

O6—C7—C9	105.7 (7)	O6'—C7'—C9'	107.0 (5)
O10—C9—C7	110.6 (8)	O10'—C9'—C7'	111.9 (7)
O10—C11—C12	116.0 (9)	O10'—C11'—C12'	114.6 (8)
O13—C12—C11	111.0 (9)	O13'—C12'—C11'	110.4 (8)
O13—C14—C15	109.5 (9)	O13'—C14'—C15'	110.4 (8)
O16—C15—C14	115.7 (9)	O16'—C15'—C14'	114.8 (8)
O16—C17—C18	109.4 (8)	O16'—C17'—C18'	108.3 (8)
C17—C18—O20	106.8 (7)	O20'—C18'—C17'	106.9 (7)
O20—C21—C23	113.5 (7)	O20'—C21'—C23'	112.0 (7)
N1—C23—C21	116.7 (7)	N1'—C23'—C21'	117.7 (7)
C7—O6—C4—C3	172.1 (8)		
N1—C3—C4—O6	-2.9 (13)		
C4—O6—C7—C9	-155.4 (8)		
C11—O10—C9—C7	-171.7 (8)		
O6—C7—C9—O10	-70.7 (10)		
C9—O10—C11—C12	-79.8 (11)		
C14—O13—C12—C11	-172.1 (9)		
O10—C11—C12—O13	-71.2 (12)		
C12—O13—C14—C15	-172.7 (9)		
C17—O16—C15—C14	70.8 (12)		
O13—C14—C15—O16	67.1 (13)		
C15—O16—C17—C18	172.1 (7)		
O16—C17—C18—O20	74.0 (10)		
C21—O20—C18—C17	-157.2 (9)		
C18—O20—C21—C23	-169.8 (8)		
C3—N1—C23—C21	177.7 (9)		
O20—C21—C23—N1	-33.7 (13)		
C7'—O6'—C4'—C3'	177.7 (4)		
N1'—C3'—C4'—O6'	-8.0 (5)		
C4'—O6'—C7'—C9'	-153.8 (5)		
C11'—O10'—C9'—C7'	-175.4 (7)		
O6'—C7'—C9'—O10'	-69.5 (8)		
C9'—O10'—C11'—C12'	-79.2 (10)		
C14'—O13'—C12'—C11'	-171.5 (8)		
O10'—C11'—C12'—O13'	-71.3 (10)		
C12'—O13'—C14'—C15'	-175.2 (9)		
C17'—O16'—C15'—C14'	75.7 (11)		
O13'—C14'—C15'—O16'	68.7 (12)		
C15'—O16'—C17'—C18'	171.3 (7)		
C21'—O20'—C18'—C17'	-152.1 (9)		
O16'—C17'—C18'—O20'	71.1 (9)		
C18'—O20'—C21'—C23'	-170.0 (8)		
C3'—N1'—C23'—C21'	178.9 (7)		
O20'—C21'—C23'—N1'	-36.7 (13)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

The authors wish to thank Chinoin Pharmaceuticals for supporting the project with manpower and instrumentation. JSB and RMI are grateful for the financial support of the Office of Naval Research. One of us (GMK) is grateful for the Magyary Zoltán fellowship of the Foundation for Hungarian Higher Education and Research.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1127). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 466–468

1:1 Adduct of Tris(4-hydroxy-3,5-dimethylbenzyl)amine and Hexamethylenetetramine

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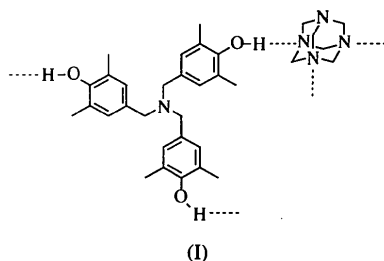
(Received 23 March 1995; accepted 10 August 1995)

Abstract

The title compound {4,4',4''-(nitrotrimethylene)tris(2,6-dimethylphenol)-1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]}decane (1/1), C₂₇H₃₃NO₃·C₆H₁₂N₄ crystallizes in the space group *R*3̄, with hydrogen-bonded layers perpendicular to the symmetry axes. All molecules lie on threefold rotation axes. Each triphenol molecule is hydrogen bonded to three hexamethylenetetramine molecules and each hexamethylenetetramine molecule is hydrogen bonded to three triphenol molecules. The hydrogen bonds are similar to those found in other adducts of hexamethylenetetramine with phenols.

