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1-Cyclohexyl-5-cyclohexylaminotetrazole

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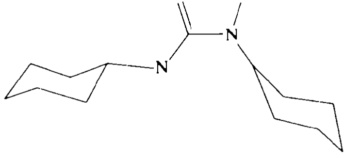
Abstract

The title compound, $C_{13}H_{23}N_5$, consists of a planar tetrazole moiety and two cyclohexane rings substituted equatorially. Both cyclohexane rings adopt the chair conformation. The two cyclohexane rings are inclined to the mean plane of the tetrazole ring at 52.9 (1) and 70.1 (1)° and are at an angle of 74.5 (1)° with each other. N—H···N and C—H···N hydrogen bonds join the molecules in chains running along the *a* axis.

Comment

A rather small number of structures with a tetrazole ring has been described earlier (Gallardo *et al.*, 1997; Destro & Soave, 1995). Tetrazole derivatives have potential affinities for angiotensin II receptor antagonistic activity (Sung-eun *et al.*, 1997; Terukage *et al.*, 1997). They acts as acids and as nucleophilic catalysts in pyrophosphate bond formation (Valentin & Chi-Huey, 1997). Tetrazole compounds are used in the preparation of explosives (Duke, 1971; Bryden, 1958). The X-ray structure determination of the title compound, (I), was carried out in order to establish the conformation of the tetrazole moiety with respect to cyclohexane rings and also to study the nature of the hydrogen-bond formation in the crystalline state.



(I)

The tetrazole ring can be described in terms of electron-density delocalization around the ring. The N4—N5 distance is clearly a double bond, significantly shorter than the N1—N5 and N3—N4 single bonds (Table 1). These values are consistent with those observed previously for the tetrazole ring (Duke, 1971; Rogers *et al.*, 1991). Using the criteria of Burke-Laing & Laing (1976), the sum of bond orders over the three N—N bonds is nearly four, as expected. Evidently, subtle differences between these molecules result in different degrees of electron delocalization in the sensitive tetrazole ring. It is clear that electron delocalization occurs over these bonds and involves the N6 atom as well. Thus the tetrazole ring can be described in terms of electron-density delocalization around the whole ring (Gowda *et al.*, 1984; Steel, 1996).

Steric repulsion between the substituents is reflected in the asymmetry of the exocyclic angles C2—N1—C13, N1—C2—N6, N5—N1—C13 and N3—C2—N6 (see Table). The five endocyclic tetrazole angles average to 108° (Rogers *et al.*, 1991). Bonds at N6 exhibit a significant pyramidalization and this is indicative that N6 is involved in π-conjugation with the ring. The molecule contains two equatorially substituted cyclohexane rings adopting chair conformations, with torsion-angle magnitudes agreeing closely with related structures (Gauthier *et al.*, 1997). The Cremer & Pople (1975) total puckering amplitudes, Q_T, are: 0.570 (2)

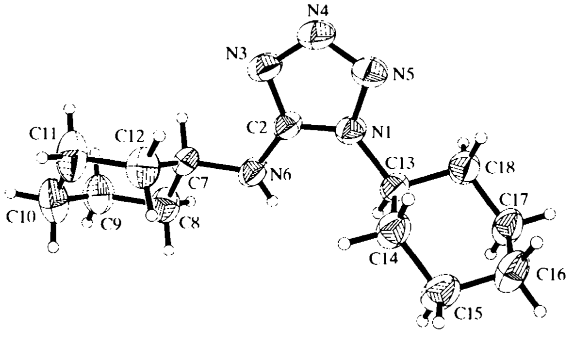


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids and the atom-labelling scheme.

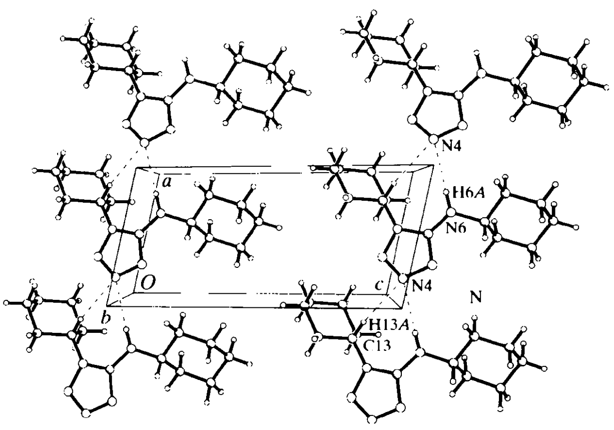


Fig. 2. A view of the molecular packing and the intermolecular hydrogen bonding, viewed down the *b* axis.

and 0.568 (2) Å for rings *A* (C7–C12) and *B* (C13–C18), respectively.

The two cyclohexane rings are inclined to the plane of the tetrazole ring by 52.9 (1) (ring *A*) and 70.1 (1)° (ring *B*), while they form an angle of 74.5 (1)° with each other. The N6 atom is involved in an N—H···N hydrogen bond with N4 of an adjacent tetrazole ring that, together with a C13—H···N4 interaction (Table 2), joins the molecules in chains running along the *a* axis as shown in Fig. 2.

Experimental

A mixture of azido acetamide (1 g, 5.5 mmol) and *N*-substituted malcimide (0.91 g, 5.1 mmol) was refluxed in benzene (940 ml) for 4 h. The separated solid was washed using aqueous solution. The final product was recrystallized from an acetone–*N*,*N*-dimethylformamide mixture (0.87 g, 70%).

