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# 2,6-Bis[(4-methyl-1-piperazinyl)methyl]-4-nitrophenol

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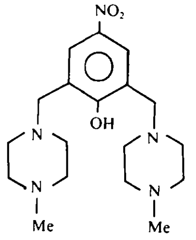
## Abstract

In the title compound, $C_{18}H_{29}N_5O_3$, each piperazine ring assumes a 'perfect chair' conformation with the exocyclic methyl group in an equatorial position. The nitro group makes a dihedral angle of 5.5 (1)° with the mean plane of the phenyl ring. Best planes through the four non-N atoms of each of the two piperazine rings make a dihedral angle of 29.9 (1)° with one another.

## Comment

As part of a study of the chemistry of bidentate ligands containing N-atom donors the title compound (I) was synthesized by the Mannich reaction (Hodgkin, 1984) between *p*-nitrophenol, formaldehyde and *N*-methylpiperazine, and crystallized from light petroleum ether by slow evaporation. Bond lengths and angles have the expected values.



(I)

The methyl groups at N15 and N23 of the piperazine rings are in equatorial positions (Allinger, Carpenter & Karkowski, 1965). Both the piperazine rings (*A* and *B*) assume 'perfect chair' conformations (Bassi & Scordamaglia, 1977; Sbit, Dupont, Dideberg, Liegeois & Delarge, 1992). Packing of the molecules in the unit cell depends mainly on van der Waals forces. A short intermolecular contact distance of 3.203 (3) Å occurs between atoms C18 and O10($x$, $y - 1$, $z + 1$).

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 relative orientations with respect to the phenyl ring. Atom N20 of piperazine ring *B* lies almost in the plane of the phenyl ring [torsion angle C3—C2—C19—N20 = 3.9 (3)°]. The intramolecular distance C3···N20 of 2.820 (3) Å is suggestive of a possible C—H···N interaction. On the other hand, ring *A* is rotated by about −36° to displace atom N12 significantly away from the plane of the phenyl

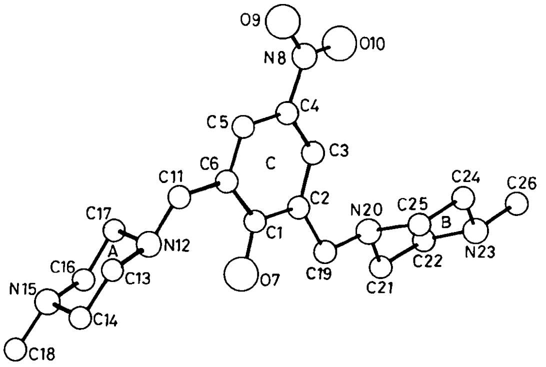


Fig. 1. Perspective view and numbering scheme of the title molecule.

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† DCB contribution No. 829.

ring, possibly to enable N12 to interact with the proton on the phenyloxy group to form an intramolecular hydrogen bond (the H atom at O7 could not be located).

## Experimental

### *Crystal data*

$C_{18}H_{29}N_5O_3$
$M_r = 363.46$
Triclinic
$P\bar{1}$
$a = 9.369$ (1) Å
$b = 10.762$ (3) Å
$c = 11.510$ (1) Å
$\alpha = 76.31$ (1)°
$\beta = 72.18$ (1)°
$\gamma = 64.14$ (2)°
$V = 987.0$ (4) Å$^3$
$Z = 2$

$D_x = 1.23$ Mg m$^{-3}$
$D_m = 1.22$ Mg m$^{-3}$
$D_m$ measured by flotation
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 20 reflections
$\theta = 10\text{-}20°$
$\mu = 0.657$ mm$^{-1}$
$T = 295$ K
Needle
0.2 × 0.2 × 0.15 mm
Yellow

### *Data collection*

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3755 measured reflections
3523 independent reflections
2955 observed reflections $[I > 3\sigma(I)]$

$R_{\text{int}} = 0.011$
$\theta_{\text{max}} = 70°$
$h = 0 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity variation: 1.2%