Comment

Hexamethylenetetramine (HMTA) is used industrially as a crosslinking agent (Knop & Pilato, 1985) and its reaction with model phenols has been the subject of a study directed at elucidating the curing mechanism of a phenolic resin (Looney & Solomon, 1995). HMTA forms a variety of crystalline complexes with phenol and substituted phenols (Jordan & Mak, 1970; Tse, Wong & Mak, 1977; Mak, Yu & Lam, 1978). The crystal structure of the 1:3 adduct of HMTA and phenol was shown to be comprised of three phenol molecules linked to each HMTA molecule through O—H...N hydrogen bonds (Jordan & Mak, 1970), while in the 1:2 adduct with *m*-cresol (Mak, Yu & Lam, 1978), two *m*-cresol molecules are hydrogen bonded to each HMTA molecule. With resorcinol and hydroquinone (Mahmoud & Wallwork, 1979; Mak, Tse, Chong & Mok, 1977), which contain two phenolic groups, HMTA forms 1:1 adducts in which hydrogen bonds link the phenolic and HMTA molecules into zigzag chains. As the ligand involved in the title adduct, (I), has three phenol units tethered by an amine functionality, a more extensive polymeric structure may be envisaged.



The central N atom on the triphenol molecule, N(1), and one of the N atoms of the HMTA molecule, N(2), both lie on sites of threefold symmetry, and thus one third of the two molecules forms the asymmetric unit. The phenol rings are almost perpendicular to the *ab* plane, with the dihedral angle between the normal to the ring plane and the *c* axis being 87.14°. Each triphenol molecule is hydrogen bonded to three HMTA molecules (Fig. 1) and each HMTA molecule is hydrogen bonded to three triphenol molecules, giving rise to hydrogen-bonded layers which lie perpendicular to the symmetry axes (Fig. 2); all molecules lie on threefold axes. Within each layer, O—H...N linkages give rise to large pear-shaped rings comprising three HMTA and three triphenol molecules. Packing of these layers occurs in a space-filling manner, which precludes the formation of any channels. There are no unusually short intermolecular interactions between the layers. The hydrogen bonds that link the triphenol and HMTA molecules [O—H(O) 0.88 (2), H(O)...N(3) 1.97 (2), O...N(3) 2.793 (2) Å and O—H(O)...N(3) 154 (2)°] are similar to those found in other adducts of HMTA and phenols.

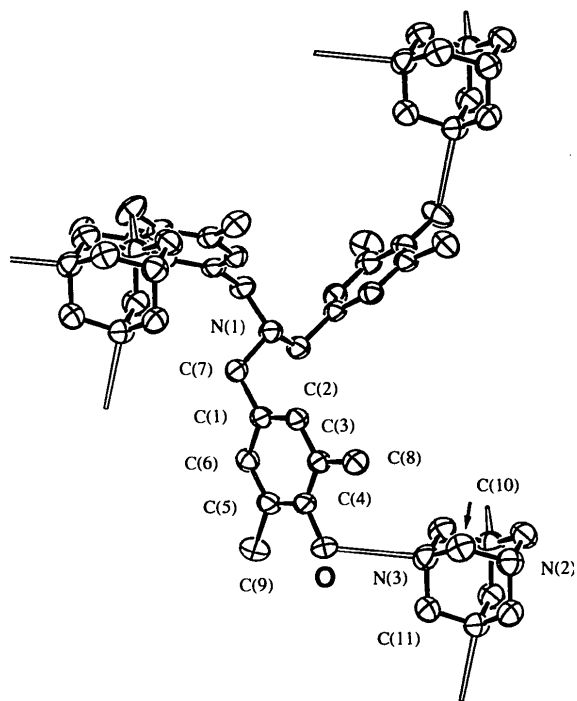


Fig. 1. ORTEP (Johnson, 1976) drawing of adduct (I). Atoms of the asymmetric unit are labelled. Displacement ellipsoids are drawn at the 50% probability level. Double lines represent hydrogen bonds.

