

References

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1,3-Bis(2-methylphenyl)-2-(4-morpholino)-isothiourea

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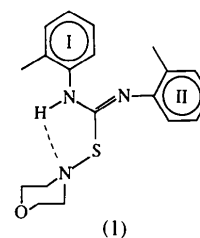
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Abstract

The title molecule, C₁₉H₂₃N₃OS, consists of two aromatic rings and a morpholine ring attached to an isothiourea moiety. The morpholine ring adopts a chair conformation and the sum of the angles around the N atom is 337.5 (2)°. The molecular conformation is stabilized by an intramolecular N—H···N hydrogen bond.

Comment

The molecular conformation and atomic numbering scheme of the title compound, (1), are shown in Fig. 1. We have previously reported the crystal structures of related compounds (Sudha, Senthil Selvan, Subramanian, Steiner, Koellner, Srinivasan & Ramdas, 1995*a,b*).



The morpholine ring in (1) is in a chair conformation. A survey of structures with morpholine rings shows wide variability of the N-atom pyramidality, with the sum of the angles at the N atom ranging from 336 to 359° (Wong-Ng, Nyburg, Awwal, Jankie & Kresge, 1982). In the present case, the sum of the angles at N(12) is 337.5 (2)°. The morpholine ring is oriented in such a way that the N(12) lone pair can accept an intramolecular hydrogen bond from the N(8)—H group [N···N 2.724 (3) and H···N 2.07 Å; Fig. 1 and Table 3]. To achieve this favourable intramolecular interaction, the torsion angle N(8)—C(9)—S(11)—N(12) has a value of -1.0 (2)°, while the best planes of the isothiourea and morpholino groups are almost perpendicular to one another [dihedral angle 88.6 (1)°]. The geometry around the S atom is normal [N—S 1.708 (2), C—S 1.801 (3) Å and N—S—C 101.2 (1)°].

The two aromatic rings have very different orientations. Ring II is almost perpendicular to the isothiourea moiety [angle between least-squares planes 85.2 (1)°], thereby avoiding short intramolecular contacts. This is the geometry that we have typically observed in related compounds (Sudha *et al.*, 1995*a,b*). Ring I, however, is located almost in the isothiourea plane [angle between least-squares planes 15.9 (2)°; torsion angles C(2)—C(1)—N(8)—C(9) 171.1 (2) and C(1)—N(8)—C(9)—N(10) -7.5 (4)°]. This leads to an unusually short intramolecular C(6)—H···N(10) contact, with H···N

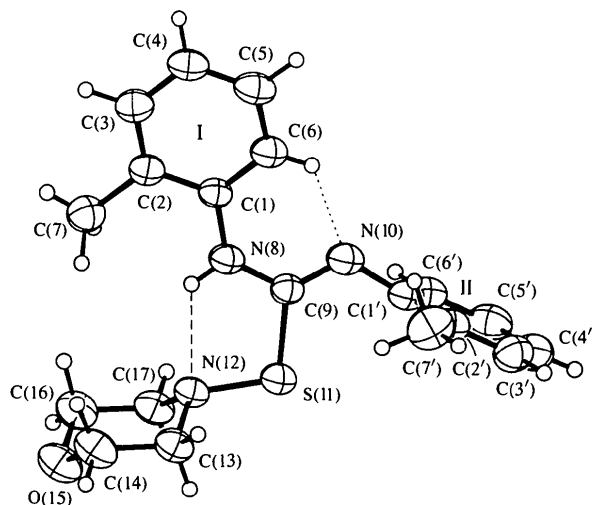


Fig. 1. The molecular structure and atomic numbering scheme of (1). Displacement ellipsoids are shown at the 30% probability level.

2.24 Å (Fig. 1 and Table 3), which is associated with appreciable widening of the angle at N(8) [129.3 (2)°]. The orientation of ring I is somewhat surprising because it is sterically free to avoid the strain at N(8) by rotation out of the isothiourea plane.

The packing of the molecules in the unit cell is shown in Fig. 2. The packing forces are almost entirely of the van der Waals type.

