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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

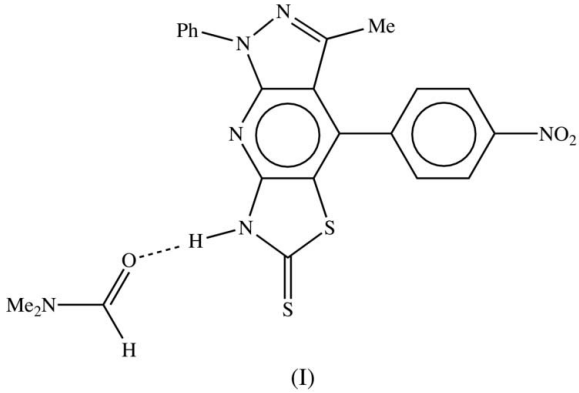
Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.051
wR factor = 0.141
Data-to-parameter ratio = 16.4

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

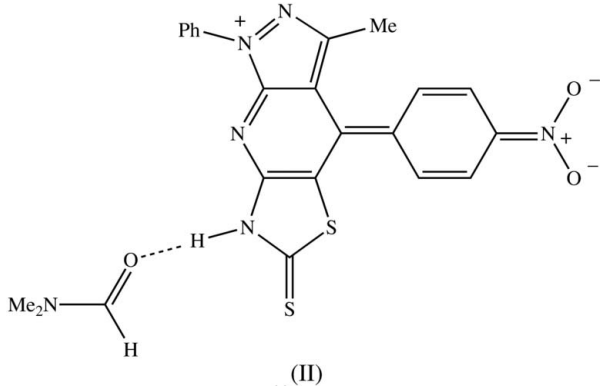
The title compound is a stoichiometric solvate, $C_{20}H_{13}N_5O_2S_2\cdot C_3H_7NO$, in which the two components are linked by an N—H···O hydrogen bond. The heterocyclic molecules are linked into chains by a combination of a C—H···S=C hydrogen bond and a π–π stacking interaction.

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).

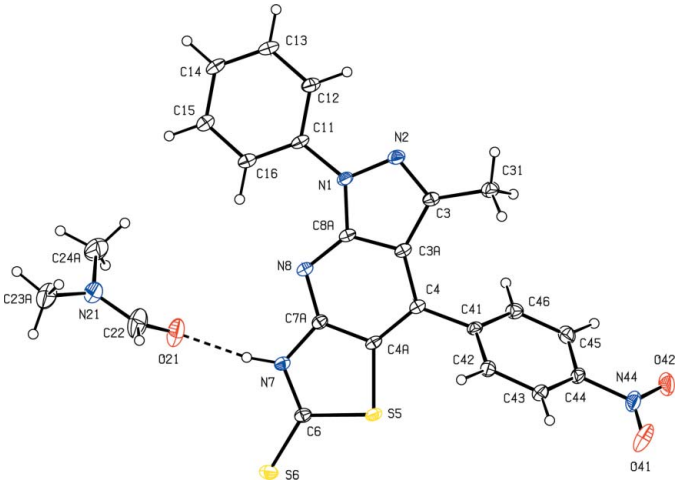


Figure 1
The independent components of (I), showing displacement ellipsoids drawn at the 30% probability level. For the sake of clarity, only the major orientation of the dimethylformamide component is shown, with only one orientation of the methyl groups. The dashed line indicates a hydrogen bond.

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—

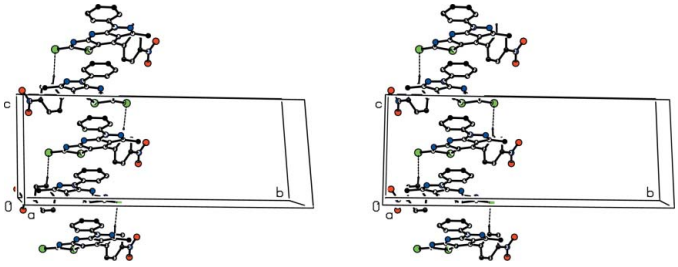


Figure 2
Stereoview of part of the crystal structure of (I), showing the formation of a [101] chain built from C—H···S═C hydrogen bonds (dashed lines) and π–π stacking interactions. For the sake of clarity, the solvent molecules and the H atoms not involved in the motif shown have been omitted.