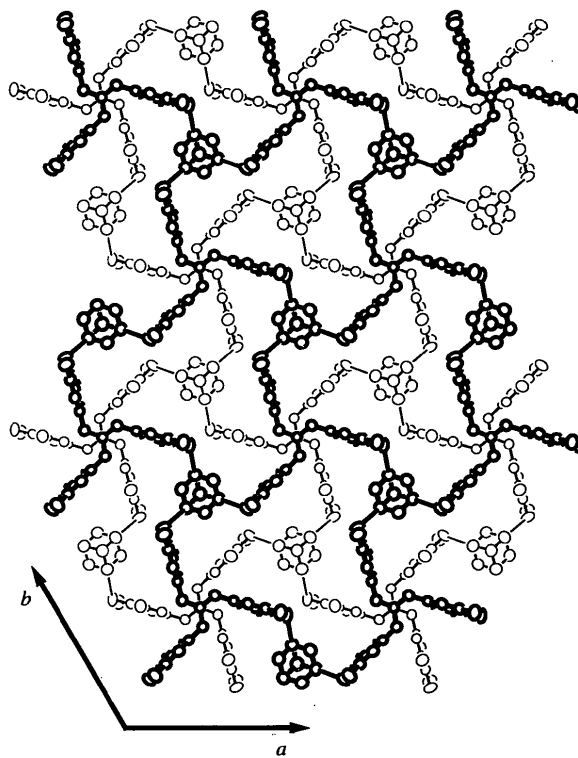


Fig. 2. A projection down *c* showing the packing of two adjacent layers centrosymmetrically related through the origin.

Experimental

The title compound was prepared by the reaction of 2,6-dimethylphenol and HMTA (mole ratio 1:2) (Zinke, Zigeuner, Weiss & Wiesenberger, 1949). The adduct of the resulting tris(4-hydroxy-3,5-dimethylbenzyl)amine was purified by recrystallization from ethanol and then from toluene. Crystals were grown from acetonitrile (m.p. 453–455 K).

Crystal data

C ₂₇ H ₃₃ NO ₃ ·C ₆ H ₁₂ N ₄	Mo K α radiation
$M_r = 559.74$	$\lambda = 0.71073 \text{ \AA}$
Rhombohedral	Cell parameters from 25 reflections
$R\bar{3}$	$\theta = 9.2\text{--}18.9^\circ$
$a = 14.1090 (10) \text{ \AA}$	$\mu = 0.079 \text{ mm}^{-1}$
$c = 26.697 (5) \text{ \AA}$	$T = 293 (1) \text{ K}$
$V = 4602.4 (10) \text{ \AA}^3$	Hexagonal needle
$Z = 6$	$0.400 \times 0.333 \times 0.200 \text{ mm}$
$D_x = 1.212 \text{ Mg m}^{-3}$	Colourless

Data collection

Enraf–Nonius CAD-4	$R_{\text{int}} = 0.0247$
MACHS diffractometer	$\theta_{\text{max}} = 24.98^\circ$
$\omega/2\theta$ scans	$h = -16 \rightarrow 3$
Absorption correction:	$k = -3 \rightarrow 16$
none	$l = -31 \rightarrow 31$
5431 measured reflections	3 standard reflections
1811 independent reflections	frequency: 150 min
1436 observed reflections	intensity decay: 6%
$[I > 2\sigma(I)]$	

Refinement

Refinement on F^2	Extinction correction:
$R(F) = 0.0353$	<i>SHELXL93</i> (Sheldrick, 1993)
$wR(F^2) = 0.0974$	Extinction coefficient:
$S = 1.036$	0.0010 (2)
1811 reflections	Atomic scattering factors
185 parameters	from <i>International Tables for Crystallography</i> (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)
$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 1.7548P]$	
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\text{max}} = -0.002$	
$\Delta\rho_{\text{max}} = 0.292 \text{ e \AA}^{-3}$	
$\Delta\rho_{\text{min}} = -0.104 \text{ e \AA}^{-3}$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