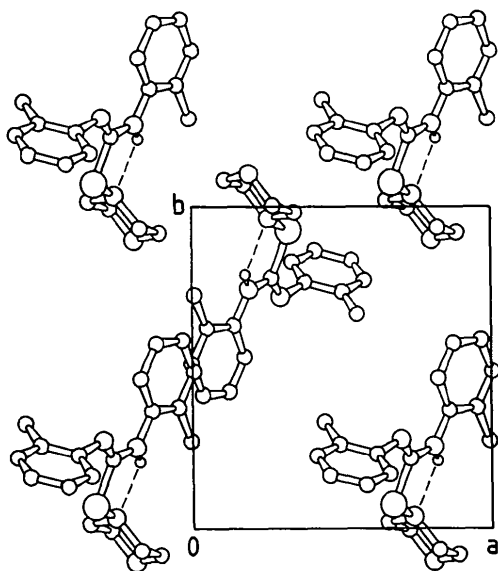


Fig. 2. The crystal packing scheme projected along the *c* axis. For clarity, only the section between $z/c = 0$ and $z/c = \frac{1}{2}$ is shown. H atoms have been omitted, except for the H(N8) atom which is involved in an intramolecular hydrogen bond.

Experimental

The title compound was synthesized and supplied by the SPIC Science Foundation, Madras, India. The density D_m was measured by flotation in KI/water solution.

Crystal data

C₁₉H₂₃N₃O₅

$M_r = 341.5$

Monoclinic

$P2_1/c$

$a = 11.773 (3) \text{ \AA}$

$b = 11.408 (1) \text{ \AA}$

$c = 14.830 (3) \text{ \AA}$

$\beta = 112.32 (2)^\circ$

$V = 1842.5 (6) \text{ \AA}^3$

$Z = 4$

$D_x = 1.23 \text{ Mg m}^{-3}$

$D_m = 1.25 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.54184 \text{ \AA}$

Cell parameters from 19 reflections

$\theta = 22\text{--}48^\circ$

$\mu = 1.63 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Prismatic

$0.6 \times 0.4 \times 0.4 \text{ mm}$

Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

ω – θ scans

Absorption correction: none

$R_{\text{int}} = 0.026$

$\theta_{\text{max}} = 59.9^\circ$

$h = -13 \rightarrow 12$

$k = 0 \rightarrow 12$

$l = 0 \rightarrow 16$

2850 measured reflections
2727 independent reflections
2683 observed reflections
[$I > 2\sigma(I)$]

Refinement

Refinement on F^2

$R(F) = 0.058$

$wR(F^2) = 0.141$

$S = 1.138$

2727 reflections

309 parameters

Only H-atom U 's refined

3 standard reflections
frequency: 60 min
intensity decay: 12%

$w = 1/[\sigma^2(F_o^2) + (0.0932P)^2 + 0.1615P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *SHELXL93*

(Sheldrick, 1993)

