Ferguson, G., Glidewell, C. & Patterson, I. L. J. (1996). *Acta Cryst.* C**52**, 420–423.
Ferguson, G., Glidewell, C., Royles, B. J. L. & Smith, D. M. (1996). *Acta Cryst.* C**52**, 2465–2468.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Glidewell, C., Ferguson, G., Nikas, S. & Varvoglis, A. (1996). *Acta Cryst.* C**52**, 1488–1490.
Glidewell, C., Lightfoot, P. & Patterson, I. L. J. (1995). *Acta Cryst.* C**51**, 1648–1651.
Hanton, L. R., Hunter, C. A. & Purvis, D. H. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1134–1136.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kohler, E. P. & Tishler, M. (1935). *J. Am. Chem. Soc.* **57**, 217–224.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Shriner, R. L., Struck, H. C. & Jorison, W. J. (1930). *J. Am. Chem. Soc.* **52**, 2060–2069.
Spek, A. L. (1996*a*). *PLATON. Molecular Geometry Program.* Version of November 1996. University of Utrecht, The Netherlands.
Spek, A. L. (1996*b*). *PLUTON. Molecular Graphics Program.* Version of August, 1996. University of Utrecht, The Netherlands.

*Acta Cryst.* (1997). C**53**, 1978–1980

# Pairwise-Interwoven $R_6^6(48)$ Hexagonal Nets in the Hydrogen-Bonded Structure of Hexamethylenetetramine–1,1,1-Tris(4-hydroxyphenyl)ethane (1/1)

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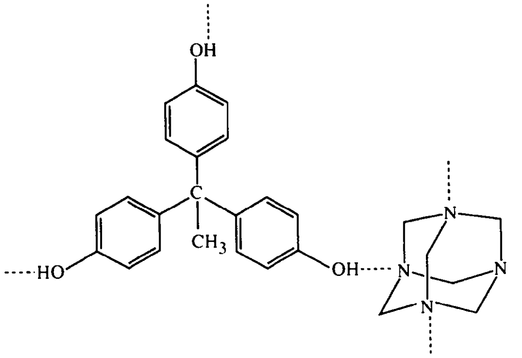
(*Received 30 April 1997; accepted 5 August 1997*)

## Abstract

In the 1:1 adduct formed by hexamethylenetetramine (HMTA) and 1,1,1-tris(4-hydroxyphenyl)ethane, $C_6H_{12}N_4.C_{20}H_{18}O_3$, the tris-phenol acts as a triple donor of hydrogen bonds of type O—H···N and the HMTA as a triple acceptor of such hydrogen bonds, with O···N distances of 2.777 (4), 2.781 (4) and 2.795 (4) Å. The components are assembled into infinite nets comprising hexagonal rings, and pairs of such nets are interwoven; the pairs of interwoven nets are, in addition, connected by C—H···O hydrogen bonds with a C···O distance of 3.339 (5) Å.

## Comment

In hydrogen-bonded adducts with aromatic hydroxy compounds, hexamethylenetetramine [HMTA, $(CH_2)_6N_4$] generally acts as a bis-acceptor of hydrogen bonds (Mak *et al.*, 1977; Mak, Yu & Lam, 1978; Mahmoud & Wallwork, 1979; Coupar, Glidewell & Ferguson, 1997). The only recorded example in which HMTA is observed to act as a tris-acceptor of hydrogen bonds is the complex with phenol, $HMTA.(phenol)_3$, where the ordered molecular aggregates lie on threefold rotation axes (Jordan & Mak, 1970). However, this precedent indicates that with an appropriate tris-phenol acting as a tris-donor of hydrogen bonds, it should be possible to design and construct a hydrogen-bonded system in which each component, HMTA and the tris-phenol, takes part in three hydrogen bonds, thereby generating a continuous molecular network. It can be estimated that a structure built from just one such network of hexagonal rings would have a density of around 0.35 Mg m$^{-3}$, so that based on the typical densities of adducts of this general type, the presence of four independent networks is to be expected, with the possibility of interweaving. The phase behaviour of the binary system HMTA/1,1,1-tris(4-hydroxyphenyl)ethane is complex, and homogeneous phases with HMTA to tris-phenol ratios of 2:1, 3:2 and 1:1 can all be crystallized from solutions in ethanol or propanol (Coupar, Glidewell & Ferguson, 1997). We report here the structure of the 1:1 adduct, (I), which indeed proves to contain HMTA acting as a tris-acceptor of hydrogen bonds in a continuous network structure.