Crystal data

$C_{13}H_{23}N_5$
$M_r = 249.36$
Triclinic
$P\bar{1}$
$a = 6.039 (2)$ Å
$b = 9.587 (3)$ Å
$c = 12.598 (6)$ Å
$\alpha = 80.32 (3)°$
$\beta = 77.51 (2)°$
$\gamma = 89.48 (3)°$
$V = 701.7 (5)$ Å^3
$Z = 2$
$D_x = 1.180$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3270 reflections
$\theta = 1.37–33.22°$
$\mu = 0.075$ mm^{-1}
$T = 293 (2)$ K
Block
0.38 × 0.28 × 0.12 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
4162 measured reflections
2707 independent reflections

2057 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\rm max} = 26°$
$h = -6 \rightarrow 7$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.156$
$S = 1.021$
2707 reflections
255 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.1001P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.207$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.215$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C2	1.344 (2)	C2—N6	1.348 (2)
N1—N5	1.366 (2)	N3—N4	1.356 (2)
N1—C13	1.469 (2)	N4—N5	1.292 (2)
C2—N3	1.331 (2)	N6—C7	1.463 (2)
C2—N1—N5	108.2 (1)	N1—C2—N6	126.1 (1)
C2—N1—C13	129.3 (1)	C2—N3—N4	105.5 (1)
N5—N1—C13	121.9 (1)	N5—N4—N3	111.9 (1)
N3—C2—N1	108.5 (1)	N4—N5—N1	105.8 (1)
N3—C2—N6	125.4 (1)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6*A*···N4$^{\rm i}$	0.87 (2)	2.32 (2)	3.185 (2)	170 (2)
C13—H13*A*···N4$^{\rm i}$	0.95 (2)	2.56 (2)	3.494 (3)	167 (2)

Symmetry code: (i) $x - 1, y, z$.

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was −35°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1996). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1380). Services for accessing these data are described at the back of the journal.

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4-(Phenothiazin-10-yl)benzene-1,2-dicarbonitrile

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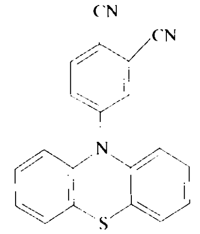
Abstract

The title compound, $C_{20}H_{11}N_3S$, crystallizes with two molecules in the asymmetric unit. The molecules are non-planar, with a central ring in a boat conformation. The dihedral angle between the least-squares planes of the benzo rings fused to the central ring is 44.6 (1)° in one molecule, and 50.1 (1)° in the other.

Comment

The title compound, (I), was isolated as a reaction intermediate in the preparation of a phthalocyanine (Şaşmaz & Ağar, 1999). For many years, phthalocyanines have attracted great interest in various research fields such as chemical sensors, electrochromism, batteries, photodynamic therapy, semiconductive materials, liquid crystals and nonlinear optics (Moser & Thomas, 1983; Leznoff & Lever, 1989–1993).



(I)

In compound (I) there are two independent molecules in the asymmetric unit. In both molecules the bond lengths and angles show normal values and are comparable to 1-isopropyl-10-methylphenothiazine (Shirley *et al.*, 1984). The benzo and phenyl rings are nearly planar in each case, with a maximum deviation of −0.021 (2) Å for C19*A*. In molecule *A*, the folding angle between the least-squares planes of the two benzo

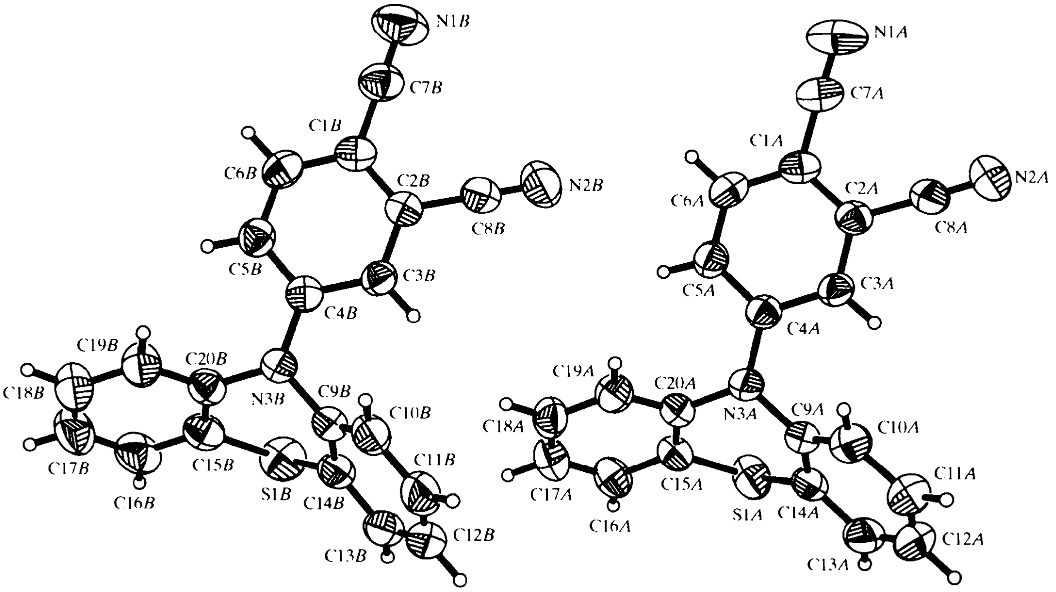


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

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