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

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^* \cdot \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(1)	0.8613 (2)	0.3683 (2)	0.6590 (2)	0.056 (1)
C(2)	0.9520 (2)	0.3783 (2)	0.6200 (2)	0.060 (1)
C(3)	1.0033 (3)	0.4880 (2)	0.6200 (2)	0.070 (1)
C(4)	0.9662 (3)	0.5859 (3)	0.6556 (2)	0.077 (1)
C(5)	0.8763 (3)	0.5750 (2)	0.6925 (2)	0.077 (1)
C(6)	0.8244 (3)	0.4666 (2)	0.6950 (2)	0.069 (1)
C(7)	0.9942 (3)	0.2744 (3)	0.5790 (3)	0.075 (1)
C(1')	0.6185 (2)	0.2334 (2)	0.7990 (2)	0.062 (1)
C(2')	0.4945 (3)	0.2637 (2)	0.7571 (2)	0.072 (1)
C(3')	0.4189 (3)	0.2279 (3)	0.8042 (3)	0.085 (1)
C(4')	0.4619 (3)	0.1656 (3)	0.8889 (2)	0.086 (1)
C(5')	0.5834 (3)	0.1364 (3)	0.9301 (2)	0.087 (1)
C(6')	0.6620 (3)	0.1698 (3)	0.8847 (2)	0.076 (1)
C(7')	0.4444 (5)	0.3328 (5)	0.6648 (4)	0.108 (1)
N(8)	0.8089 (2)	0.2567 (2)	0.6569 (2)	0.062 (1)
C(9)	0.7317 (2)	0.2201 (2)	0.6995 (2)	0.059 (1)
N(10)	0.7013 (2)	0.2795 (2)	0.7589 (2)	0.071 (1)
S(11)	0.6739 (1)	0.0736 (1)	0.6665 (1)	0.065 (1)
N(12)	0.7416 (2)	0.0360 (2)	0.5871 (1)	0.060 (1)
C(13)	0.6548 (3)	0.0182 (3)	0.4863 (2)	0.074 (1)
C(14)	0.7255 (4)	−0.0037 (3)	0.4221 (2)	0.087 (1)
O(15)	0.8054 (2)	−0.1011 (2)	0.4542 (2)	0.091 (1)
C(16)	0.8893 (3)	−0.0809 (3)	0.5509 (2)	0.083 (1)
C(17)	0.8243 (3)	−0.0658 (3)	0.6195 (2)	0.071 (1)

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

C(1)—C(6)	1.381 (4)	C(3')—C(4')	1.363 (5)
C(1)—C(2)	1.399 (3)	C(4')—C(5')	1.367 (5)
C(1)—N(8)	1.410 (3)	C(5')—C(6')	1.388 (4)
C(2)—C(3)	1.389 (4)	N(8)—C(9)	1.355 (3)
C(2)—C(7)	1.501 (4)	C(9)—N(10)	1.267 (3)
C(3)—C(4)	1.375 (4)	C(9)—S(11)	1.801 (3)
C(4)—C(5)	1.370 (4)	S(11)—N(12)	1.708 (2)
C(5)—C(6)	1.387 (4)	N(12)—C(13)	1.470 (4)
C(1')—C(6')	1.382 (4)	N(12)—C(17)	1.473 (3)
C(1')—C(2')	1.396 (4)	C(13)—C(14)	1.504 (4)
C(1')—N(10)	1.421 (3)	C(14)—O(15)	1.416 (4)
C(2')—C(3')	1.385 (4)	O(15)—C(16)	1.418 (4)
C(2')—C(7')	1.494 (5)	C(16)—C(17)	1.497 (4)
C(6)—C(1)—C(2)	119.7 (2)	C(3')—C(4')—C(5')	119.9 (3)
C(6)—C(1)—N(8)	122.8 (2)	C(4')—C(5')—C(6')	119.6 (3)
C(2)—C(1)—N(8)	117.4 (2)	C(1')—C(6')—C(5')	120.5 (3)
C(3)—C(2)—C(1)	118.2 (2)	C(9)—N(8)—C(1)	129.3 (2)
C(3)—C(2)—C(7)	120.1 (2)	N(10)—C(9)—N(8)	125.2 (2)
C(1)—C(2)—C(7)	121.7 (2)	N(10)—C(9)—S(11)	120.6 (2)
C(4)—C(3)—C(2)	122.0 (3)	N(8)—C(9)—S(11)	114.2 (2)
C(5)—C(4)—C(3)	119.1 (3)	C(9)—N(10)—C(1')	120.9 (2)
C(4)—C(5)—C(6)	120.4 (3)	N(12)—S(11)—C(9)	101.2 (1)