(I)

The structure analysis (Figs. 1 and 2) confirms not only the 1:1 ratio of the two components deduced from microanalytical data (Coupar, Glidewell & Ferguson, 1997), but also the presence of four independent networks built from hexagonal rings. The two components are connected by O—H···N hydrogen bonds, with the tris-phenol acting as a triple donor of hydrogen bonds and the HMTA acting as a triple acceptor. There are no O—H···O hydrogen bonds, although such interactions are found in the adducts of 1,1,1-tris(4-hydroxyphenyl)ethane with both 1,4-diazabicyclo[2.2.2]octane and piperazine (Ferguson, Bell, Coupar & Glidewell, 1997). Overall, the structure is built from layers of HMTA molecules around $y = 0$ and $y = \frac{1}{2}$, separated by thicker layers of tris-phenol molecules (Fig. 2).

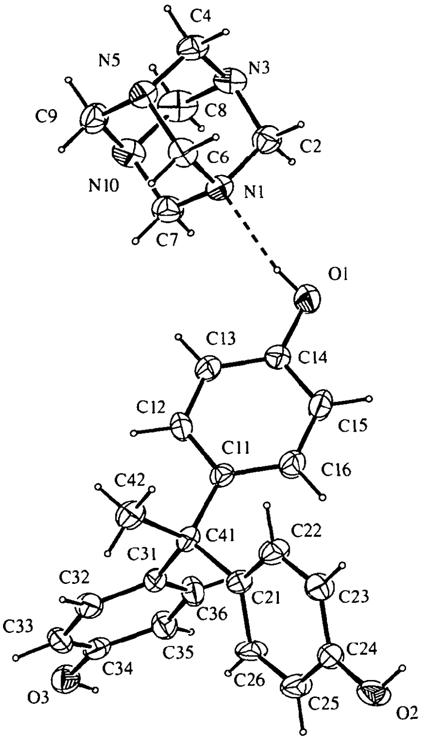


Fig. 1. A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

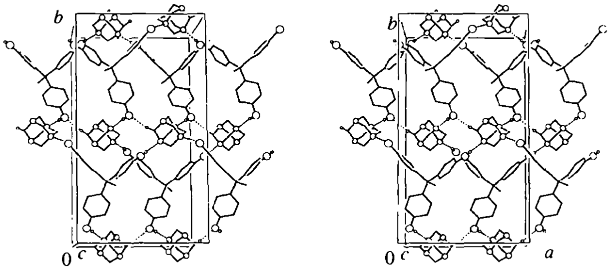


Fig. 2. Stereoview of part of the crystal structure, showing the twofold interweaving of the nets. Large, medium and small circles represent O, N and H atoms, respectively.

The asymmetric unit (Fig. 1) contains one molecule of each component, and within this unit, atom O1 acts as hydrogen-bond donor to N1. Atom O3 in the unit at ($x$, $y$, $z$) acts as donor to atom N5 in the unit at ($-1+x$, $y$, $z$), giving rise to a chain formation parallel to the *a* direction. The unitary graph set (Etter, 1990; Bernstein, Davis, Shimoni & Chang, 1995) for the hydrogen-bond motifs n this chain is *DD* and the binary graph set is $C_4^4(16)$. The remaining O atom, O2, in the unit at ($x$, $y$, $z$) acts as hydrogen-bond donor to atom N3 in the unit at ($1-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$), while atom O2 in this latter unit acts as donor to atom N3 at ($x$, $-1+y$, $z$), so giving rise to a spiral chain parallel to the **b** direction, generated by the $2_1$ axis, and having unitary and binary graph sets *DD* and $C_4^4(16)$.

