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1-[(4-Nitrophenoxy)acetyl]-3-(5-thioxo-4,5-dihydro-1,3,4-thiadiazolin-2-yl)urea dimethylformamide solvate

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Key indicators

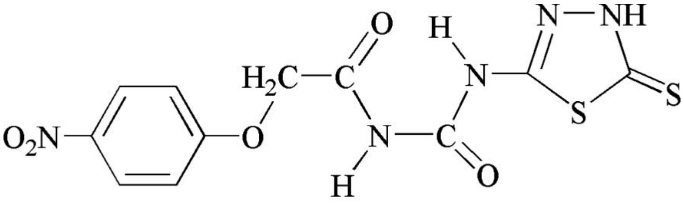
Single-crystal X-ray study
T = 292 K
Mean σ(C–C) = 0.005 Å
R factor = 0.047
wR factor = 0.131
Data-to-parameter ratio = 12.8

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

In the title compound, $C_{11}H_9N_5O_5S_2{\cdot}C_3H_7NO$, the urea scaffold, which adopts a planar configuration mediated by intramolecular N—H···O hydrogen bonds, is nearly coplanar with the thiadiazole ring and the benzene ring. Intermolecular paired N—H···N hydrogen bonds result in the formation of an $R_2^2(6)$ motif. Intermolecular π–π stacking interactions are also present.

Comment

1,3,4-Thiadiazole derivatives are known to display a broad spectrum of pesticidal activity (Nakagawa *et al.*, 1996; Wang *et al.*, 2004). Aroyl ureas have been reported to possess diverse biological effects, such as insecticidal, fungicidal, herbicidal and plant growth regulating activities (Wang *et al.*, 1998; Zhang *et al.*, 2005). In an extensive search for new plant growth regulators, compounds incorporating both the 1,3,4-thiadiazole nucleus and aroyl urea groups have been synthesized in our laboratory, including the title compound, (I). The crystal structure of (I) has been investigated by X-ray diffraction as part of our ongoing structural studies of this class (Song, Tan *et al.*, 2005; Song, Zhang *et al.*, 2005) and to provide a basis for consideration of stereochemical structure–activity relationships.



(I)

The asymmetric unit of the crystal structure contains a solvent molecule of dimethylformamide (DMF; Fig. 1). The acyl urea scaffold is essentially planar for the formation of intramolecular N—H···O hydrogen bonds, thus assuming the most stable configuration. The molecule is nearly planar, the dihedral angle formed by the thiadiazole ring with the benzene ring being 7.3 (1)°. Bond lengths and angles in (I) are as expected (Table 1). In the crystal structure, two neighbouring molecules are linked by complementary N—H···N hydrogen bonds into an $R_2^2(6)$ motif in a head-to-head manner, as shown in Fig. 2. Also present are π–π stacking interactions (Fig. 2) between thiadiazole and benzene rings. The interplanar spacing is 3.655 (2) Å, the centroid-to-centroid separation is 3.874 (2) Å and the centroid offset is 1.284 (2) Å.

Experimental

The required 2-amino-5-mercapto-1,3,4-thiadiazole was prepared by addition cyclocondensation of thiosemicarbazide and carbon disulfide according to a literature method (Wang *et al.*, 1999). The title compound was then synthesized according to the procedure of Wang *et al.* (2003). Suitable crystals for the X-ray analysis were obtained by slow evaporation of an acetone–DMF (3:1) solution at room temperature (m.p. 510–511 K). IR (KBr, cm^{-1}): ν 3339, 3081, 1724, 1706, 1602, 1256; ^{1}H NMR (DMSO-d_6): δ 14.15 (*s*, 1H), 11.40 (*s*, 1H), 11.07 (*s*, 1H), 8.22–7.10 (*m*, 4H), 4.93 (*s*, 2H). Analysis calculated for $C_{11}H_9N_5O_5S_2$: C 37.18, H 2.55, N 19.71%; found: C 36.97, H 2.73, N 19.82%.

