Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(*E*)-Methyl 1,3-thiazol-2-yl ketone 2,4-dinitrophenylhydrazone

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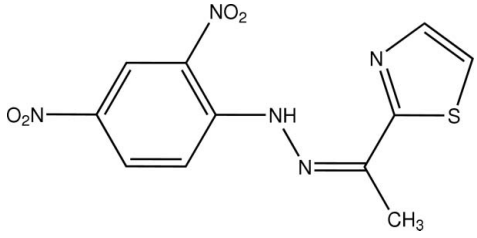
Received 16 May 2008; accepted 21 May 2008

Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.120; data-to-parameter ratio = 15.3.

Crystals of the title compound, $C_{11}H_9N_5O_4S$, were obtained from a condensation reaction of 2,4-dinitrophenylhydrazine and methyl 1,3-thiazol-2-yl ketone. Excluding two methyl H atoms, the molecule displays a planar structure, the dihedral angle between the terminal thiazole and benzene rings being 1.82 (8)°. The imino group links with adjacent nitro and thiazole groups by intramolecular bifurcated hydrogen bonding. The centroid–centroid separation of 3.7273 (11) Å between nearly parallel benzene and thiazole rings of adjacent molecules indicates the existence of π–π stacking in the crystal structure. Weak intermolecular C—H···O hydrogen bonding is also observed.

Related literature

For general background, see: Okabe *et al.* (1993); Shan *et al.* (2003, 2006). For a related structure, see: Shan *et al.* (2008).



Experimental

Crystal data

$C_{11}H_9N_5O_4S$ M_r = 307.29
Monoclinic, $P2_1/c$
a = 8.0126 (5) Å
b = 7.3239 (4) Å
c = 21.8683 (12) Å
β = 92.610 (2)°
V = 1281.98 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.28 mm^{-1}
T = 295 (2) K
0.46 × 0.42 × 0.36 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Absorption correction: none
12253 measured reflections
2943 independent reflections
1845 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.119
S = 1.11
2943 reflections
192 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O1	0.86	2.03	2.628 (2)	126
N3—H3···N5	0.86	2.03	2.686 (2)	133
C9—H9···O1^{i}	0.93	2.58	3.289 (3)	133

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The work was supported by the Natural Science Foundation of Zhejiang Province, China (No. M203027).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2236).

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supporting information

Acta Cryst. (2008). E**64**, o1156 [doi:10.1107/S1600536808015298]

(*E*)-Methyl 1,3-thiazol-2-yl ketone 2,4-dinitrophenylhydrazone

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S1. Comment

As some phenylhydrazone derivatives have shown to be potentially DNA damaging and mutagenic agents (Okabe *et al.*, 1993), a series of new phenylhydrazone derivatives have been synthesized in our laboratory (Shan *et al.*, 2003; Shan *et al.*, 2006). As part of the ongoing investigation, the title compound has recently been prepared and its crystal structure is reported here.

The molecular structure of the title compound is shown in Fig. 1. The molecule displays a coplanar structure, except methyl H atoms, the dihedral angle between the thiazole and benzene rings being 1.82 (8)°. The N4—C7 bond distance is significantly shorter than N3—N4 and N3—C1 bond distances (Table 1), and indicates the typical C?N double bond. The phenylhydrazone and thiazole are located on the opposite sides of the C?N double bond, the molecule has an E-configuration, similar to that found in a related compound, (E)-2-furlyl methylketone 2,4-dinitrophenylhydrazone (Shan *et al.*, 2008). The imino group links with adjacent nitro and thiazole groups by intra-molecular bifurcated hydrogen bonding (Fig. 1 and Table 2).

A partially overlapped arrangement between nearly parallel benzene ring and thiazole ring of the adjacent molecule is illustrated in Fig. 2. The dihedral angle and centroid-to-centroid separation are 1.82 (8)° and 3.7273 (11) Å, these suggest the existence of π-π stacking between adjacent molecules in the crystal. The crystal structure also contains intermolecular weak C—H···O hydrogen bonding (Table 2).

S2. Experimental

2,4-Dinitrophenylhydrazine (0.4 g, 2 mmol) was dissolved in ethanol (10 ml), and H_2SO_4 solution (98%, 0.5 ml) was slowly added to the ethanol solution with stirring. The solution was heated at 333 K for several min until the solution cleared. 2-Thiazolyl methyl ketone (0.25 g, 2 mmol) was added to the above solution with continuous stirring, and the mixture was refluxed for 30 min. When the solution had cooled to room temperature yellow powder crystals appeared. The powder crystals were separated and washed with water three times. Recrystallization from an absolute ethanol yielded well shaped single crystals.

