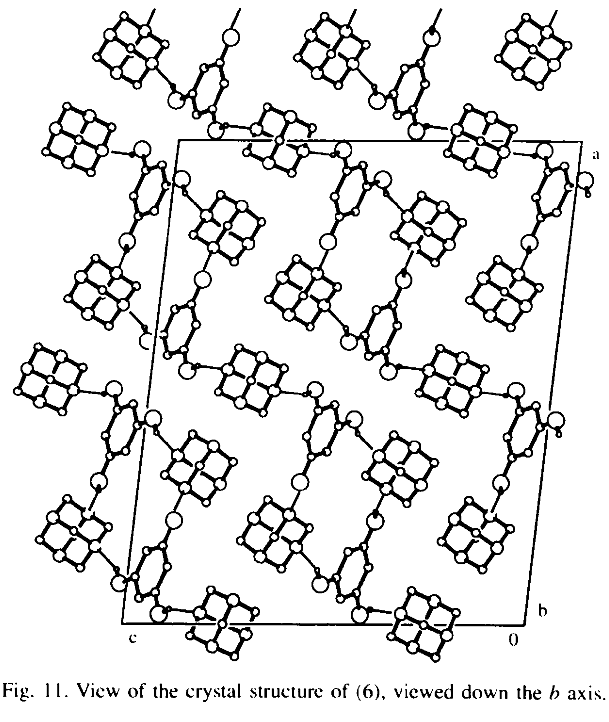

Fig. 11. View of the crystal structure of (6), viewed down the *b* axis.

is subject to conglomerate crystallization in the non-centrosymmetric space group $P2_12_12_1$. The fact that very similar structures can occur in different space groups has been commented upon elsewhere (Brock & Dunitz, 1994) and clearly the factors underlying the spontaneous folding of even these simple hydrogen-bonded chains are rather subtle and require further study before reliable structural predictions can be made. The other notable difference between (4*g*) and (5*a*), other than the external HMTA units in (5*a*), and probably an important factor in their folding regimes, lies in the patterns of the weak, soft (Braga, Grepioni, Biradha, Pedireddi & Desiraju, 1995) C—H· · ·O hydrogen bonds occurring between different multiple helices.

3.2.4. *1,3,5-Trihydroxybenzene–HMTA (2/3) adduct (6).* If all three hydroxyl groups of a trisphenol were acting as hydrogen-bond donors to a double-acceptor diamine, in all molecules of which two N atoms were acting as hydrogen-bond acceptors, then a trisphenol:diamine stoichiometry of 2:3 may be expected, as then there would be an exact match between the numbers of hydrogen-bond donors and active acceptors; such a stoichiometric ratio would inevitably lead to some degree of structural complexity, as is indeed observed in adduct (6). In this structure the 1,3,5-trihydroxybenzene component utilizes all three hydroxyl groups as hydrogen-bond donors, while the HMTA components do act as only bis-acceptors. The triol and one HMTA unit (defined by N10, N11, N13 and N15, Fig. 10) lie in general positions in *C*2/*c*, while a second HMTA (defined by N21 and N23, Fig. 10) lies on a twofold rotation axis, consistent with the 2:3 triol:HMTA stoichiometry. Within the asymmetric unit, O1 acts as a hydrogen-bond donor to N11; additionally, O3 in the molecule at ($x$, $y$, $z$) acts as a donor to N13 in HMTA at ($\frac{1}{2} - x$, $-\frac{1}{2} - y$, $1 - z$), while O3 in the triol at ($\frac{1}{2} - x$, $-\frac{1}{2} - y$, $1 - z$) acts as a donor to N13 in the HMTA at ($x$, $y$, $z$). These paired O3· · ·N13 hydrogen bonds generate a centrosymmetric ring lying around the centre of inversion at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{2}$), with similar rings about the inversion centres at ($\frac{1}{4}$, $\frac{3}{4}$, 0), ($\frac{3}{4}$, $\frac{1}{4}$, 0) and ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{1}{2}$) (Fig. 11). These rings are linked into a chain-of-rings; O5 of the triol at ($x$, $y$, $z$) acts as a donor towards N21 of the HMTA lying on the twofold axis at (0, $y$, $\frac{1}{4}$), while O5 of the triol at ($-x$, $y$, $\frac{1}{2} - z$) acts as a donor to the symmetry-related N21*A* atom of the same HMTA. Overall, therefore, the structure comprises chains of rings linked by spacer HMTA units, lying in the $[\bar{1}01]$ direction; the rings are themselves made up from a combination of cages and smaller rings and a schematic representation of this structural motif is given in Fig. 12.

