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1-Cyclohexyl-3-phenylthiourea

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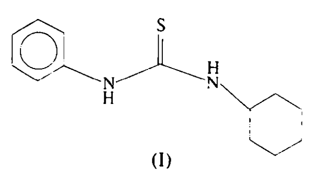
Abstract

The cyclohexane ring in the title compound, $C_{13}H_{18}N_2S$, is in a chair conformation. The molecule adopts a *cis–trans* configuration with respect to the thiourea moiety. The molecules are linked by N—H···S intermolecular hydrogen bonds in the crystal lattice to form two-dimensional layers parallel to the *bc* plane.

Comment

Unsymmetrically substituted thioureas are found to exhibit agrochemical properties (Sarkis & Faisal, 1985). The title compound, (I), was synthesized in view of its agrochemical importance (Ramadas, Srinivasan & Janarthanan, 1993). The crystal structure determination of this compound forms part of our studies on a series of thiourea derivatives. We are interested in the solid-state conformation of these molecules and the nature of the N—H···S hydrogen bonds present in these compounds.



(I)

Fig. 1 shows the displacement ellipsoid plot of the molecule of (I) with the numbering scheme. The bond lengths and angles observed in this structure are normal and comparable to those of 1-cyclohexyl-3-(2-tolyl)-thiourea [(II); Ramnathan *et al.*, 1995*a*]. The dihedral angle between the planes of the thiourea moiety and the phenyl ring is 56.1 (1)°.

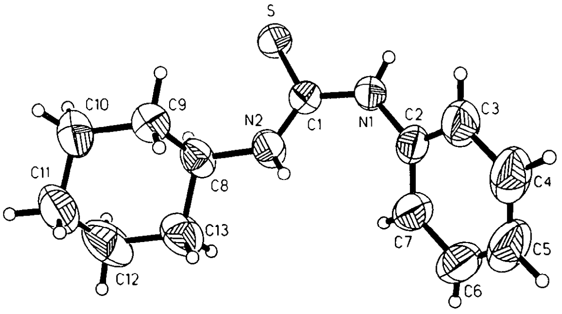


Fig. 1. A 50% probability displacement ellipsoid plot of molecule (I) with the atomic numbering scheme.

The two substituent groups (phenyl and cyclohexyl) are oriented in a *cis–trans* configuration with respect to the C=S bond. So far, the *cis–cis* configuration has been observed in both (II) and 1,3-diphenylthiourea (Ramnathan *et al.*, 1995*b*). Contrary to our expectation that molecule (II), with the methyl group in an *ortho* position (C7), would prefer the *cis–trans* configuration and molecule (I) the *cis–cis* configuration, the results turn out be the other way around. The phenyl groups of the two molecules are oriented in exactly opposite directions and the cyclohexane ring is rotated about the N2—C8 bond by nearly 10° for the two molecules; the torsion angles S—C1—N1—C2, C1—N2—C8—C9 and C1—N2—C8—C13 are −168.5 (2), −90.3 (2) and 146.6 (2)°, respectively, for (I), and −0.4 (2), −79.3 (2) and 157.3 (2)°, respectively, for (II). The *cis–trans* and *cis–cis* configurations show major differences in the N1—C1—N2 and S—C1—N1 angles, while the S—C1—N2 angle is unchanged; N1—C1—N2 is 117.3 (2) for (I) and 114.6 (1)° for (II), and S—C1—N1 is 119.1 (1) for (I) and 121.8 (1)° for (II). The molecules are more linear in the *cis–cis* configuration than in the *cis–trans* configuration. The packing of molecules of (I) in the crystal lattice is shown in Fig. 2.

