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Bis(1,2-dihydroxybenzene) hexamethylenetetramine

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Key indicators

Single-crystal X-ray study

$T = 298$ K

Mean σ(C–C) = 0.004 Å

R factor = 0.051

wR factor = 0.119

Data-to-parameter ratio = 12.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title binary complex, $2C_6H_6O_2 \cdot C_6H_{12}N_4$, is constructed from hexamethylenetetramine, positioned about a twofold symmetry operator, and 1,2-dihydroxybenzene. Each of the four tertiary amine N atoms participates in O—H$\cdots$N contacts that produce molecular strands that propagate along the c axis.

Comment

The controlled construction of molecular assemblies has progressed over the past several decades owing, in part, to the improved understanding of non-bonded contacts. The extension of these efforts to multicomponent systems is a current topic of interest that frequently follows the rational selection of building blocks with complementary molecular features. Although various modes of molecular alignment have been generated using this strategy, the extension of predictable low-dimensional motifs (discrete and one-dimensional patterns) to two- and three-dimensional patterns remains a current challenge.

In many ways hexamethylenetetramine (HMTA) is a model candidate for use in cocrystallization studies. The hydrogen-bond ability and tetrahedral arrangement of the four tertiary N atoms provide attractive features that could, in principle, form extended molecular architectures *via* selective cocrystallization with donor molecules. We were somewhat surprised to discover that a search of the Cambridge Structural Database (CSD; Version 5.27 with August 2006 update; Allen, 2002) for HMTA cocrystalline compounds revealed relatively few structures that involve all HMTA N atoms in intermolecular contacts. Of the 30 reported structures that contain neutral HMTA and OH donor components (alcohols and carboxylic acids), only two [2,2′-biphenol (MacLean *et al.*, 1999) and (1*R*,3*S*)-camphoric acid (Zakaria *et al.*, 2003)] adopt motifs that involve all N atoms. A parallel search for protonated HMTA molecular salts with $C—O^-$ acceptors (carboxylates and alkoxides) uncovered an additional ten structures of which none exhibit tertacoordination *via* either $N\cdots H—O$ or $N^+—H\cdots\,^-O—C$ intermolecular contacts.

The title binary complex, (I), was prepared and crystallographically assessed as part of our continuing effort to understand the cocrystallization tendencies and specificities of HMTA (Sakwa & Wheeler, 2003). The asymmetric unit of (I) (Fig. 1) comprises a molecule of 1,2-dihydroxybenzene and one half-molecule of HMTA positioned about a twofold rotation axis upon which are located atoms C8 and C10. As anticipated, both hydroxyl groups participate in hydrogen bonds (Table 1). Hydroxy atom O2 forms an intramolecular interaction, while atom O1 forms a contact to a neighboring HMTA molecule. Owing to crystallographic symmetry, the
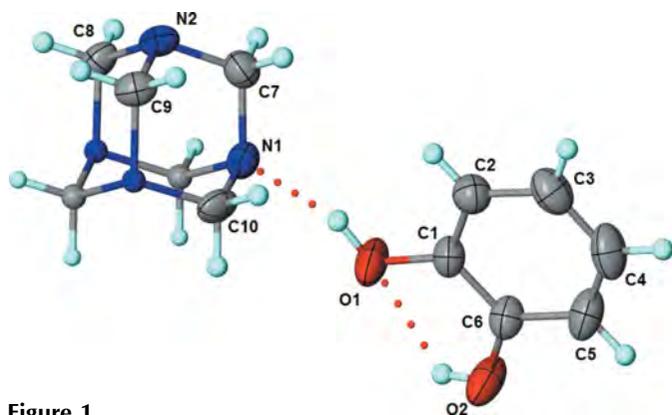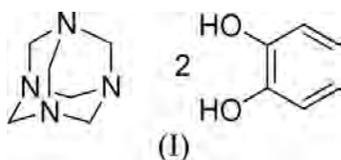
Figure 1
The structure of the component molecules of (I), showing the atom-labeling scheme and displacement ellipsoids at the 50% probability level. Atoms C8 and C10 of the HMTA molecule lie on a twofold axis. Dotted lines indicate hydrogen bonds.
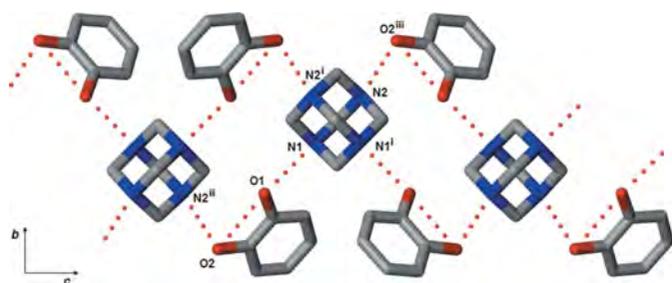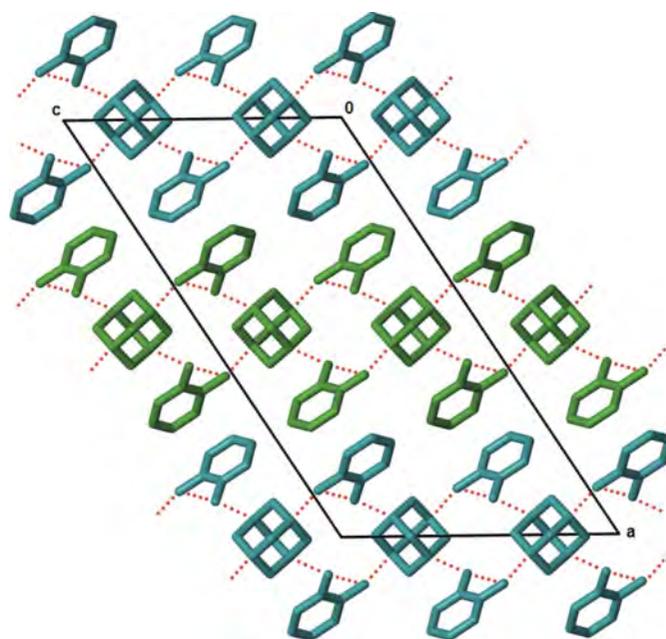