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).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England. JC thanks the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support. PD and SC thank COLCIENCIAS, UNIVALLE (Universidad del Valle, Colombia) and Universidad de Nariño for financial support.

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supporting information

Acta Cryst. (2005). E**61**, o3998–o4000 [https://doi.org/10.1107/S1600536805035270]

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$F(000) = 1024$
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Cell parameters from 5163 reflections
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$T = 120$ K
Block, yellow
0.62 × 0.44 × 0.22 mm

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Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
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$R_{int} = 0.004$
$\theta_{max} = 27.6°$, $\theta_{min} = 3.4°$
$h = -12\rightarrow12$
$k = -32\rightarrow33$
$l = -13\rightarrow13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.141$
$S = 1.04$
5163 reflections
315 parameters
4 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
$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2 + 2.3558P]$ 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}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S5	0.04959 (6)	0.23186 (2)	0.42860 (6)	0.02374 (15)	
S6	0.02305 (7)	0.11493 (2)	0.43299 (7)	0.03246 (17)	
O41	−0.3219 (3)	0.46091 (10)	0.3239 (3)	0.0649 (7)	
O42	−0.1921 (3)	0.48677 (8)	0.5375 (3)	0.0534 (6)	
N1	0.6937 (2)	0.29852 (7)	0.6336 (2)	0.0238 (4)	
N2	0.6898 (2)	0.35265 (8)	0.6311 (2)	0.0266 (4)	
N7	0.2870 (2)	0.17113 (7)	0.4987 (2)	0.0236 (4)	
N8	0.5055 (2)	0.22780 (7)	0.57145 (19)	0.0225 (4)	
N44	−0.2077 (3)	0.45932 (9)	0.4352 (3)	0.0416 (6)	
C3	0.5410 (3)	0.36700 (9)	0.5849 (2)	0.0245 (5)	
C3A	0.4412 (2)	0.32185 (9)	0.5548 (2)	0.0221 (5)	
C4	0.2784 (2)	0.31267 (9)	0.5036 (2)	0.0206 (4)	
C4A	0.2353 (2)	0.26033 (9)	0.4831 (2)	0.0212 (4)	
C6	0.1294 (3)	0.16877 (9)	0.4549 (2)	0.0242 (5)	
C7A	0.3511 (2)	0.22072 (9)	0.5187 (2)	0.0216 (4)	
C8A	0.5441 (2)	0.27860 (9)	0.5853 (2)	0.0213 (4)	
C11	0.8420 (2)	0.27248 (9)	0.6862 (2)	0.0236 (5)	
C12	0.9776 (3)	0.30312 (10)	0.7410 (3)	0.0296 (5)	
C13	1.1232 (3)	0.27921 (10)	0.7969 (3)	0.0314 (5)	
C14	1.1366 (3)	0.22527 (10)	0.7992 (2)	0.0293 (5)	
C15	1.0010 (3)	0.19517 (10)	0.7431 (2)	0.0289 (5)	
C16	0.8536 (3)	0.21845 (10)	0.6862 (3)	0.0272 (5)	
C31	0.4970 (3)	0.42329 (10)	0.5684 (3)	0.0317 (5)	
C41	0.1576 (2)	0.35366 (8)	0.4808 (2)	0.0214 (4)	
C42	0.0288 (3)	0.35766 (9)	0.3520 (2)	0.0264 (5)	
C43	−0.0918 (3)	0.39259 (9)	0.3358 (3)	0.0307 (5)	
C44	−0.0803 (3)	0.42273 (9)	0.4488 (3)	0.0285 (5)	
C45	0.0474 (3)	0.42075 (10)	0.5768 (3)	0.0319 (5)	
C46	0.1674 (3)	0.38572 (9)	0.5925 (3)	0.0277 (5)	
O21	0.4894 (3)	0.08967 (9)	0.5501 (2)	0.0591 (6)	
N21	0.6802 (3)	0.03981 (10)	0.5281 (3)	0.0533 (7)	
C22	0.5487 (4)	0.06737 (13)	0.4825 (4)	0.0596 (9)	
C23A	0.7141 (10)	0.0072 (3)	0.4277 (10)	0.059 (2)	0.598 (8)
C24A	0.7980 (6)	0.0502 (3)	0.6634 (5)	0.0647 (17)	0.598 (8)
C23B	0.7698 (16)	0.0199 (5)	0.4515 (16)	0.059 (2)	0.402 (8)
C24B	0.7343 (11)	0.0154 (4)	0.6705 (6)	0.0647 (17)	0.402 (8)
H7	0.3435	0.1426	0.5089	0.028*	
H12	0.9698	0.3402	0.7399	0.036*	
H13	1.2154	0.3001	0.8343	0.038*	
H14	1.2370	0.2090	0.8384	0.035*	
H15	1.0091	0.1581	0.7436	0.035*	
H16	0.7616	0.1975	0.6477	0.033*	
H22	0.4942	0.0698	0.3831	0.071*	
H31A	0.4672	0.4341	0.6449	0.048*	
H31B	0.4081	0.4287	0.4778	0.048*	

