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5-(2-Chlorophenyl)-4-phenyl-3,4-dihydro-2H-1,2,4-triazole-3-thione

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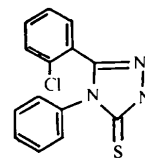
Abstract

The title compound, C₁₄H₁₀ClN₃S, was prepared by the reaction of benzhydrazide and 2-chlorophenyl isothiocyanate. The triazole ring is planar to within 0.003 (2) Å. The dihedral angles between the phenyl rings and the 1,2,4-triazole ring are 59.2(1) and 58.9(1)°. The dihedral angle between the two phenyl rings is 63.7(1)°. The molecules are linked by N—H···S hydrogen bonds.

Comment

Bridging systems based on the 1,2,4-triazole ring are interesting owing to their similarity to the 1,3-imidazole bridging found in the Cu–Zn protein superoxide dismutase (Feiters, 1990). Condensed 1,2,4-triazoles are biologically important compounds (Kottke *et al.*, 1983; Francis *et al.*, 1988). The ability of triazoles to form a bridge between metal ions makes these complexes particularly important for magnetochemistry applications (Groenveeld *et al.*, 1982). The 1,2,4-triazole ring systems are typical planar 6π-electron partially aromatic systems. They possess an extensive chemistry (Temple, 1981; Benson, 1967). 1,2,4-Triazole and its derivatives are starting materials for the synthesis of many heterocycles (Desenko, 1995). Thiosemicarbazones and related compounds with S—C—N linkages display a wide range of biological activities. Metal complexes of these compounds have been synthesized in order to gauge their activity compared with that of the free ligand and to determine the coordination behaviour of the ligand towards the metal (Offiong, 1995; West *et*

al., 1993). Apart from its extensive chemical significance, the 1,2,4-triazole nucleus is also found to be associated with diverse medicinal properties, such as analgesic, anti-asthmatic, diuretic, antifungal and anti-inflammatory activities (Mohamed *et al.*, 1993). Knowledge of the molecular structure of these compounds is important for understanding their reactivity under condensation reaction conditions. Therefore, the crystal structure analysis of the title compound, (I), was undertaken.



(I)

The structure of (I) (Fig. 1) consists of one 1,2,4-triazole-3-thione moiety with two benzene rings substituted at N1 (ring A) and C2 (ring B). The C=S bond length [1.6781 (18) Å] agrees with literature values (Allen *et al.*, 1987; Sen *et al.*, 1996). The triazole ring is planar and the maximum deviation observed is –0.003 (2) Å for atom N3. The S atom is also located in the plane. The C14—C11 bond length [1.734 (2) Å] conforms with those found in 3,5-bis(2-pyridyl)-4-*p*-chlorophenyl-4*H*-1,2,4-triazole (Wang *et al.*, 1998). The Cl atom deviates by 0.127 (1) Å from the mean plane of the phenyl ring B. The average bond lengths and angles in ring A are 1.380 (3) Å and 120.0 (2)°; similarly, the average bond lengths and angles in ring B are 1.381 (3) Å and 120.0 (2)°. The orientation of the 1,2,4-triazole ring with respect to the two phenyl rings is given by the torsion angles C2—N1—C3—C8 = –125.3 (2), C1—N1—C3—C4 = –117.6 (2), N2—C2—C9—C14 = –120.4 (2) and N1—C2—C9—C10 = –120.3 (2)°. The

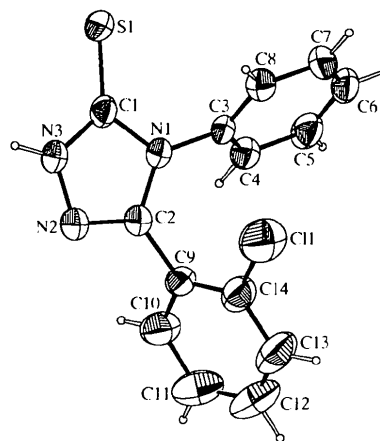


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of an arbitrary radius.

phenyl rings are inclined at an angle of 63.7(1)° with respect to each other.

In the crystal, the molecules of (I) form chains *via* intermolecular N3—H(N3)···S¹ hydrogen bonds, characterized by H···S 2.42(2) Å and N—H···S 176(2)° [symmetry code: (i) $-x, 1-y, -z$].

Experimental

A mixture of benzhydrazide (1.4 g, 0.01 mol) and 2-chlorophenyl isothiocyanate (1.7 g, 0.01 mol) was refluxed in NaOH solution (8 g, 100 ml) for 5 h, then cooled and filtered and the filtrate washed with ether. The aqueous layer was acidified with cold dilute HCl. The resulting solid was filtered and washed with water to give the title compound [yield 59%; m.p. 495–497 K (EtOH)] (Jayanthi *et al.*, 1997).