### *Refinement*

Refinement on $F$
$R = 0.058$
$wR = 0.073$
$S = 0.574$
2955 reflections
351 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.0352F^2]$
$(\Delta/\sigma)_{\text{max}} = 0.002$
$\Delta\rho_{\text{max}} = 0.186$ e Å$^{-3}$
$\Delta\rho_{\text{min}} = -0.338$ e Å$^{-3}$
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\text{eq}}$ |
|---|---|---|---|---|
| C1 | 0.2543 (2) | 0.6866 (2) | 0.0244 (1) | 0.0478 (9) |
| C2 | 0.1511 (2) | 0.7599 (2) | −0.0571 (1) | 0.0490 (8) |
| C3 | 0.1407 (2) | 0.8919 (2) | −0.1108 (1) | 0.0512 (8) |
| C4 | 0.2334 (2) | 0.9490 (2) | −0.0849 (1) | 0.0516 (8) |
| C5 | 0.3327 (2) | 0.8789 (2) | −0.0018 (1) | 0.0518 (9) |
| C6 | 0.3430 (2) | 0.7480 (2) | 0.0538 (1) | 0.0499 (8) |
| O7 | 0.2630 (2) | 0.5587 (1) | 0.0756 (1) | 0.0592 (9) |
| N8 | 0.2254 (2) | 1.0849 (2) | −0.1451 (1) | 0.0623 (9) |
| O9 | 0.3158 (2) | 1.1319 (2) | −0.1284 (1) | 0.0788 (9) |
| O10 | 0.1281 (2) | 1.1514 (2) | −0.2115 (2) | 0.0876 (9) |
| C11 | 0.4554 (2) | 0.6663 (2) | 0.1407 (2) | 0.0572 (8) |
| N12 | 0.3888 (2) | 0.5770 (1) | 0.2392 (1) | 0.0498 (9) |
| C13 | 0.5150 (2) | 0.4732 (2) | 0.3029 (2) | 0.0620 (9) |
| C14 | 0.4480 (2) | 0.3813 (2) | 0.4014 (2) | 0.0668 (9) |
| N15 | 0.3078 (2) | 0.4614 (2) | 0.4899 (1) | 0.0596 (9) |
| C16 | 0.1825 (2) | 0.5595 (2) | 0.4251 (2) | 0.0583 (8) |
| C17 | 0.2471 (2) | 0.6568 (2) | 0.3285 (1) | 0.0564 (8) |
| C18 | 0.2446 (3) | 0.3707 (2) | 0.5862 (2) | 0.0774 (14) |
| C19 | 0.0498 (2) | 0.6935 (2) | −0.0783 (1) | 0.0544 (9) |
| N20 | −0.0485 (2) | 0.7793 (1) | −0.1663 (1) | 0.0513 (9) |
| C21 | −0.1879 (2) | 0.7443 (2) | −0.1531 (2) | 0.0667 (8) |
| C22 | −0.2942 (2) | 0.8474 (3) | −0.2365 (2) | 0.0771 (11) |
| N23 | −0.2035 (2) | 0.8456 (2) | −0.3646 (2) | 0.0695 (8) |
| C24 | −0.0590 (3) | 0.8727 (2) | −0.3785 (2) | 0.0665 (9) |
| C25 | 0.0459 (2) | 0.7693 (2) | −0.2931 (1) | 0.0572 (9) |
| C26 | −0.3049 (4) | 0.9479 (3) | −0.4454 (3) | 0.1106 (18) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| C1—C2 | 1.406 (2) | N12—C17 | 1.464 (2) |
| C1—C6 | 1.414 (3) | C13—C14 | 1.494 (3) |
| C1—O7 | 1.340 (2) | C14—N15 | 1.454 (2) |
| C2—C3 | 1.382 (3) | N15—C16 | 1.460 (2) |
| C2—C19 | 1.512 (3) | N15—C18 | 1.457 (3) |
| C3—C4 | 1.390 (3) | C16—C17 | 1.513 (3) |
| C4—C5 | 1.393 (2) | C19—N20 | 1.454 (2) |
| C4—N8 | 1.443 (3) | N20—C21 | 1.467 (3) |
| C5—C6 | 1.377 (3) | N20—C25 | 1.458 (2) |
| C6—C11 | 1.518 (3) | C21—C22 | 1.504 (3) |
| N8—O9 | 1.237 (3) | C22—N23 | 1.459 (3) |
| N8—O10 | 1.235 (3) | N23—C24 | 1.461 (4) |
| C11—N12 | 1.474 (2) | N23—C26 | 1.457 (4) |
| N12—C13 | 1.475 (2) | C24—C25 | 1.513 (3) |
| C6—C1—O7 | 121.1 (2) | C13—N12—C17 | 109.9 (1) |
| C2—C1—O7 | 118.2 (2) | N12—C13—C14 | 111.0 (2) |
| C2—C1—C6 | 120.7 (2) | C13—C14—N15 | 111.6 (2) |
| C1—C2—C19 | 118.5 (2) | C14—N15—C18 | 111.1 (2) |
| C1—C2—C3 | 119.0 (2) | C14—N15—C16 | 108.8 (2) |
| C3—C2—C19 | 122.4 (2) | C16—N15—C18 | 110.6 (2) |
| C2—C3—C4 | 119.8 (2) | N15—C16—C17 | 110.3 (2) |
| C3—C4—N8 | 119.0 (2) | N12—C17—C16 | 110.0 (1) |
| C3—C4—C5 | 121.7 (2) | C2—C19—N20 | 112.7 (2) |
| C5—C4—N8 | 119.3 (2) | C19—N20—C25 | 112.4 (1) |
| C4—C5—C6 | 119.3 (2) | C19—N20—C21 | 112.4 (1) |
| C1—C6—C5 | 119.4 (2) | C21—N20—C25 | 108.3 (2) |
| C5—C6—C11 | 120.7 (2) | N20—C21—C22 | 109.4 (2) |
| C1—C6—C11 | 119.8 (2) | C21—C22—N23 | 111.0 (2) |
| C4—N8—O10 | 119.2 (2) | C22—N23—C26 | 111.1 (2) |
| C4—N8—O9 | 119.1 (2) | C22—N23—C24 | 109.9 (2) |
| O9—N8—O10 | 121.8 (2) | C24—N23—C26 | 110.1 (2) |
| C6—C11—N12 | 111.8 (2) | N23—C24—C25 | 110.8 (2) |
| C11—N12—C17 | 112.6 (1) | N20—C25—C24 | 109.5 (1) |
| C11—N12—C13 | 111.0 (2) | | |
| C1—C2—C19—N20 | −178.9 (2) | N12—C13—C14—N15 | −57.1 (2) |
| C3—C2—C19—N20 | 3.9 (3) | C13—C14—N15—C16 | 58.7 (2) |
| C1—C6—C11—N12 | −36.0 (3) | C14—N15—C16—C17 | −59.9 (2) |
| C5—C6—C11—N12 | 147.4 (2) | N15—C16—C17—N12 | 60.1 (2) |
| C3—C4—N8—O10 | 5.0 (3) | C21—N20—C25—C24 | 61.5 (2) |
| C3—C4—N8—O9 | −175.3 (3) | C25—N20—C21—C22 | −61.8 (2) |
| C5—C4—N8—O9 | 5.2 (3) | N20—C21—C22—N23 | 59.8 (3) |
| C5—C4—N8—O10 | −174.5 (3) | C21—C22—N23—C24 | −56.4 (3) |
| C13—N12—C17—C16 | −57.0 (2) | C22—N23—C24—C25 | 56.1 (3) |
| C17—N12—C13—C14 | 55.6 (2) | N23—C24—C25—N20 | −59.4 (2) |