Figure 2
View of the packing of (I), showing the catemeric O—H···N interactions as dashed lines. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $x, 2 - y, -\frac{1}{2} + z$; (iii) $x, 2 - y, \frac{1}{2} + z$.]

latter interactions form two contacts for each HMTA molecule (Fig. 2). The remaining N atoms (N2) also participate in contacts with neighboring dihydroxybenzene molecules *via* two symmetry related O2—H2O···N2 hydrogen bonds. This collection of non-bonded contacts involves each of the four HMTA N atoms and forms molecular strands that propagate along the *c* axis. A perspective of the parallel alignment of several of these strands in the unit cell is shown in Fig. 3

(I)

Figure 3
Projection of the unit-cell contents of (I), showing the assembly of molecular strands (gray and green).

Crystal data

$2C_6H_6O_2 \cdot C_6H_{12}N_4$	$Z = 4$
$M_r = 360.41$	$D_x = 1.326$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 23.794$ (2) Å	$\mu = 0.10$ mm^{-1}
$b = 6.8422$ (5) Å	$T = 298$ (2) K
$c = 13.244$ (1) Å	Plate, colorless transparent
$\beta = 123.135$ (6)°	$0.41 \times 0.41 \times 0.20$ mm
$V = 1805.5$ (3) Å^3	

Data collection

Siemens P4 diffractometer	$R_{int} = 0.022$
$\omega/2\theta$ scans	$\theta_{max} = 25.4°$
Absorption correction: none	3 standard reflections
1921 measured reflections	every 97 reflections
1626 independent reflections	intensity decay: none
1054 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$+ 0.6351P]$
$wR(F^2) = 0.119$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
1626 reflections	$\Delta\rho_{max} = 0.15$ e Å^{-3}
127 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Experimental

Single crystals of (I) were prepared by slow evaporation at room temperature of a methanol solution (20 ml) of 1:2 hexamethylene-tetramine (0.250 g, 1.79 mmol) and 1,2-dihydroxybenzene (0.393 g, 3.60 mmol) (m.p. 422–425 K). ^{1}H NMR (acetone-d_6): δ 4.63 (*s*, 12H, HMTA-CH$_2$), 6.62 (*dd*, *J* = 5.8 and 3.5 Hz, 4H, H-2, 5), 6.78 (*dd*, *J* = 5.8 and 3.5 Hz, 4H, H-3, 4). ^{13}C NMR (acetone-d_6): δ 145.6 (C7—C10), 119.4 (C3, 4), 115.7 (C2, 5), 74.4 (C1, 6).

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O···N1	0.91 (3)	1.89 (3)	2.764 (3)	162 (3)
O2—H2O···O1	0.79 (3)	2.34 (3)	2.717 (3)	111 (2)
O2—H2O···N2^i	0.79 (3)	2.10 (3)	2.832 (3)	155 (3)

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

Phenoxy H atoms were refined without constraint. All other H atoms were included in the riding-model approximation, with C—H = 0.93–0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *XSCANS* (Bruker, 1999); cell refinement: *XSCANS*; data reduction: *XPREP* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED*.

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