C(1)—C(6)—C(5)	120.5 (3)	C(13)—N(12)—C(17)	109.9 (2)
C(6')—C(1')—C(2')	119.9 (2)	C(13)—N(12)—S(11)	114.2 (2)
C(6')—C(1')—N(10)	120.4 (2)	C(17)—N(12)—S(11)	113.4 (2)
C(2')—C(1')—N(10)	119.3 (2)	N(12)—C(13)—C(14)	109.2 (3)
C(3')—C(2')—C(1')	117.8 (3)	O(15)—C(14)—C(13)	112.0 (3)
C(3')—C(2')—C(7')	120.8 (3)	C(14)—O(15)—C(16)	109.4 (2)
C(1')—C(2')—C(7')	121.4 (3)	O(15)—C(16)—C(17)	111.5 (3)
C(4')—C(3')—C(2')	122.3 (3)	N(12)—C(17)—C(16)	108.4 (2)
C(2)—C(1)—N(8)—C(9)	171.1 (2)		
C(6)—C(1)—N(8)—C(9)	-10.6 (4)		
C(1)—N(8)—C(9)—N(10)	-7.5 (4)		
C(1)—N(8)—C(9)—S(11)	173.4 (2)		
N(8)—C(9)—N(10)—C(1')	179.4 (2)		
N(8)—C(9)—S(11)—N(12)	-1.0 (2)		
C(9)—N(10)—C(1')—C(2')	-97.4 (3)		
C(9)—N(10)—C(1')—C(6')	89.6 (3)		
C(9)—S(11)—N(12)—C(13)	-114.4 (2)		
C(9)—S(11)—N(12)—C(17)	118.6 (2)		

Table 3. Parameters of the intramolecular hydrogen bonding (\AA , $^\circ$)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$H_{\text{norm}} \cdots A \uparrow$	$D-H_{\text{norm}} \cdots A$
N(8)—H \cdots N(12)	0.83 (3)	2.18 (3)	2.724 (3)	2.07	119
C(6)—H \cdots N(10)	0.88 (3)	2.35 (3)	2.932 (4)	2.24	120

\uparrow Data for normalized H-atom positions are based on bond lengths of N—H = 1.04 and C—H = 1.09 \AA .

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: KA1178). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,2,6,6-Tetramethylpiperidinium Chloride

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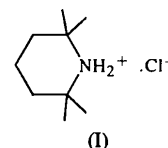
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Abstract

Crystals of 2,2,6,6-tetramethylpiperidinium chloride, $\text{C}_9\text{H}_{20}\text{N}^+\cdot\text{Cl}^-$, crystallized from dichloromethane solution. Hydrogen bonding between the piperidinium and chloride ions [$d(\text{N}-\text{H} \cdots \text{Cl}) = 3.16$ and 3.30\AA] links the units into alternating chains running parallel to the crystallographic b axis.

Comment

We have proposed that the reaction of molybdenum hexacarbonyl with certain bis-dialkylaminophosphine oxides to form cage-like complexes proceeds *via* the elimination of a molecule of the dialkylamine (Wong *et al.*, 1988). We have recently isolated the by-product of one such reaction and characterized it as its hydrochloride salt, (I).



2,2,6,6-Tetramethylpiperidinium chloride crystallized from dichloromethane solution as small prisms. The molecular structure is shown in Fig. 1. The coordinates of the N—H protons were refined using a fixed isotropic displacement parameter, while all other protons were refined using a fixed riding model.

The structure shows the expected deviations from idealized cyclohexane geometry seen in other structures containing this cation (Johnson, Polborn & Noth, 1991;

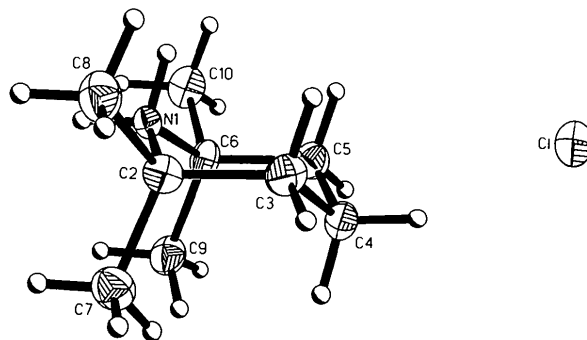


Fig. 1. Molecular structure of 2,2,6,6-tetramethylpiperidinium chloride showing 50% probability ellipsoids.