S3. Refinement

Methyl H atoms were placed in calculated positions with C—H = 0.96 Å and the torsion angle was refined to fit the electron density, U_{iso}(H) = 1.5U_{eq}(C). Other H atoms were placed in calculated positions with C—H = 0.93 and N—H = 0.86 Å, and refined in riding mode with U_{iso}(H) = 1.2U_{eq}(C,*N*).

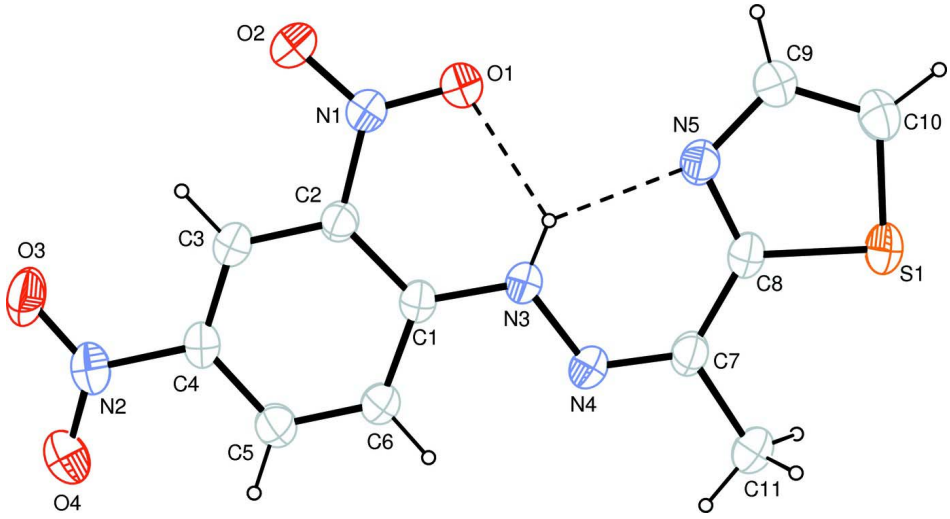

Figure 1

The molecular structure of the title compound with 30% probability displacement ellipsoids for non-H atoms, dashed lines indicate hydrogen bonding.

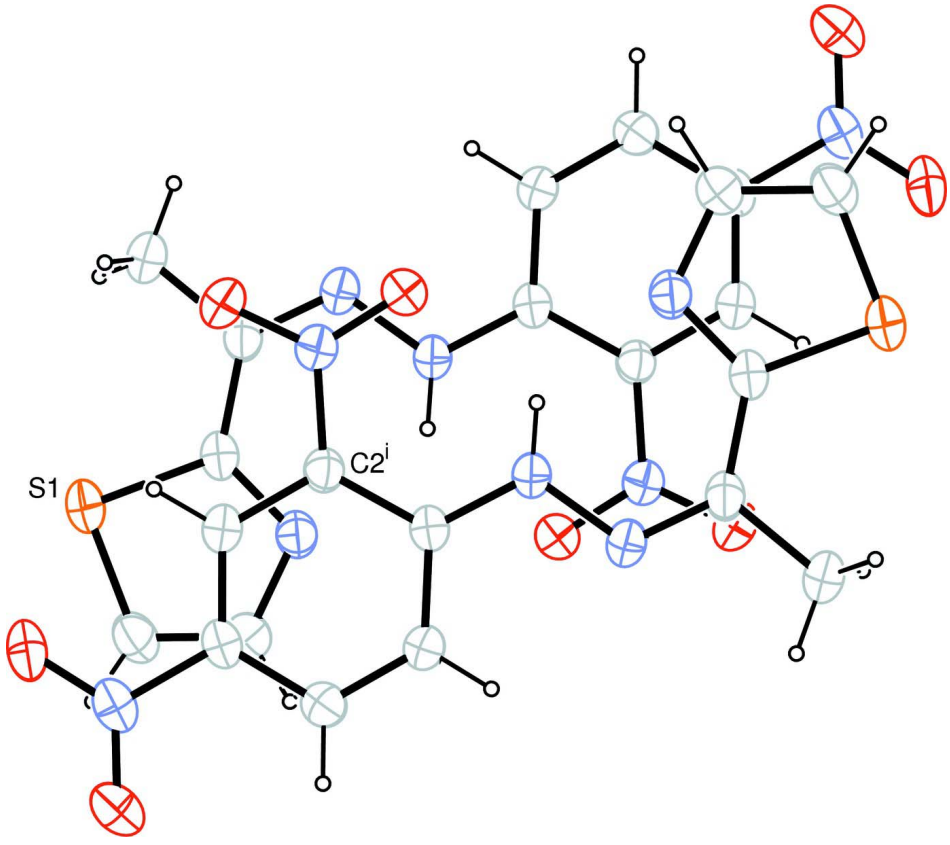

Figure 2

A diagram showing the partially overlapped arrangement of benzene and thiazole rings [symmetry code: (i) 1 - *x*,1 - *y*,1 - *z*].

