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1,4-Bis[3-(*N*-ethyliminomethyl)-2-hydroxy-5-methylbenzyl]piperazine†

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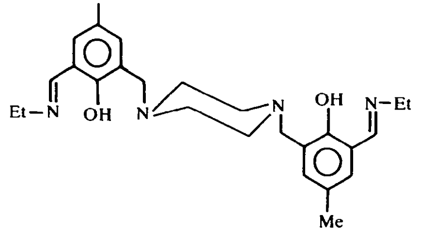
Abstract

In the title compound, $C_{26}H_{36}N_4O_2$, the piperazine ring adopts a chair conformation with the substituents at the N atoms both lying in equatorial positions so that the molecule has an extended conformation and is pseudo-centrosymmetric. The two phenyl rings lie almost in a plane making a dihedral angle of 9.06 (3)°. The structure is stabilized by hydrogen bonding, as well as van der Waals interactions.

Comment

The design and synthesis of binucleating ligands that incorporate dissimilar metal ions to form discrete hetero-dinuclear complexes is of importance in attempts to mimic some physical and chemical properties of the active sites of metalloenzymes such as cytochrome *c* oxidase (Palmer *et al.*, 1976) and bovine erythrocyte superoxide dismutase, and to search for the appropriate system for binding and activating simple molecules (Aratake *et al.*, 1990). On the basis of these considerations, the title compound, (I), was synthesized and its structure studied.



(I)

Phenyl rings *A* (C1–C6) and *B* (C15–C20) are nearly coplanar, and the dihedral angle between their mean planes is 9.06 (3)°. The torsion angles C5—C6—C7—N8 and C16—C15—C14—N11 [31.0 (2) and −28.4 (2)°, respectively] define the orientation of the substituents at the piperazine ring; both are in equatorial positions. As expected, the piperazine ring has a chair conformation and the molecule as a whole is pseudo-centrosymmetric with an extended conformation.

The piperazine moiety makes dihedral angles of 69.69 (6) and 74.76 (6)° with rings *A* and *B*, respectively. The C—O and C=N distances [1.361 (2) and 1.266 (2) Å, respectively] are comparable with reported average values (Allen *et al.*, 1987). Intramolecular hydrogen bonding determines the orientations of the C=N—Et substituents, so they only influence the packing of the molecules indirectly. The structure is stabilized by van der Waals forces.

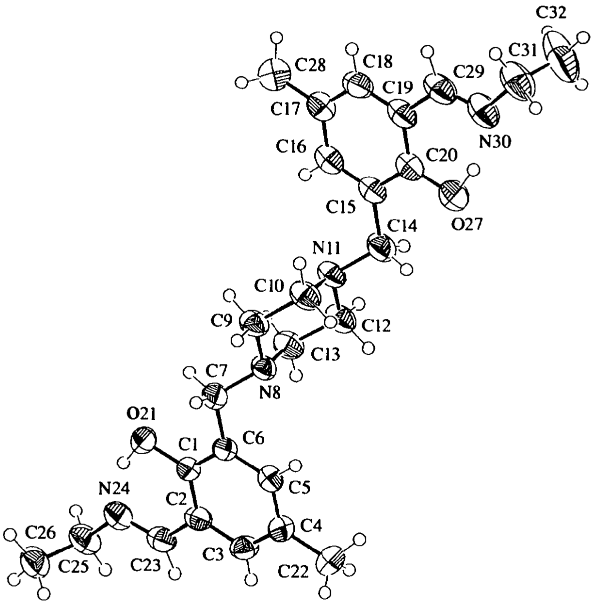


Fig. 1. *ORTEP*II (Johnson, 1976) plot of (I) showing 50% probability displacement ellipsoids.