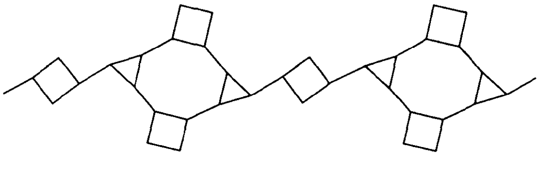

Fig. 12. Schematic view of the chain-forming motif in (6). Triangles and squares represent 1,3,5-trihydroxybenzene and HMTA units, respectively, and single lines represent O—H· · ·N hydrogen bonds.

An alternative description of this structure, which arises from the pattern of hydrogen bonds and which is particularly apparent from the *b*-axis projection (Fig. 11), is of almost linear strings of (3 HMTA + 2 triol) units lying in the (204) planes, with similarly linear strings in the $(\bar{4}02)$ planes.

### 3.3. *Molecular dimensions and conformations*

In each of (4*c*), (4*d*), (4*g*), (5*a*) and (6) the HMTA contain two types of C—N bond; those where the nitrogen is involved in an O—H· · ·N hydrogen bond and those where the nitrogen is involved in no hydrogen bonding. The C—N bonds where nitrogen acts as a hydrogen-bond acceptor are consistently longer that the remainder. In individual adducts the mean difference between the two types of C—N bond distance ranges from 0.011 Å in (4*g*) and (6) to 0.018 Å in (4*d*); overall, in this series of adducts the mean value of 39 C—N bond lengths involving hydrogen-bond acceptors is 1.472 (10) Å, while the mean value of 45 C—N bond lengths not involving hydrogen bonds is 1.458 (10) Å. In contrast to these values, in the adduct of HMTA with ferrocene-1,1′-diylbis(diphenylmethanol), a tertiary alcohol and thus a weaker hydrogen-bond donor than phenols, the difference between the two mean values is negligible (Ferguson, Glidewell, Lewis & Zakaria, 1995), while in salts of HMTA with strong acids where complete proton transfer occurs to yield the cation $[C_6H_{13}N_4]^+$, the differences are typically in the range 0.050–0.060 Å (Mak, Li & Yip, 1983; Chou, Lessinger & Chiang, 1987; Tebbe & Nagel, 1995). In adduct (4*c*) the C—S bond length, 1.781 (3) Å, is above the upper quartile value for bonds of this type; otherwise, all the intramolecular dimensions are typical of their types (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

In adduct (4*c*) the bisphenol fragments lie across mirror planes so that their symmetry is $C_s$; however, the C—S—C—C torsional angles [93.0 (2) and −88.3 (2)°] mean that the skeletal conformation is very close to local $C_{2v}$ symmetry. In (4*d*) the corresponding angles are 87.9 (3) and −90.8 (3)°, so that, again, the skeletal conformation is very close to local $C_{2v}$ symmetry. No crystallographic symmetry is imposed upon the bisphenol fragment in (4*g*) and the values of the torsion angles C11—C3—C21—C22 and C21—C3—C11—C12 of 74.6 (4) and 20.7 (5)°, respectively, indicate that the local symmetry of this fragment is only $C_1$. Similarly, in (5*a*) the values of the torsional angles C2—C1—C*n*1—C*n*2 [for $n$ = 1–3; 30.0 (7), 68.2 (6) and 24.2 (7)°, respectively] indicate that the local symmetry of the trisphenol component is again only $C_1$.

