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5-Phenyl-1,3,4-oxadiazole-2(3*H*)-thione

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Key indicators

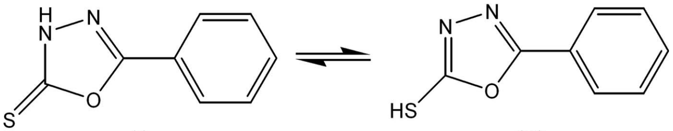
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.002 Å
R factor = 0.040
wR factor = 0.106
Data-to-parameter ratio = 26.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_8H_6N_2OS$, the planar oxadiazole ring is effectively coplanar with the phenyl ring. This facilitates the formation of N—H···S interactions, leading to a thione tautomer in the solid state, and the formation of centrosymmetric dimers.

Comment

Oxadiazole derivatives belong to an important group of heterocyclic compounds and have been the subject of extensive study in recent years. Numerous reports have highlighted their chemistry and their biological and industrial uses (see, for example, Naito *et al.*, 1999; Xu *et al.*, 2000; Eissa, 1998; Holla *et al.*, 2000; Tinperciuc *et al.*, 1999; Potts, 1984; Kulkarni & Rowhani, 1989; Obi *et al.*, 1995). Their capacity to act as a building blocks for the generation of supramolecular architectures associated with diverse biological activities increases their manifold applications.



(I) (II)

Owing to the presence of the NHC=S group, the title compound can exhibit thione–thiol tautomerism (Horning & Muchowski, 1972) to give (I) and (II). Although the thiol tautomer is commercially available, an effort was made to crystallize 5-(4-phenyl)-1,3,4-oxadiazole-2(3*H*)-thione. This was accomplished by a ring-closure reaction of the product formed by the reaction of CS_2 and Et_3N with benzoic acid hydrazide (Hoggarth, 1952). A search of the Cambridge Structural Database (Version 5.27, November 2005; Allen, 2002) for related derivatives showed that both a thione (Ziyaev *et al.*, 1992) and a thiol derivative (Qiu & Xu, 2004) have been structurally characterized. However, the title compound has not been structurally characterized.

The title compound adopts tautomeric form (I), as shown in Fig. 1. The molecule as a whole is almost planar, since the dihedral angle between the two rings is 6.93 (2)°. Comparison of C=S and C=N bond lengths with earlier reports containing similar systems (Öztürk *et al.*, 2004; Du *et al.*, 2004; Ziyaev *et al.*, 1992; Qiu & Xu, 2004) confirms a high degree of delocalization in the 1,3,4-oxadiazole-2-thione ring. The planarity, π-electron delocalization and some intermolecular interactions contribute to stabilize the structure.

The observed tautomeric form allows for an intermolecular hydrogen-bonding interaction, as shown in Fig. 2 and Table 2.

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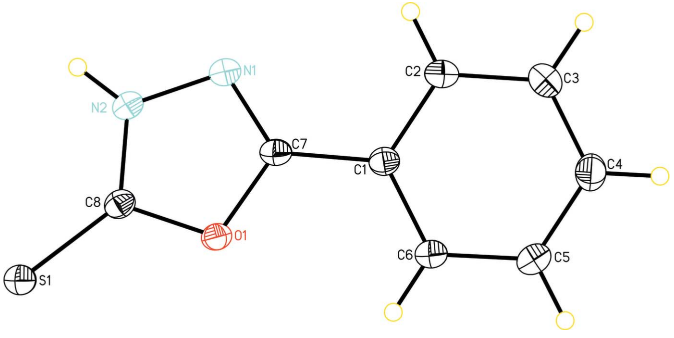

Figure 1
The molecular structure of (I), with atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii.