Crystal data

C₁₄H₁₀ClN₃S

$M_r = 287.76$

Triclinic

$P\bar{1}$

$a = 6.9675(1) \text{ \AA}$

$b = 9.5232(2) \text{ \AA}$

$c = 11.0979(3) \text{ \AA}$

$\alpha = 97.556(1)^\circ$

$\beta = 104.298(1)^\circ$

$\gamma = 95.403(1)^\circ$

$V = 701.20(3) \text{ \AA}^3$

$Z = 2$

$D_x = 1.363 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 39 reflections

$\theta = 5.38\text{--}12.51^\circ$

$\mu = 0.410 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Square

$0.52 \times 0.36 \times 0.32 \text{ mm}$

Colourless

Data collection

Siemens P4 diffractometer

$\theta/2\theta$ scans

Absorption correction: none

4570 measured reflections

3099 independent reflections

2554 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\text{max}} = 27.5^\circ$

$h = -9 \rightarrow 8$

$k = -9 \rightarrow 12$

$l = -14 \rightarrow 14$

3 standard reflections

every 97 reflections

frequency: 60 min

intensity decay: <3%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.109$

$S = 1.018$

3099 reflections

176 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 0.2548P]$

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

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

$\Delta\rho_{\text{max}} = 0.350 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.448 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

C1—N1—C2	107.5(1)	N2—C2—N1	111.3(2)
C1—N1—C3	125.5(1)	N2—C2—C9	123.2(2)
C2—N1—C3	126.7(1)	N1—C2—C9	125.4(2)
C2—N2—N3	103.7(1)	C4—C3—N1	118.7(2)
C1—N3—N2	114.2(1)	C8—C3—N1	120.0(2)
N3—C1—N1	103.3(2)	C13—C14—C11	118.8(2)
N3—C1—S1	128.5(1)	C9—C14—C11	120.5(2)
N1—C1—S1	128.2(1)		

The H atom on N3 was located by a difference Fourier synthesis, while the other H atoms were placed at their calculated positions using a riding model. All H atoms were given fixed isotropic U values.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997b). Molecular graphics: ZORTEP (Zsolnai, 1997). Software used to prepare material for publication: SHELXL97 and PARST (Nardelli, 1983, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1044). Services for accessing these data are described at the back of the journal.

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Table 1. Selected geometric parameters (\AA , $^\circ$)

S1—C1	1.6781(18)	N2—C2	1.299(2)
C11—C14	1.734(2)	N2—N3	1.374(2)
N1—C1	1.381(2)	N3—C1	1.332(2)
N1—C2	1.384(2)	C2—C9	1.476(2)
N1—C3	1.439(2)		

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(R)-(+)-2-(4-Chlorophenoxy)propionic acid

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Abstract

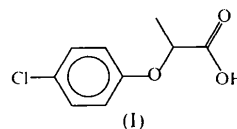
The crystal structure of optically active 2-(4-chlorophenoxy)propionic acid (C₉H₉ClO₃) has been determined. The carboxylic acid group is in an antiplanar conformation and hydrogen bonds along the twofold screw axis link the carboxylic acid groups to form a catemer motif, in contrast to the hydrogen-bonded cyclic dimers observed in the equivalent racemic compound. Also, the weaker intermolecular interactions display significant differences.

Comment

Crystallization of a racemic mixture of the two enantiomers of a chiral compound will most frequently lead to the formation of a racemic compound, *i.e.* crystals with a well defined structure composed of the two enantiomers in equal amounts. More rarely, a spontaneous resolution occurs which leads to a conglomerate of crystals containing the pure enantiomers. In a description of the crystallization habits of racemates, Jacques *et al.* (1981) estimated that racemic compounds were formed in *ca* 90% of cases. The racemic compound can have either a higher or a lower melting point than the pure enantiomer. A recent survey of 1114 racemic and enantiomer pairs indicates that the average melting point of

racemates, T_r , is 402 K, only slightly higher than that of the enantiomers, T_a , which is 399 K. Moreover, the average difference, $T_r - T_a$, is a symmetrical bell-shaped distribution with an s.u. of ± 20 K (Collet, 1998).

The difference in melting point and melting enthalpy between the enantiomer and the equivalent racemic compound is closely linked to differences in their crystal structures. Comparative studies of enantiomers and racemic compounds for a series of related compounds, *e.g.* monofluoro mandelic acids and halogen-substituted 3-hydroxy-3-phenylpropionic acids (Larsen & Marthi, 1997), containing identical functional groups, showed a significant degree of diversity in their hydrogen-bond patterns. From the structural comparisons, it became obvious that weaker interactions, such as C—H...O hydrogen bonds and halogen–hydrogen interactions, should be taken into account to explain the variation in melting behaviour from the structural differences. However, in most of these systems the enantiomer melts at a higher temperature than the racemic compound; therefore, we looked for systems where the racemic compound is the higher melting one. The 2-phenoxypropionic acids were selected, since some of the cases with the largest differences in melting point and melting enthalpy between the racemic compound and the enantiomer are found in these compounds (Gabard & Collet, 1986). In addition, they contain only one functional group that could be expected to take part in the hydrogen bonding, which reduces the number of possible hydrogen-bond patterns. This paper describes the work with (R)-(+)-2-(4-chlorophenoxy)propanoic acid, (I).



Two independent structure determinations have been conducted previously for racemic 2-(4-chlorophenoxy)propionic acid (Kennard *et al.*, 1982; Raghunathan *et al.*, 1982) at room temperature, with a reported melting point of 386 K (Gabard & Collet, 1986). The structure determination for the equivalent enantiomeric compound, with a melting point of 359 K (Gabard & Collet, 1986), should enable us to relate these differences in thermodynamic behaviour to differences between the two crystal structures. The ORTEPII (Johnson, 1976) drawing in Fig. 1 shows 2-(4-chlorophenoxy)propionic acid as found in crystals of the pure enantiomer. The bond lengths and angles listed in Table 1 are virtually identical to those found in the racemic compound (Kennard *et al.*, 1982). All of them agree within 2 s.u., apart from the O7—C8—C9 angle, which displays the largest difference of 4 s.u. The *exo* angles around C1 show the same difference of *ca* 10° that was observed in the racemic compound.