	$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$			
	x	y	z	U_{eq}
N(1)	0	0	0.09940 (7)	0.0382 (4)
O	0.42258 (9)	-0.04761 (10)	0.05476 (5)	0.0624 (4)
C(1)	0.19289 (10)	0.03737 (10)	0.09999 (5)	0.0386 (3)
C(2)	0.20759 (11)	0.02567 (10)	0.04963 (5)	0.0409 (3)
C(3)	0.28396 (11)	-0.00189 (11)	0.03262 (5)	0.0415 (3)
C(4)	0.34497 (10)	-0.02068 (11)	0.06823 (5)	0.0432 (4)
C(5)	0.33297 (11)	-0.00911 (11)	0.11916 (5)	0.0448 (4)
C(6)	0.25737 (11)	0.02075 (11)	0.13395 (5)	0.0428 (3)
C(7)	0.11227 (10)	0.07063 (11)	0.11783 (6)	0.0420 (4)
C(8)	0.3008 (2)	-0.0085 (2)	-0.02246 (6)	0.0558 (4)
C(9)	0.3987 (2)	-0.0309 (2)	0.15694 (8)	0.0664 (5)
N(2)	1/3	-1/3	-0.08533 (8)	0.0549 (6)

N(3)	0.36290 (10)	-0.22191 (10)	-0.01134 (5)	0.0502 (3)
C(10)	0.3621 (2)	-0.22526 (13)	-0.06621 (6)	0.0566 (4)
C(11)	0.44196 (13)	-0.25354 (13)	0.00624 (7)	0.0533 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

N(1)—C(7)	1.4717 (14)	C(3)—C(8)	1.500 (2)
O—C(4)	1.374 (2)	C(4)—C(5)	1.390 (2)
C(1)—C(2)	1.383 (2)	C(5)—C(6)	1.386 (2)
C(1)—C(6)	1.385 (2)	C(5)—C(9)	1.502 (2)
C(1)—C(7)	1.508 (2)	N(2)—C(10)	1.460 (2)
C(2)—C(3)	1.392 (2)	N(3)—C(10)	1.466 (2)
C(3)—C(4)	1.394 (2)	N(3)—C(11)	1.470 (2)
C(7)—N(1)—C(7')	109.40 (9)	C(6)—C(5)—C(4)	118.16 (12)
C(2)—C(1)—C(6)	117.77 (12)	C(6)—C(5)—C(9)	121.23 (15)
C(2)—C(1)—C(7)	121.72 (12)	C(4)—C(5)—C(9)	120.60 (14)
C(6)—C(1)—C(7)	120.49 (12)	C(1)—C(6)—C(5)	122.38 (13)
C(1)—C(2)—C(3)	122.26 (13)	N(1)—C(7)—C(1)	114.05 (11)
C(2)—C(3)—C(4)	117.95 (13)	C(10)—N(2)—C(10 ⁱⁱ)	108.46 (11)
C(2)—C(3)—C(8)	120.42 (13)	C(10)—N(3)—C(11 ⁱⁱ)	107.77 (13)
C(4)—C(3)—C(8)	121.62 (13)	C(10)—N(3)—C(11)	107.70 (12)
O—C(4)—C(5)	116.69 (12)	C(11 ⁱⁱ)—N(3)—C(11)	108.21 (15)
O—C(4)—C(3)	121.82 (13)	N(2)—C(10)—N(3)	112.14 (14)
C(5)—C(4)—C(3)	121.45 (12)	N(3 ⁱⁱⁱ)—C(11)—N(3)	112.40 (13)

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

The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1990). Refinement was by *SHELXL93* (Sheldrick, 1993) using full-matrix least squares, with anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for H atoms. The figures were prepared using *ORTEPII* (Johnson, 1976) and the tables prepared using *SHELXL93*. All calculations were carried out on a VAXstation 4000VLC computer system.

ACP and DHS wish to thank the Australian Industry Research and Development Board (grant No. 15068), the Australian Research Council for supporting this research and Comalco Aluminium Ltd for financial support. We thank Dr Mark Looney for the suggestion of carrying out this study.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: TA1031). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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