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Crystal data

$C_{11}H_9N_5O_4S$
$M_r = 307.29$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.0126$ (5) Å
$b = 7.3239$ (4) Å
$c = 21.8683$ (12) Å
$\beta = 92.610$ (2)°
$V = 1281.98$ (13) Å^3
$Z = 4$
$F(000) = 632$
$D_x = 1.592$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5366 reflections
$\theta = 3.1$–25.5°
$\mu = 0.28$ mm^{-1}
$T = 295$ K
Prism, orange
0.46 × 0.42 × 0.36 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.00 pixels mm^{-1}
ω scans
12253 measured reflections
2943 independent reflections
1845 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
$h = -10 \rightarrow 10$
$k = -9 \rightarrow 8$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.119$
$S = 1.11$
2943 reflections
192 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.1169P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.029 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.18922 (7)	0.17161 (8)	0.69372 (2)	0.0610 (2)
N1	0.3851 (2)	0.1710 (2)	0.39844 (7)	0.0550 (4)
N2	0.9262 (2)	0.3699 (2)	0.33512 (8)	0.0614 (5)
N3	0.49462 (19)	0.2538 (2)	0.52598 (6)	0.0488 (4)

H3	0.3946	0.2130	0.5201	0.059*
N4	0.5583 (2)	0.2973 (2)	0.58348 (7)	0.0523 (4)
N5	0.20975 (19)	0.1562 (2)	0.57733 (7)	0.0508 (4)
O1	0.28243 (18)	0.1495 (2)	0.43763 (7)	0.0762 (5)
O2	0.35547 (19)	0.1322 (2)	0.34454 (7)	0.0777 (5)
O3	0.8766 (2)	0.3374 (3)	0.28262 (7)	0.0865 (5)
O4	1.0639 (2)	0.4328 (2)	0.34849 (8)	0.0820 (5)
C1	0.5967 (2)	0.2783 (2)	0.47889 (8)	0.0436 (4)
C2	0.5482 (2)	0.2422 (2)	0.41680 (8)	0.0439 (4)
C3	0.6570 (2)	0.2710 (2)	0.37046 (8)	0.0475 (4)
H3A	0.6232	0.2463	0.3301	0.057*
C4	0.8131 (2)	0.3355 (2)	0.38400 (8)	0.0487 (5)
C5	0.8673 (2)	0.3689 (3)	0.44448 (9)	0.0565 (5)
H5	0.9754	0.4101	0.4534	0.068*
C6	0.7610 (2)	0.3408 (3)	0.49027 (8)	0.0531 (5)
H6	0.7982	0.3638	0.5304	0.064*
C7	0.4663 (2)	0.2727 (3)	0.62965 (8)	0.0498 (4)
C8	0.2965 (2)	0.2023 (2)	0.62794 (8)	0.0469 (4)
C9	0.0559 (3)	0.0960 (3)	0.59096 (9)	0.0571 (5)
H9	−0.0221	0.0579	0.5608	0.069*
C10	0.0226 (3)	0.0947 (3)	0.65099 (10)	0.0622 (5)
H10	−0.0778	0.0568	0.6666	0.075*
C11	0.5480 (3)	0.3213 (3)	0.69085 (9)	0.0675 (6)
H11A	0.6545	0.3770	0.6849	0.101*
H11B	0.5635	0.2127	0.7150	0.101*
H11C	0.4781	0.4052	0.7116	0.101*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0664 (4)	0.0751 (4)	0.0428 (3)	0.0004 (3)	0.0172 (2)	−0.0027 (2)
N1	0.0516 (9)	0.0714 (11)	0.0421 (9)	−0.0039 (8)	0.0013 (7)	0.0003 (8)
N2	0.0643 (11)	0.0655 (11)	0.0558 (11)	−0.0015 (9)	0.0195 (9)	0.0047 (9)
N3	0.0477 (8)	0.0626 (10)	0.0361 (8)	−0.0014 (7)	0.0045 (7)	−0.0016 (7)
N4	0.0549 (10)	0.0648 (10)	0.0371 (8)	−0.0011 (8)	0.0022 (7)	−0.0041 (7)
N5	0.0541 (9)	0.0563 (9)	0.0424 (9)	0.0006 (7)	0.0060 (7)	0.0014 (7)
O1	0.0560 (9)	0.1221 (14)	0.0507 (9)	−0.0217 (8)	0.0066 (7)	−0.0024 (8)
O2	0.0684 (9)	0.1195 (13)	0.0448 (8)	−0.0168 (8)	−0.0027 (7)	−0.0133 (8)
O3	0.0966 (12)	0.1204 (14)	0.0444 (9)	−0.0222 (10)	0.0232 (8)	−0.0015 (9)
O4	0.0623 (10)	0.1066 (13)	0.0786 (11)	−0.0139 (9)	0.0215 (8)	0.0070 (10)
C1	0.0478 (10)	0.0452 (9)	0.0382 (9)	0.0027 (8)	0.0062 (8)	0.0007 (8)
C2	0.0456 (10)	0.0477 (10)	0.0385 (9)	0.0024 (8)	0.0026 (8)	0.0017 (8)
C3	0.0560 (11)	0.0490 (10)	0.0377 (9)	0.0027 (9)	0.0036 (8)	0.0003 (8)
C4	0.0529 (11)	0.0519 (10)	0.0424 (10)	0.0016 (9)	0.0124 (8)	0.0016 (8)
C5	0.0512 (11)	0.0659 (12)	0.0529 (11)	−0.0090 (9)	0.0073 (9)	−0.0066 (10)
C6	0.0510 (11)	0.0671 (12)	0.0412 (10)	−0.0063 (9)	0.0031 (8)	−0.0078 (9)
C7	0.0556 (11)	0.0570 (11)	0.0373 (9)	0.0036 (9)	0.0064 (8)	−0.0005 (8)
C8	0.0548 (11)	0.0487 (10)	0.0379 (9)	0.0054 (8)	0.0088 (8)	0.0017 (8)