Cell refinement and data reduction: *SDP* (Frenz, 1978). Program used to solve structure: *SHELXS*86 (Sheldrick, 1986). Program used to refine structure: *SHELX*76 (Sheldrick, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983). Program used to plot diagrams: *PLUTO* (Motherwell & Clegg, 1978). Computers used: VAX 730 and MicroVAX II.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and geometry, least-squares-planes data and torsion angles, and a stereoview of the packing in the unit cell have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71672 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1054]

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# (5-Chloro-1,3-benzoxazol-2-ylthio)-acetonitrile

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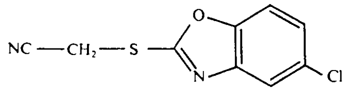
## Abstract

(5-Chloro-1,3-benzoxazol-2-ylthio)acetonitrile, $C_9H_5ClN_2OS$, was obtained by the reaction of chloroacetonitrile with 5-chloro-2-mercaptobenzoxazole. The structure of the title compound was indicated by IR, $^1$H NMR and $^{13}$C NMR spectra, and confirmed by an X-ray analysis. The cyanomethyl group is bonded to the benzoxazole ring through the S atom. The starting compound reacts in the thiol form. Intermolecular bonding includes C—H···N hydrogen bonds.

## Comment

Benzoxazole-2-thione (2-mercaptobenzoxazole) exhibits two tautomeric forms (Seidel, 1980). As a result of this prototropic ability, nucleophilic attack of an alkyl halide on the 2-mercaptobenzoxazole could occur at either the N or the S atom, depending upon whether the molecule existed in the thiol or the thione form. Therefore, mixtures of S-substituted and N-substituted benzoxazole derivatives have generally been reported (Desai, Hunter & Khalidi, 1934; Katz & Cohen, 1954).

The present investigation has been undertaken in order to determine the structure of the reactive tautomeric form. The title compound (I) was synthesized by the reaction of chloroacetonitrile with 5-chloro-2-mercaptobenzoxazole (Arçay, Şafak & Abbasoğlu, 1992). NMR spectral data are given in the *Experimental*. A long-range correlation was observed between the methylene protons ($\delta = 4.10$) and the atom C(1) ($\delta = 162.3$) in the two-dimensional $^1$H and $^{13}$C heteronuclear long-range COSY experiments. This finding is in agreement with the literature (Pretsch, Clerc, Seibl & Simon, 1981). It can be seen from this observation that the cyanomethyl group is bonded to the benzoxazole ring through the S atom as shown in Fig. 1. This is confirmed by the X-ray analysis. Consequently, the starting compound reacts in the thiol form in this synthesis. According to the values of the related angles (Table 2), the linear chain formed by the atoms C(8), C(9) and N(2) is linked with the planar 5-chloro-2-benzoxazolylthio moiety so that the



(I)

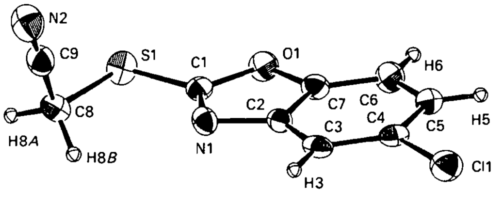


Fig. 1. A view of the molecule showing the labelling of the atoms. Displacement ellipsoids are shown at 50% probability levels.

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