The molecules of the title compound, (I), are connected by intermolecular N—H···S hydrogen bonds; one [N1···S^{i} 3.536 (2) Å, N1—H1···S^{i} 160 (2)°] forms dimers around the centre of inversion and the other

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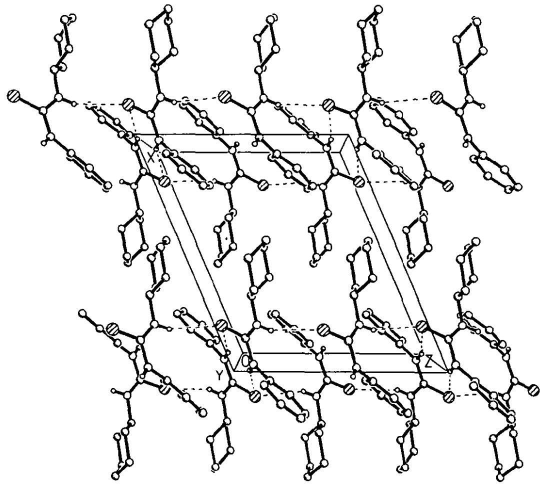

Fig. 2. A packing diagram of molecule (I).

[N2···S^{ii} 3.689 (2) Å, N2—H2···S^{ii} 159 (2)°] links the glide-related molecules in a chain along the *c* axis [symmetry codes: (i) $-x, -y, -z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$]. As a result, two-dimensional layers of the molecules are formed parallel to the *bc* plane. We have observed that among the thiourea compounds having a *cis–trans* configuration, the N—H···S hydrogen bond leading to the formation of dimers (N1—H1···S) is always stronger than the other (N2—H2···S). The present investigation further strengthens this view.

In the *cis–trans* configuration, N—H···S hydrogen bonds form a two-dimensional layer, but in the case of the *cis–cis* configuration, N—H···S hydrogen bonds form one-dimensional chains.

Experimental

Single crystals suitable for X-ray study were obtained by slow evaporation of an ethanol solution of the title compound.

Crystal data

$C_{13}H_{18}N_2S$
$M_r = 234.35$
Monoclinic
$P2_1/c$
$a = 12.163 (1)$ Å
$b = 11.359 (1)$ Å
$c = 10.309 (2)$ Å
$\beta = 113.58 (1)°$
$V = 1305.4 (3)$ Å^3
$Z = 4$
$D_x = 1.192$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8–15°$
$\mu = 0.224$ mm^{-1}
$T = 293 (2)$ K
Needle
0.54 × 0.42 × 0.24 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3784 measured reflections
2971 independent reflections
2211 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0246$

$\theta_{max} = 27.5°$
$h = -15 \rightarrow 14$
$k = -14 \rightarrow 1$
$l = -1 \rightarrow 13$
3 standard reflections monitored every 97 reflections
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0442$
$wR(F^2) = 0.1273$
$S = 1.021$
2971 reflections
217 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0789P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.287$ e Å^{-3}
$\Delta\rho_{min} = -0.156$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
S	0.16883 (4)	0.09363 (4)	−0.00100 (4)	0.0522 (2)
N1	0.00289 (13)	0.16813 (14)	0.0823 (2)	0.0560 (4)
N2	0.18300 (13)	0.26354 (14)	0.1847 (2)	0.0549 (4)
C1	0.11678 (14)	0.18164 (14)	0.0949 (2)	0.0453 (4)
C2	−0.06457 (14)	0.2434 (2)	0.1330 (2)	0.0553 (4)
C3	−0.1318 (2)	0.1934 (2)	0.1985 (3)	0.0729 (6)
C4	−0.2047 (2)	0.2642 (3)	0.2409 (3)	0.0908 (8)
C5	−0.2108 (2)	0.3823 (3)	0.2154 (3)	0.1012 (11)
C6	−0.1445 (2)	0.4332 (3)	0.1501 (3)	0.0894 (9)
C7	−0.0721 (2)	0.3631 (2)	0.1037 (3)	0.0709 (6)
C8	0.3101 (2)	0.2857 (2)	0.2173 (2)	0.0542 (4)
C9	0.3894 (2)	0.2129 (2)	0.3406 (3)	0.0697 (5)
C10	0.5219 (2)	0.2361 (3)	0.3757 (5)	0.0970 (9)
C11	0.5520 (2)	0.3631 (3)	0.4033 (4)	0.0889 (8)
C12	0.4742 (3)	0.4379 (3)	0.2855 (4)	0.0964 (9)
C13	0.3385 (2)	0.4165 (2)	0.2462 (3)	0.0772 (6)

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

S—C1	1.696 (2)	N2—C1	1.332 (2)
N1—C1	1.347 (2)	N2—C8	1.466 (2)
N1—C2	1.421 (2)		
C1—N1—C2	128.2 (2)	C3—C2—N1	118.5 (2)
C1—N2—C8	124.63 (14)	C7—C2—N1	120.5 (2)
N2—C1—N1	117.33 (15)	N2—C8—C9	111.2 (2)
N2—C1—S	123.62 (12)	N2—C8—C13	110.3 (2)
N1—C1—S	119.05 (13)		

The structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from difference maps and refined isotropically.

