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4-Hydroxy-2,6-bis[(4-methylpiperazinyl)-methyl]benzonitrile Monohydrate

K. Gunasekaran,[a] S. Shanmuga Sundara Raj,[a]
D. Velmurugan,[a]* T. M. Rajendran[b]† and
M. Kandaswamy[b]

[a]*Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600 025, India, and* [b]*Department of Inorganic Chemistry, University of Madras, Guindy Campus, Madras 600 025, India*

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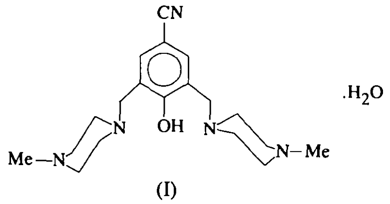
Abstract

The two piperazine rings of the title compound, $C_{19}H_{29}N_5O.H_2O$, assume a chair conformation and the exocyclic methyl groups in the piperazine rings are in equatorial positions. The best planes through the C atoms of the two piperazine rings make a dihedral angle of 40.1 (1)°. The mean puckering amplitude for the piperazine moiety is 0.598 (3) Å. The structure is stabilized by O—H···N intermolecular hydrogen bonding.

Comment

As part of our interest in the chemistry of binucleating ligands containing N-dentating atoms, the title compound, (I), was synthesized by Mannich reaction (Hodgkin, 1984). The average N—C distance in the piperazine ring is 1.468 (2) Å, in agreement with the value of 1.458 Å found in hydropiperazine (Schwarzenbach, 1968). The observed bond angles in the heterocyclic rings are distributed close to 110°, indicating that all the ring atoms including the N atoms are sp^3 hybridized (Perales, Cano & García-Blanco, 1977).



(I)

The cyano group lies in plane with the phenyl group. In piperazine ring *A*, the C atoms C9, C10, C12 and C13 form the base of the chair while the N8 atom deviates from the plane by −0.701 (3) Å and N11 by 0.673 (2) Å. Similarly, in ring *B*, atoms C17, C18, C20 and C21 lie in a plane while the N atoms N16 and N19 deviate by 0.683 (2) and −0.686 (3) Å, respectively. The methyl groups attached to N11 and N19 occupy equatorial positions. The best planes through the C atoms make a dihedral angle of 40.1 (1)°.

An interesting aspect of the molecular conformation is that even though the two piperazine rings have similar bond geometry and are substituted symmetrically with respect to the phenyl ring, they adopt different orientations with respect to the phenyl ring.

The structure is stabilized by an intramolecular O—H···N hydrogen bond [O23—H23 1.062 (4), N8···H23 1.783 (3), N8···O23 2.642 (3) Å and O23—H23···N8 134.8 (2)°]. The water molecule aids packing by forming intermolecular hydrogen bonds [OW···N11($-x+\frac{1}{2}$, $y-\frac{1}{2}$, $-z+\frac{3}{2}$) 2.949 (3) Å].

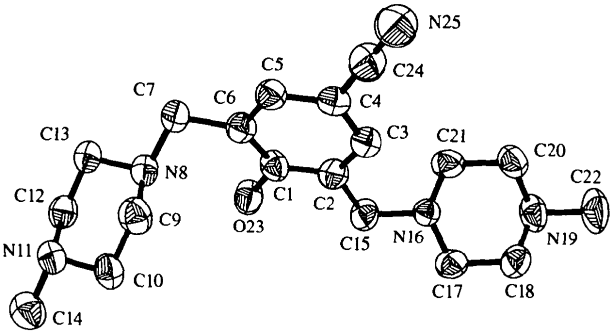


Fig. 1. A view of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

p-Cyanophenol (0.1 mol) in ethanol (150 ml) was mixed with an excess of *N*-methylpiperazine and stirred as a formaldehyde solution and refluxed. After evaporation of ethanol, compound (I) was obtained by washing with sodium carbonate solution, extracting with diethyl ether and drying.

Crystal data

$C_{19}H_{29}N_5O.H_2O$
$M_r = 361.49$
Monoclinic
$C2/c$
$a = 34.250\,(3)$ Å
$b = 9.134\,(1)$ Å
$c = 13.819\,(1)$ Å
$\beta = 112.7\,(1)°$
$V = 3988.3\,(7)$ Å^3
$Z = 8$
$D_x = 1.20$ Mg m^{-3}
$D_m = 1.251$ Mg m^{-3}
D_m measured by flotation

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 22 reflections
$\theta = 14$–$22°$
$\mu = 0.61$ mm^{-1}
$T = 298$ K
Needle
0.42 × 0.34 × 0.27 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans

2454 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.013$

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† Present address: Department of Chemistry, Pondicherry University, Pondicherry, India.