The intersection of the two chain motifs, which occurs at every tris-phenol and every HMTA molecule, generates infinite sheets built up from hexagonal nets. Each hexagonal ring in the net involves three molecules of each component: for example, the tris-phenol units at ($x$, $y$, $z$), ($-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$) and ($1-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$) using atoms O1 and O3, O2 and O3, and O1 and O2, respectively, as donors, and the HMTA units at ($x$, $y$, $z$), ($-1+x$, $y$, $z$) and ($1-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$), using N1 and N3, N5 and N3, and N1 and N5, respectively, as hydrogen-bond acceptors. The binary-level graph set for these six-component rings is $R_6^6(48)$: this is precisely the same as for the hexagonal rings in trimesic acid (Duchamp & Marsh, 1969). The formation of such an infinite net requires the use of only two molecules of each component per unit cell: since $Z = 8$, there must be four such independent nets to fill the available space. Pairs of hexagonal nets, related by the a glide plane normal to the **c** direction, are interwoven: one of the resultant bilayers lies predominantly in the half of the unit cell having $0 < z < 0.5$, while the other lies predominantly in the half of the unit cell having $0.5 < z < 1.0$. The pairwise interweaving of hexagonal $R_6^6(48)$ nets in (I) is closely analogous to the pairwise interweaving of square $R_4^4(32)$ nets in 4,4′-sulfonyldiphenol (Glidewell & Ferguson, 1996)

The O···N distances within the hydrogen bonds (Table 2) are typical of those observed in other HMTA adducts with phenols (Jordan & Mak, 1970; Mak *et al.*, 1977; Mak, Yu & Lam, 1978; Mahmoud & Wallwork, 1979; Coupar, Glidewell & Ferguson, 1997). In addition, there is a C—H···O hydrogen bond in which the bond C7—H7*A* (the C—H bond antiperiplanar to the bond N10—C9, see Fig. 1) in the HMTA unit at ($x$, $y$, $z$) acts as donor to the O2 atom in the tris-phenol at ($\frac{1}{2}-x$, $\frac{1}{2}+y$, $z$). This interaction, which generates a $C_2^2(15)$ chain parallel to the [010] direction, serves to form cross-links between the two otherwise independent components of a bilayer. The C···O and H···O distances in this interaction (Table 2) are both short in comparison with the values now accepted as indicative of C—H···O hydrogen bonds (Taylor & Kennard, 1982; Desiraju, 1991, 1996; Braga *et al.*, 1995), so that these cross-linking interactions should be regarded as fairly strong for their type. There are no significant interactions between the bilayers.

Within the molecular components, the interatomic distances are all typical (Allen *et al.*, 1987); the conformation of the tris-phenol components, as judged by the C42—C41—C*n*1—C*n*2 ($n$ = 1, 2, 3) angles (Table 1) is very far from the idealized maximum $C_3$ rotational symmetry. Examination of the structure with

*PLATON* (Spek, 1996*a*) showed that there were no solvent-accessible voids in the crystal lattice.

## Experimental

A sample of the adduct was prepared as described previously (Coupar, Glidewell & Ferguson, 1997). Crystals suitable for single-crystal X-ray diffraction were selected directly from the prepared sample.

### *Crystal data*

$C_6H_{12}N_4.C_{20}H_{18}O_3$
$M_r = 446.54$
Orthorhombic
*Pbca*
$a = 13.307$ (2) Å
$b = 24.150$ (3) Å
$c = 14.740$ (2) Å
$V = 4737.1$ (12) Å$^3$
$Z = 8$
$D_x = 1.252$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.11–16.10°$
$\mu = 0.083$ mm$^{-1}$
$T = 294$ (1) K
Plate
0.41 × 0.29 × 0.10 mm
Colourless

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4342 measured reflections
4168 independent reflections
1373 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$

$\theta_{\rm max} = 25.00°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 28$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: no decay, variation 1.0%

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.129$
$S = 0.819$
4168 reflections
301 parameters
H atoms riding (C—H 0.93–0.97, O—H 0.82 Å; OH and $CH_3$ allowed to rotate, but not to tilt)

