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3-Methyl-4-(4-nitrophenyl)-1-phenyl-1,7-dihydro-6*H*-pyrazolo[3,4-*b*]thiazolo[5,4-e]pyridine-6-thione–dimethylformamide (1/1)

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Key indicators

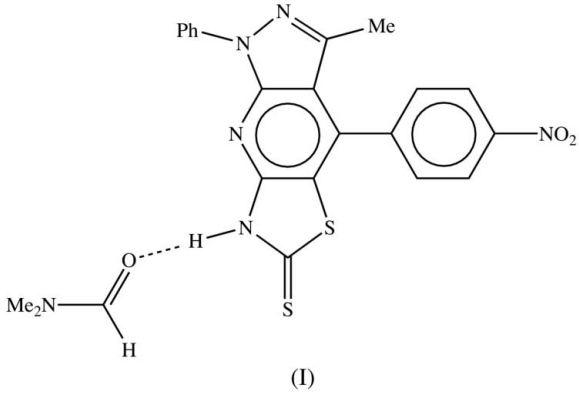
Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.051
wR factor = 0.141
Data-to-parameter ratio = 16.4

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

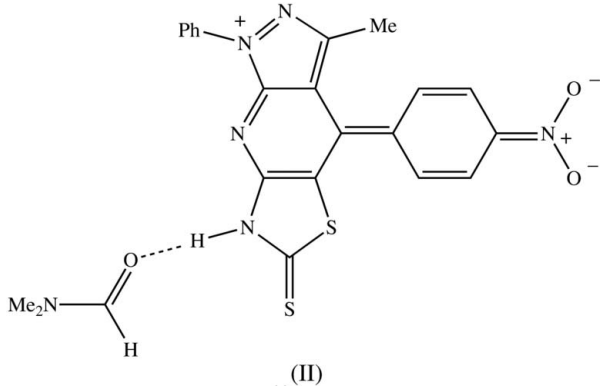
The title compound is a stoichiometric solvate, $C_{20}H_{13}N_5O_2S_2\cdot C_3H_7NO$, in which the two components are linked by an N—H···O hydrogen bond. The heterocyclic molecules are linked into chains by a combination of a C—H···S=C hydrogen bond and a π–π stacking interaction.

Comment

With the aim of preparing new classes of fused thiazolo systems, we have synthesized a novel series of 5-arylmethylene-2-thioxothiazolidin-4-ones (Delgado *et al.*, 2005) as intermediates for cyclocondensation reactions. We report here the structure of 3-methyl-4-(4-nitrophenyl)-1-phenyl-1,7-dihydro-6*H*-pyrazolo[3,4-*b*]thiazolo[5,4-*e*]pyridin-6-thione, formed by the reaction of 5-(4-nitrobenzyliden)-2-thioxothiazolidin-4-one with 5-amino-3-methyl-1-phenylpyrazole, and crystallized as its dimethylformamide solvate, (I).



(I)



(II)

The title compound (Fig. 1) is a stoichiometric solvate in which the two independent components are linked by an almost linear N—H···O hydrogen bond (Table 2).

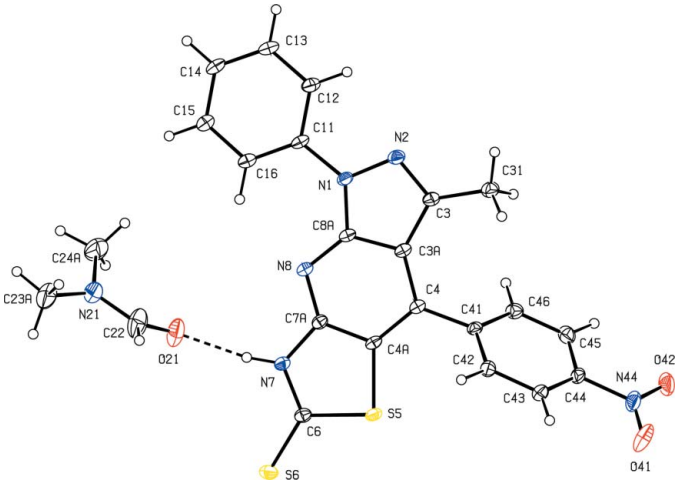


Figure 1
The independent components of (I), showing displacement ellipsoids drawn at the 30% probability level. For the sake of clarity, only the major orientation of the dimethylformamide component is shown, with only one orientation of the methyl groups. The dashed line indicates a hydrogen bond.

Within the heterocyclic component, the bond distances (Table 1) indicate electronic delocalization within the pyridine ring, with strong bond fixation in the pyrazole ring. The dihedral angle between the unsubstituted phenyl ring, C11–C16, and the pyrazole ring is only 6.1 (2)°, and this near planarity may be associated with the two intramolecular C—H···N contacts (Table 2). On the other hand, the nitrated phenyl ring, C41–C46, makes a dihedral angle of 57.7 (2)° with the pyridine ring, thus precluding the development of quinonoid forms such as (II).