Experimental

Paraformaldehyde (2 mol) and piperazine (1 mol) were stirred in 20 ml of ethanol for 1 h. 4-Methyl-2-formylphenol (2 mol) dissolved in 10 ml of acetic acid was added to this stirred solution and stirring was continued for 6 h. The 2:1:2 mixture was subjected to Schiff-base condensation with benzylamine (2 mol), and the reaction mixture refluxed for 3 h. The resulting mixture was neutralized with saturated Na_2CO_3 and the title compound was extracted with chloroform. The crude sample was purified on a silica-gel column using an *n*-hexane–chloroform (30:70 *v*/*v*) solvent mixture as eluent. The title

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† Alternative name: 6,6′-bis(*N*-ethyliminomethyl)-4,4′-dimethyl-2,2′-(piperazine-1,6-diyldimethylene)diphenol.

compound was crystallized by slow evaporation from ethanol (yield 70%, m.p. 423 K).

Crystal data

$C_{26}H_{36}N_4O_2$
$M_r = 436.59$
Monoclinic
$P2_1/c$
$a = 19.033\,(2)$ Å
$b = 13.661\,(1)$ Å
$c = 9.546\,(1)$ Å
$\beta = 95.72\,(1)^\circ$
$V = 2469.7\,(4)$ Å^3
$Z = 4$
$D_x = 1.174$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 5.39$–12.45°
$\mu = 0.075$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.88 × 0.58 × 0.36 mm
Yellow

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
7183 measured reflections
5655 independent reflections
3065 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$

$\theta_{\rm max} = 27.50^\circ$
$h = -24 \rightarrow 24$
$k = -17 \rightarrow 1$
$l = -1 \rightarrow 12$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.136$
$S = 0.908$
5655 reflections
423 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0728P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.173$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.157$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0037 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C1—O21	1.361 (2)	C20—O27	1.360 (2)
C2—C23	1.460 (2)	C23—N24	1.266 (2)
N8—C13	1.452 (2)	N24—C25	1.459 (2)
N8—C9	1.459 (2)	C29—N30	1.266 (3)
C9—C10	1.514 (2)	N30—C31	1.455 (3)
C12—C13	1.518 (2)		
O21—C1—C6	119.14 (13)	O27—C20—C15	118.9 (2)
O21—C1—C2	120.72 (13)	O27—C20—C19	121.19 (15)
C13—N8—C7	111.30 (14)	N24—C23—C2	122.9 (2)
C9—N8—C7	111.27 (13)	C23—N24—C25	118.5 (2)
C10—N11—C14	111.05 (15)	N30—C29—C19	123.2 (2)
C12—N11—C14	111.17 (14)	C29—N30—C31	117.6 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O21—H21···N24	0.97 (2)	1.71 (2)	2.604 (1)	151 (2)
O27—H27···N30	0.97 (2)	1.70 (2)	2.616 (1)	156 (2)

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1317). Services for accessing these data are described at the back of the journal.

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endo-endo-anti **Diels–Alder Diadduct of Hexachlorocyclopentadiene with 1,6-Dioxacyclodeca-3,8-diene**

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Abstract

There are two independent molecules of *endo-endo-anti*-1,7,8,9,10,16,17,18,19,19,20,20-dodecachloro-4,13-dioxapentacyclo[$14.2.1.1^{7,10}.0^{2,15}.0^{6,11}$]icosa-8,17-diene, $C_{18}H_{12}Cl_{12}O_2$, in the unit cell with different conformations. In one, the ten-membered ring adopts a chair–chair conformation, and in the other, it adopts a distorted chair–chair conformation. There are near-zero torsion angles at the ring-fusion bonds in both forms [1.5 (6) and 8.1 (5)° in the chair–chair molecule, and 2.9 (5) and 2.5 (5)° in the distorted chair–chair molecule]. The torsion angles about the bonds comprising the sides of the chair–chair are 158.5 (3), −160.7 (3), −146.8 (4) and 155.7 (3)°, and those of the distorted chair–chair are 148.0 (3), −146.8 (3), 175.7 (3) and −52.3 (4)°. The norbornene C═C bonds have lengths

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