$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.169$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.238$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O1—C14 | 1.376 (4) | N5—C6 | 1.460 (4) |
| O2—C24 | 1.366 (4) | N5—C9 | 1.471 (5) |
| O3—C34 | 1.376 (4) | N10—C7 | 1.452 (5) |
| N1—C2 | 1.470 (4) | N10—C8 | 1.453 (5) |
| N1—C6 | 1.469 (4) | N10—C9 | 1.461 (5) |
| N1—C7 | 1.479 (4) | C11—C41 | 1.543 (5) |
| N3—C2 | 1.459 (4) | C21—C41 | 1.537 (5) |
| N3—C4 | 1.471 (4) | C31—C41 | 1.530 (5) |
| N3—C8 | 1.488 (5) | C41—C42 | 1.560 (4) |
| N5—C4 | 1.474 (4) | | |
| C32—C31—C41—C42 | −14.8 (5) | C26—C21—C41—C42 | 115.4 (4) |
| C36—C31—C41—C42 | 163.2 (3) | C16—C11—C41—C42 | 128.8 (4) |
| C22—C21—C41—C42 | −60.6 (4) | C12—C11—C41—C42 | −53.0 (5) |

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···N1 | 0.82 | 1.97 | 2.777 (4) | 169 |
| O2—H2···N3$^{\rm i}$ | 0.82 | 1.96 | 2.781 (4) | 175 |
| O3—H3···N5$^{\rm ii}$ | 0.82 | 1.99 | 2.795 (4) | 166 |
| C7—H7A···O2$^{\rm iii}$ | 0.97 | 2.40 | 3.339 (5) | 163 |

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

The title compound crystallized in the orthorhombic system; space group *Pbca* was chosen from the systematic absences.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET4* and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD2* in *NRCVAX94* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX94*. Program(s) used to refine structure: *NRCVAX94* and *SHELXL93* (Sheldrick, 1993). Molecular graphics: *NRCVAX94*, *ORTEPII* (Johnson, 1976), *PLATON* (Spek, 1996*a*) and *PLUTON* (Spek 1996*b*). Software used to prepare material for publication: *NRCVAX94*, *SHELXL93* and *WordPerfect* macro *PREPCIF* (Ferguson, 1996).

GF thanks NSERC (Canada) for Research Grants.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1225). Services for accessing these data are described at the back of the journal.

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## References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Braga, D., Grepioni, F., Biradha, K., Pedireddi, V. R. & Desiraju, G. R. (1995). *J. Am. Chem. Soc.* **117**, 3156–3166.
Coupar, P. I., Glidewell, C. & Ferguson, G. (1997). *Acta Cryst.* B**53**, 521–533.
Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–296.
Desiraju, G. R. (1996). *Acc. Chem. Res.* **29**, 441–449.
Duchamp, D. J. & Marsh, R. E. (1969). *Acta Cryst.* B**25**, 5–19.
Enraf–Nonius (1992). *CAD-4-PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Ferguson, G. (1996). *PREPCIF97. A WordPerfect-5.1 Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL93 Programs.* University of Guelph, Canada.
Ferguson, G., Bell, W., Coupar, P. I. & Glidewell, C. (1997). *Acta Cryst.* B**53**, 534–543.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Glidewell, C. & Ferguson, G. (1996). *Acta Cryst.* C**52**, 2528–2530.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Jordan, T. H. & Mak, T. C. W. (1970). *J. Chem. Phys.* **52**, 3790–3794.
Mahmoud, M. M. & Wallwork, S. C. (1979). *Acta Cryst.* B**35**, 2370–2374.
Mak, T. C. W., Tse, C.-S., Chong, Y.-H. & Mok, F.-C. (1977). *Acta Cryst.* B**33**, 2980–2982.
Mak, T. C. W., Yu, W.-H. & Lam, Y.-S. (1978). *Acta Cryst.* B**34**, 2061–2063.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1996*a*). *PLATON. Molecular Geometry Program.* Version of August, 1996. University of Utrecht, The Netherlands.
Spek, A. L. (1996*b*). *PLUTON. Molecular Graphics Program.* Version of August, 1996. University of Utrecht, The Netherlands.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.