C9	0.0526 (11)	0.0641 (12)	0.0551 (12)	−0.0006 (10)	0.0069 (9)	−0.0011 (10)
C10	0.0585 (12)	0.0690 (13)	0.0607 (13)	−0.0011 (10)	0.0186 (10)	−0.0012 (11)
C11	0.0678 (14)	0.0945 (16)	0.0401 (11)	−0.0064 (12)	0.0029 (10)	−0.0083 (10)

Geometric parameters (Å, º)

S1—C10	1.691 (2)	C2—C3	1.383 (2)
S1—C8	1.7239 (19)	C3—C4	1.357 (3)
N1—O1	1.225 (2)	C3—H3A	0.9300
N1—O2	1.225 (2)	C4—C5	1.395 (3)
N1—C2	1.447 (2)	C5—C6	1.359 (3)
N2—O4	1.219 (2)	C5—H5	0.9300
N2—O3	1.221 (2)	C6—H6	0.9300
N2—C4	1.454 (2)	C7—C8	1.454 (3)
N3—C1	1.356 (2)	C7—C11	1.505 (3)
N3—N4	1.373 (2)	C9—C10	1.352 (3)
N3—H3	0.8600	C9—H9	0.9300
N4—C7	1.290 (2)	C10—H10	0.9300
N5—C8	1.324 (2)	C11—H11A	0.9600
N5—C9	1.355 (3)	C11—H11B	0.9600
C1—C6	1.405 (2)	C11—H11C	0.9600
C1—C2	1.420 (2)		
C10—S1—C8	89.63 (10)	C6—C5—C4	119.59 (18)
O1—N1—O2	122.43 (17)	C6—C5—H5	120.2
O1—N1—C2	118.64 (15)	C4—C5—H5	120.2
O2—N1—C2	118.92 (17)	C5—C6—C1	122.14 (17)
O4—N2—O3	123.44 (18)	C5—C6—H6	118.9
O4—N2—C4	118.47 (18)	C1—C6—H6	118.9
O3—N2—C4	118.07 (18)	N4—C7—C8	126.66 (16)
C1—N3—N4	116.93 (15)	N4—C7—C11	114.95 (17)
C1—N3—H3	121.5	C8—C7—C11	118.38 (17)
N4—N3—H3	121.5	N5—C8—C7	124.57 (17)
C7—N4—N3	118.86 (16)	N5—C8—S1	113.67 (14)
C8—N5—C9	110.35 (17)	C7—C8—S1	121.76 (13)
N3—C1—C6	120.08 (16)	C10—C9—N5	115.95 (19)
N3—C1—C2	123.59 (16)	C10—C9—H9	122.0
C6—C1—C2	116.32 (16)	N5—C9—H9	122.0
C3—C2—C1	121.21 (16)	C9—C10—S1	110.40 (16)
C3—C2—N1	116.32 (15)	C9—C10—H10	124.8
C1—C2—N1	122.46 (16)	S1—C10—H10	124.8
C4—C3—C2	119.92 (17)	C7—C11—H11A	109.5
C4—C3—H3A	120.0	C7—C11—H11B	109.5
C2—C3—H3A	120.0	H11A—C11—H11B	109.5
C3—C4—C5	120.79 (18)	C7—C11—H11C	109.5
C3—C4—N2	119.92 (17)	H11A—C11—H11C	109.5
C5—C4—N2	119.30 (18)	H11B—C11—H11C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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