Data collection: *XSCANS* (Fait, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93. Geometric calculations: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1207). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Rigid Bis-Bidentate Bridging Ligand: 1,4-Bis(2,2′-bipyrid-4-yl)benzene

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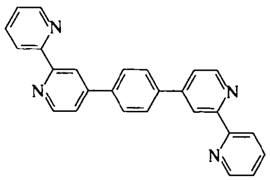
Abstract

The title compound, $C_{26}H_{18}N_4$, possesses crystallographically imposed centrosymmetry. The bipyridyl moieties adopt an *anti* conformation and have a torsion angle of 24.3 (1)° with respect to the attached benzene ring.

Comment

Polymetallic Ru^{II}–diimine complexes are efficient sensitizers for large-band-gap semiconductors and photoelectrochemical cells constructed from these sensitized electrodes exhibit very high incident photon-to-current efficiencies (Bard & Fox, 1995; Pechy *et al.*, 1995; Nazeeruddin *et al.*, 1993; O'Regan & Grätzel, 1991; Bignozzi, Argazzi, Indelli & Scandola, 1994; Meyer *et al.*, 1994; Amadelli, Argazzi, Bignozzi & Scandola, 1990). As a result, this class of sensitized electrodes offers a promising approach to the development of active solar-energy conversion devices. A key feature in these systems is the ease of migration of energy from the absorbing metal center to that attached to the semiconductor surface. We have found recently that in $[(bpy)_2Ru(\mu\text{-bphb})Ru(tpy)(CN)](PF_6)_3$ [bpy is 2,2′-bipyridyl, bphb is 1,4-bis(2,2′-bipyrid-4-yl)benzene, (1), and tpy is 2,2′,6′,2″-terpyridyl] energy transfer from the $\{(bpy)_2Ru(bphb)\}$ chromophore to the tpy-containing chromophore is 100% efficient even in frozen matrices at 20 K, implying that a nearly activationless intramolecular electronic energy migration occurs (Liang, Baba & Schmehl, 1995). In order to evaluate electronic coupling more thoroughly in bimetallic complexes bridged by the bphb ligand in light of recent theoretical work on the extent of electronic coupling through adjacent aromatic ring systems (Cave, Marcus & Sidars, 1986), the structure of bphb was determined.



(1)

Compound (1) possesses crystallographically imposed centrosymmetry and therefore the bipyridyl moieties adopt an *anti* conformation about the central benzene ring. Additionally, the two rings of the bipyridyl unit have an *anti* conformation. These two rings show a dihedral angle of 6.5 (4)° between their planes, while that between the benzene ring and the attached pyridyl ring is 24.3 (1)°. This latter angle is within the range considered to favor efficient energy migration between linked aromatic rings (Cave, Marcus & Sidars, 1986) and while a comparable angle would not necessarily be adopted by a bphb-bridged bimetallic complex, it is clear that there are no structural features of the bphb ligand itself that would prevent this.

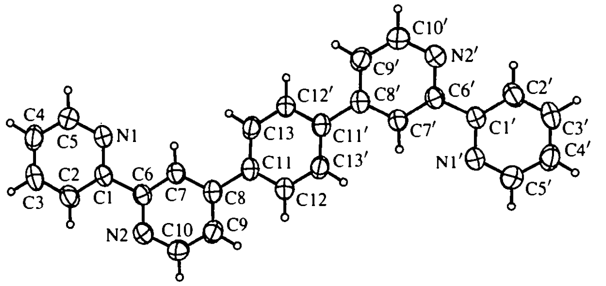


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of compound (1). Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. H atoms are represented by spheres of arbitrary radii.