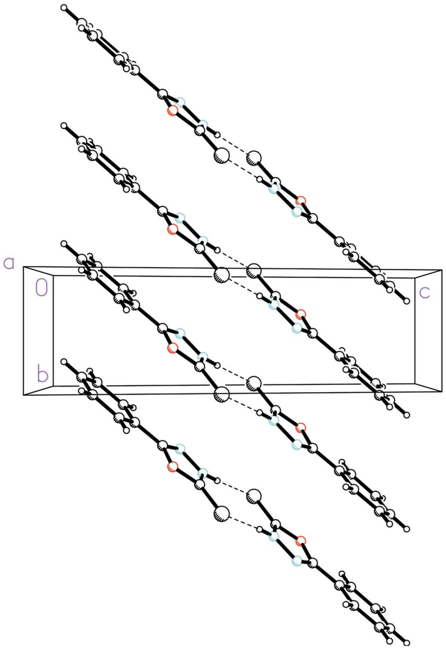

Figure 2
A projection of the crystal packing of (I), down the *a* axis. Hydrogen bonds are indicated as dashed lines.

The molecules at (x, y, z) and ($1 - x$, $-y$, $2 - z$) are linked by N—H···S bonds forming centrosymmetric dimers in a fashion similar to that observed by Dinçer *et al.* (2005) in 4-amino-5-(2-hydroxyphenyl)-2*H*-1,2,4-triazole-3(4*H*)-thione, generating an $R_2^2(8)$ ring (Grell *et al.*, 2002). The crystal packing is reinforced by a weak intermolecular π–π interaction involving the *S*-oxadiazole ring system at a centroid-to-centroid distance of 3.479 Å, forming chains along the *b* axis.

Experimental

Compound (I) was synthesized by the reaction of CS_2 (0.93 ml, 0.014 mmol) with a suspension of benzoic acid hydrazide (2 g, 0.014 mmol) in chloroform (20 ml) in the presence of Et_3N (2 ml, 0.014 mmol). After stirring the reaction mixture for 3 h, the resulting solution was filtered and acidified with acetic acid (5 ml, 20% *v*/*v*). On evaporation of the solvent, the solid obtained was washed twice with an ethanol–water mixture (1:4) and finally dried *in vacuo*. Single crystals of (I) (m.p. 486 K) suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution over a period of 4 d (yield 1.94 g, 86%). IR (KBr, ν, cm^{-1}): 3108 (–NH), 1610 (C═N), 1145 (–C═S); ^1H NMR (DMSO-d_6, TMS, δ, p.p.m.): 13.56 (*s*, 1H, NH), 8.55–7.25 (*m*, 5H, phenyl); ^{13}C NMR (DMSO-d_6, TMS, δ, p.p.m.): 131.48 (C1), 128.68 (C2, C6), 125.29 (C3, C5), 121.73 (C4), 159.72 (C7), 176.74 (C8). The IR and NMR data confirm the presence of the thione tautomer in the solid state as well as in solution.

Crystal data

$C_8H_6N_2OS$
$M_r = 178.21$
Monoclinic, $P2_1/n$
$a = 11.3414$ (15) Å
$b = 4.6589$ (16) Å
$c = 16.0242$ (7) Å
$\beta = 103.845$ (5)°
$V = 822.1$ (3) Å^3

$Z = 4$
$D_x = 1.440$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 0.34$ mm^{-1}
$T = 298$ (2) K
Plate, colourless
0.79 × 0.23 × 0.07 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.775$, $T_{max} = 0.977$

12966 measured reflections
2888 independent reflections
2386 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 30.7°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.106$
$S = 1.01$
2888 reflections
110 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Table 1
Selected bond lengths (Å).

S1—C8	1.6574 (15)	C7—N1	1.2850 (19)
O1—C8	1.3672 (16)	C8—N2	1.3281 (17)
O1—C7	1.3739 (16)	N1—N2	1.3761 (18)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*B*···S1^i	0.86	2.44	3.2907 (13)	173

Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.

The crystal was a two-component twin. The data were processed using two orientation matrices corresponding to the two twin components. The structure was solved using only non-overlapping reflections, but all reflections were used in the refinement with a scale factor for each component [0.670 (1) for the major component]. All H atoms were initially located in a difference Fourier map. The C—H distances were then constrained to an ideal geometry (0.93 Å) with $U_{iso}(H) = 1.2U_{eq}(C)$. The N—H distances were idealized, with an N—H distance of 0.86 Å and with $U_{iso}(H) = 1.2U_{eq}(N)$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure:

SHELXTL (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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