### 3.4. *Hydrogen bonding*

3.4.1. *Hydrogen-bond dimensions.* In Table 4 are collected metrical data for the three types of hydrogen bond, O—H···N, C—H···O and C—H···π(arene), which are observed in the structures of (4*c*), (4*d*), (4*g*), (5*a*) and (6) described above. Hydrogen bonds of the type O—H···N occur in all five structures with O···N distances ranging from 2.713 (4) Å in (4*d*) to 2.789 (3) Å in (4*g*). These values are comparable with the values observed, typically *ca* 2.74 Å, in HMTA adducts of simple phenols (Jordan & Mak, 1970; Tse, Wong & Mak, 1977; Mak, Yu & Lam, 1978; Mahmoud & Wallwork, 1979), but they are very much shorter those found (Ferguson, Glidewell, Lewis & Zakaria, 1995) in the HMTA adduct with ferrocene-1,1′-diylbis(diphenylmethanol), 2.861 (3) and 2.921 (3) Å; this is fully consistent with the higher acidity of phenolic hydroxyl groups, as compared with those in tertiary alcohols.

Hydrogen bonds of the type C—H···O are observed in (4*d*) (involving a sulfone O atom) and in (4*g*) and (5*a*) (both involving phenolic O atoms). The C···O distances in the examples observed here (Table 4) range from 3.306 (5) to 3.522 (5) Å, both in (4*g*), but all are fairly short in comparison with the values now accepted as indicative of C—H···O hydrogen bonds (Taylor & Kennard, 1982; Desiraju, 1991; Braga, Grepioni, Biradha, Pedireddi & Desiraju, 1995): similarly, the H···O distances are fairly short for interactions of this type. These values taken together indicate that the C—H groups in phenols, as well as the familiar O—H groups, have fairly high acidity, comparable with the C—H acidity in alkynes (Desiraju, 1991).

In addition to the highly localized O—H···N and C—H···O hydrogen bonds, (4*c*) and (4*d*) also exhibit weak delocalized C—H···π(arene) hydrogen bonding. In these examples, the shortest H···C distances, to C11, C12 and C13 in (4*c*) and to C11, C15 and C16 in compound (4*d*), are comparable with the shortest intermolecular H···C distances observed in alkynes (Steiner, 1995).

3.4.2. *Hydrogen-bonding motifs.* The essential features of the localized hydrogen-bonding patterns in the adducts studied here can readily be codified using the graph-set approach (Etter, 1990; Etter, MacDonald & Bernstein, 1990; Bernstein, Davis, Shimoni & Chang, 1995). In each of (4*c*), (4*d*), (4*g*) and (5*a*) the basic chain-forming motif, encompassing an entire bisphenol/HMTA pair has the graph set $C_2^2(16)$. In addition, in (4*d*) there is a motif involving spiral formation by means of C—H···O═S hydrogen bonds which has the graph set $C_2^2(11)$, so that for (4*d*) the overall graph set descriptor is $C_2^2(16)C_2^2(11)$. In (4*g*) there are two additional motifs involving C—H···O hydrogen bonds: the bonding motif between the two strands within a double helix has graph set $C(7)$, while the motif linking different double helices has graph set $C(5)$, so that the overall descriptor for (4*g*) is $C(5)C(7)C_2^2(16)$. For (5*a*) the O—H···N hydrogen bonds external to the triple helix have graph set $D$, giving the overall descriptor for this triple helix as $DC_2^2(16)$. In (6) the centrosymmetric rings have unitary graph set $R_4^4(20)$, while the chain-forming motif arising from the linkage of these rings has binary graph set $C_4^4(20)$; this structure provides an example of the chain-of-rings pattern, with overall descriptor $C_4^4(20)[R_4^4(20)]$ (Bernstein, Davis, Shimoni & Chang, 1995).

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