There are two weak intermolecular interactions between the heterocyclic molecules, which may be of structural significance. Aryl atom C46 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the thione atom S6 in the molecule at ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$), thereby forming a $C(8)$ (Bernstein *et al.*, 1995) chain running parallel to the [101] direction and generated by the *n*-glide plane at $y = 0.25$ (Fig. 2). This chain is reinforced by a π–π stacking interaction between the unsubstituted phenyl ring in the molecule at (x, y, z) and the pyridine ring in the molecule at ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$); these rings are nearly parallel, with a dihedral angle between them of only 5.8 (2)°. The ring-centroid separation is 3.545 (2) Å and the interplanar spacing is *ca* 3.41 Å, corresponding to a ring-centroid offset of *ca* 0.97 Å. Two [101] chains pass through each unit cell, but there are no direction-specific interactions between adjacent chains.

Experimental

A solution containing equimolar quantities (1 mmol of each component) of 5-amino-3-methyl-1-phenylpyrazole and 5-(4-nitrobenzyliden)-2-thioxothiazolidin-4-one in dimethylformamide (DMF; 3 ml) was heated under reflux for 6 h. The reaction mixture was cooled, and ethanol was added before the combined solvents were removed under reduced pressure. The resulting solid product was recrystallized from DMF to yield **orange** crystals suitable for single-crystal X-ray diffraction. Yield 90%; m.p. 530 K. MS (70 eV) *m*/*z* (%) 421 (13, M^++2); 420 (28, M^++1); 419 (100, M^+); 372 (6).

Crystal data

$C_{20}H_{13}N_5O_2S_2\cdot C_3H_7NO$
$M_r = 492.57$
Monoclinic, $P2_1/n$
$a = 9.3023$ (2) Å
$b = 25.5447$ (7) Å
$c = 10.3794$ (2) Å
$\beta = 113.7660$ (13)°
$V = 2257.25$ (9) Å^3
$Z = 4$
$D_x = 1.449$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5163 reflections
$\theta = 3.4$–27.6°
$\mu = 0.28$ mm^{-1}
$T = 120$ (2) K
Block, yellow
0.62 × 0.44 × 0.22 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.848$, $T_{max} = 0.942$
25526 measured reflections
5163 independent reflections
4088 reflections with $I > 2\sigma(I)$
$R_{int} = 0.004$
$\theta_{max} = 27.6°$
$h = -12 \rightarrow 12$
$k = -32 \rightarrow 33$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.141$
$S = 1.04$
5163 reflections
315 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2 + 2.3558P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.12$ e Å^{-3}
$\Delta\rho_{min} = -0.80$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.383 (3)	N7—C7*A*	1.380 (3)
N2—C3	1.322 (3)	C7*A*—N8	1.328 (3)
C3—C3*A*	1.433 (3)	N8—C8*A*	1.339 (3)
C3*A*—C4	1.408 (3)	C8*A*—N1	1.373 (3)
C4—C4*A*	1.387 (3)	C3*A*—C8*A*	1.412 (3)
C4*A*—S5	1.745 (2)	C4*A*—C7*A*	1.414 (3)
S5—C6	1.749 (2)	C6—S6	1.656 (2)
C6—N7	1.350 (3)		
N2—N1—C11—C12	3.8 (3)	C3*A*—C4—C41—C42	128.2 (2)
C8*A*—N1—C11—C12	−174.1 (2)	C4*A*—C4—C41—C42	−56.1 (3)
N2—N1—C11—C16	−177.4 (2)	C3*A*—C4—C41—C46	−56.6 (3)
C8*A*—N1—C11—C16	4.8 (4)	C4*A*—C4—C41—C46	119.1 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H7···O21	0.88	1.84	2.711 (3)	170
C12—H12···N2	0.95	2.41	2.758 (4)	102
C16—H16···N8	0.95	2.32	2.975 (4)	126
C46—H46···S6^{i}	0.95	2.80	3.743 (3)	176

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

All H atoms were located in difference maps and subsequently treated as riding atoms with C—H = 0.95 (CH) or 0.98 Å (CH_3), and N—H = 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}$(C,N), or $1.5U_{eq}$(C) for the methyl groups. It was apparent from an early stage that the methyl groups of the dimethylformamide component were disordered over two sets of sites, corresponding to two conformations of this molecule. This disorder was modelled using common sites for the N—

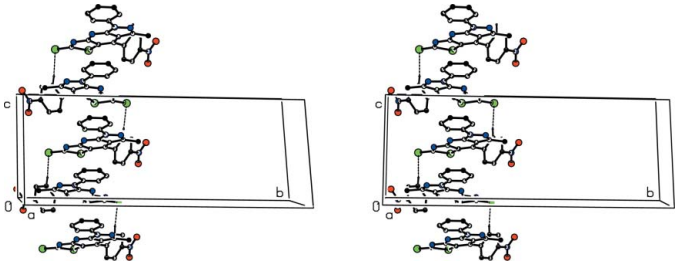


Figure 2
Stereoview of part of the crystal structure of (I), showing the formation of a [101] chain built from C—H···S═C hydrogen bonds (dashed lines) and π–π stacking interactions. For the sake of clarity, the solvent molecules and the H atoms not involved in the motif shown have been omitted.

CHO fragment in the two conformations and two distinct sets of sites for the methyl C atoms; the refined values of the site occupancy factors were 0.598 (8) and 0.402 (8). In addition, it was necessary to model each of the methyl groups using six half-occupancy H-atom sites, offset from one another by 60°. The crystals of (I) were very fragile, and attempts to cut small fragments from larger crystals consistently led to the shattering of the crystals. The highest peak in the difference map is located 1.05 Å from one of the methyl H atoms in the minor orientation of the disordered solvent component.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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