Absorption correction:
empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.832$, $T_{\max} = 0.998$
2992 measured reflections
2812 independent reflections

$\theta_{\max} = 60°$
$h = 0 \rightarrow 38$
$k = 0 \rightarrow 10$
$l = -15 \rightarrow 15$
3 standard reflections
every 200 reflections
frequency: 120 min
intensity decay: <1.3%

Refinement

Refinement on F
$R = 0.06$
$wR = 0.082$
$S = 0.878$
2454 reflections
346 parameters
All H atoms refined
$w = 1/[\sigma^2(F) + 0.019F^2]$

$(\Delta/\sigma)_{\max} = 0.023$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

C1—C2	1.392 (5)	C10—N11	1.462 (5)
C1—C6	1.408 (4)	N11—C12	1.472 (3)
C1—O23	1.363 (3)	N11—C14	1.463 (3)
C2—C3	1.387 (4)	C12—C13	1.521 (4)
C2—C15	1.521 (4)	C15—N16	1.464 (5)
C3—C4	1.402 (4)	N16—C17	1.469 (4)
C4—C5	1.395 (5)	N16—C21	1.473 (3)
C4—C24	1.430 (4)	C17—C18	1.515 (5)
C5—C6	1.373 (4)	C18—N19	1.454 (4)
C6—C7	1.523 (5)	N19—C20	1.464 (4)
C7—N8	1.480 (3)	N19—C22	1.470 (6)
N8—C9	1.478 (3)	C20—C21	1.522 (5)
N8—C13	1.472 (5)	C24—N25	1.151 (4)
C9—C10	1.517 (4)		
C6—C1—O23	120.7 (3)	C9—C10—N11	110.7 (2)
C2—C1—O23	118.1 (3)	C10—N11—C14	109.9 (3)
C2—C1—C6	121.2 (3)	C10—N11—C12	109.6 (2)
C1—C2—C15	118.2 (2)	C12—N11—C14	110.5 (2)
C1—C2—C3	119.7 (3)	N11—C12—C13	110.4 (2)
C3—C2—C15	122.1 (3)	N8—C13—C12	109.4 (3)
C2—C3—C4	119.2 (3)	C2—C15—N16	112.6 (2)
C3—C4—C24	120.0 (3)	C15—N16—C21	110.3 (2)
C3—C4—C5	120.5 (2)	C15—N16—C17	110.7 (2)
C5—C4—C24	119.4 (3)	C17—N16—C21	109.3 (2)
C4—C5—C6	120.7 (3)	N16—C17—C18	109.9 (2)
C1—C6—C5	118.7 (3)	C17—C18—N19	109.9 (3)
C5—C6—C7	119.7 (3)	C18—N19—C22	111.4 (3)
C1—C6—C7	121.6 (2)	C18—N19—C20	109.1 (3)
C6—C7—N8	111.5 (3)	C20—N19—C22	110.6 (3)
C7—N8—C13	110.5 (2)	N19—C20—C21	110.3 (2)
C7—N8—C9	111.8 (2)	N16—C21—C20	109.8 (2)
C9—N8—C13	109.1 (2)	C4—C24—N25	177.8 (3)
N8—C9—C10	109.3 (2)		
C9—N8—C13—C12	−60.3 (3)	C17—N16—C21—C20	−58.0 (3)
C13—N8—C9—C10	60.3 (3)	C21—N16—C17—C18	58.9 (3)
N8—C9—C10—N11	−59.7 (3)	N16—C17—C18—N19	−60.6 (3)
C9—C10—N11—C12	58.3 (3)	C17—C18—N19—C20	60.3 (3)
C10—N11—C12—C13	−58.0 (3)	C18—N19—C20—C21	−59.6 (3)
N11—C12—C13—N8	59.4 (3)	N19—C20—C21—N16	58.8 (3)

Refinement was performed by full-matrix least-squares methods. All the H atoms were located from the difference Fourier map, except the two of the water molecule (O*W*), and were included in the refinement. Calculations were performed using VAX730 and MicroVAX II computers.

Data collection: *SDP* (Frenz, 1978). Cell refinement: *SDP*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: PT1043). Services for accessing these data are described at the back of the journal.

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3-(1,8-Naphthalenedicarboximido)benzonitrile [or *N*-(3-Cyanophenyl)-1,8-naphthalimide], $C_{19}H_{10}N_2O_2$

Rhys A. Batchelor,[a] Christopher A. Hunter[b] and Jim Simpson[a]

[a]*Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand, and* [b]*Department of Chemistry, University of Sheffield, Sheffield S3 7HF, England. E-mail: jsimpson@alkali.otago.ac.nz*

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Abstract

The reaction of 3-cyanoaniline and naphthalic anhydride in refluxing dimethylformamide yielded the title compound. In the crystal, the naphthalimide and benzonitrile ring planes are inclined at 69.36(16)°. The molecules pack in columnar stacks parallel to the *c* axis.