Crystal data

$C_{11}H_9N_5O_5S_2\cdot C_3H_7NO$
$M_r = 428.47$
Triclinic, $P\overline{1}$
$a = 7.9981\ (12)$ Å
$b = 11.3139\ (16)$ Å
$c = 12.0232\ (17)$ Å
$\alpha = 68.893\ (2)^\circ$
$\beta = 70.744\ (2)^\circ$
$\gamma = 70.897\ (2)^\circ$
$V = 931.0\ (2)$ Å^3
$Z = 2$
$D_x = 1.528$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1691 reflections
$\theta = 2.4$–27.5°
$\mu = 0.33$ mm^{-1}
$T = 292\ (2)$ K
Block, yellow
0.20 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.936$, $T_{\max} = 0.936$
4982 measured reflections
3253 independent reflections
2384 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.051$
$\theta_{\max} = 25.0^\circ$
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 13$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.131$
$S = 1.02$
3253 reflections
255 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2 + 0.0083P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C8—O4	1.216 (3)	C10—N3	1.374 (3)
C8—N2	1.364 (3)	C10—S1	1.736 (3)
C9—O5	1.205 (3)	C11—N5	1.335 (3)
C9—N3	1.356 (3)	C11—S2	1.656 (3)
C9—N2	1.389 (3)	C11—S1	1.740 (3)
C10—N4	1.282 (3)	N4—N5	1.370 (3)
O3—C7—C8	110.7 (2)	S2—C11—S1	126.19 (17)
O4—C8—N2	124.2 (3)	O1—N1—O2	122.9 (3)
N2—C8—C7	117.8 (2)	C8—N2—C9	126.9 (2)
O5—C9—N2	121.7 (2)	C10—N4—N5	108.3 (2)
N3—C9—N2	115.2 (2)	C11—N5—N4	119.7 (2)
N4—C10—S1	115.9 (2)	C4—O3—C7	117.8 (2)
N5—C11—S1	107.1 (2)	C10—S1—C11	88.96 (13)
O4—C8—N2—C9	−2.0 (5)	S2—C11—N5—N4	−179.0 (2)
O5—C9—N2—C8	177.5 (3)	C5—C4—O3—C7	4.3 (4)
N2—C9—N3—C10	−177.6 (2)	C8—C7—O3—C4	171.9 (2)
S1—C10—N3—C9	1.2 (4)	S2—C11—S1—C10	179.1 (2)

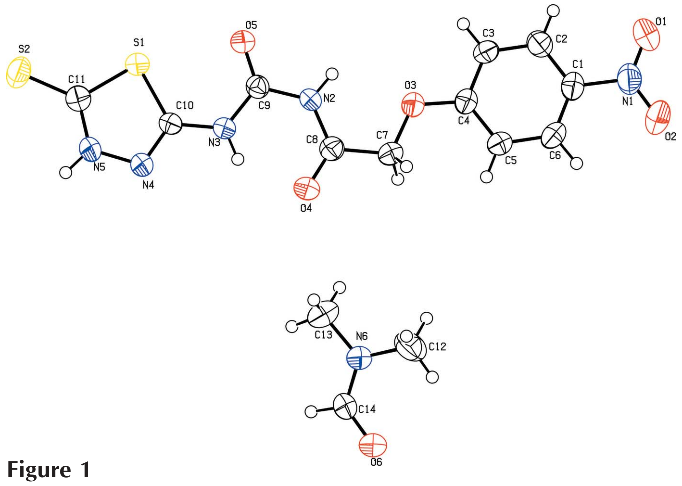


Figure 1
The asymmetric unit of (I), with 50% probability displacement ellipsoids.

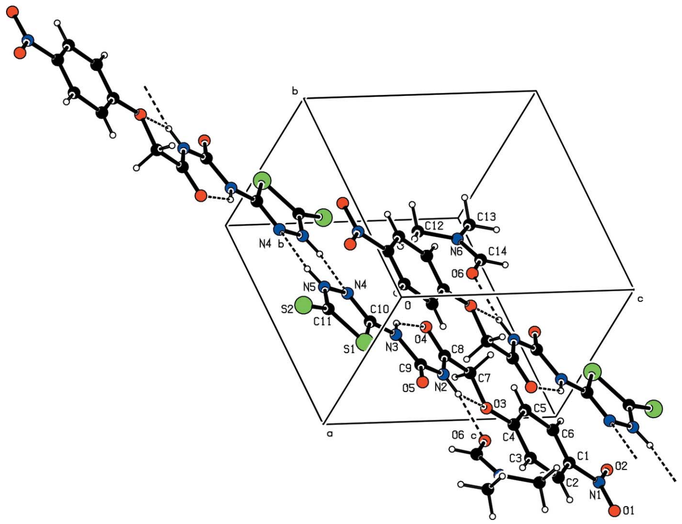


Figure 2
Packing diagram of (I), showing hydrogen bonds (dashed lines) and π–π stacking interactions [symmetry codes: (*a*) x, y, z; (*b*) $1 - x, 1 - y, -z$; (*c*) $1 - x, -y, 1 - z$].

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O6$^{\text{i}}$	0.86	2.02	2.852 (3)	162
N5—H5A···N4$^{\text{ii}}$	0.86	2.30	2.991 (3)	137
N2—H2A···O3	0.86	2.23	2.652 (3)	110
N3—H3A···O4	0.86	1.91	2.601 (3)	136

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + 1, -y + 1, -z + 2$.

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with C—H distances of 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, but each group was allowed to rotate freely about its C—C bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å for aromatic and aldehyde H, C—H = 0.97 Å for methylene H, N—H = 0.86 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

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structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL*.

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