H31C	0.5867	0.4442	0.5717	0.048*	
H42	0.0235	0.3365	0.2750	0.032*	
H43	−0.1802	0.3955	0.2485	0.037*	
H45	0.0531	0.4428	0.6523	0.038*	
H46	0.2563	0.3836	0.6796	0.033*	
H23A	0.8136	−0.0113	0.4769	0.088*	0.299 (4)
H23B	0.7220	0.0294	0.3538	0.088*	0.299 (4)
H23C	0.6293	−0.0183	0.3853	0.088*	0.299 (4)
H23D	0.6297	0.0112	0.3338	0.088*	0.299 (4)
H23E	0.7212	−0.0296	0.4568	0.088*	0.299 (4)
H23F	0.8140	0.0181	0.4254	0.088*	0.299 (4)
H24A	0.8872	0.0266	0.6817	0.097*	0.299 (4)
H24B	0.7552	0.0445	0.7345	0.097*	0.299 (4)
H24C	0.8330	0.0866	0.6678	0.097*	0.299 (4)
H24D	0.7631	0.0785	0.7076	0.097*	0.299 (4)
H24E	0.8951	0.0606	0.6548	0.097*	0.299 (4)
H24F	0.8172	0.0186	0.7215	0.097*	0.299 (4)
H23G	0.8696	0.0055	0.5183	0.088*	0.201 (4)
H23H	0.7905	0.0485	0.3984	0.088*	0.201 (4)
H23I	0.7095	−0.0076	0.3864	0.088*	0.201 (4)
H23J	0.7101	0.0255	0.3504	0.088*	0.201 (4)
H23K	0.7893	−0.0176	0.4703	0.088*	0.201 (4)
H23L	0.8702	0.0385	0.4823	0.088*	0.201 (4)
H24G	0.7390	−0.0227	0.6617	0.097*	0.201 (4)
H24H	0.6605	0.0241	0.7130	0.097*	0.201 (4)
H24I	0.8389	0.0287	0.7301	0.097*	0.201 (4)
H24J	0.7533	0.0428	0.7415	0.097*	0.201 (4)
H24K	0.8318	−0.0040	0.6902	0.097*	0.201 (4)
H24L	0.6534	−0.0086	0.6731	0.097*	0.201 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S5	0.0136 (2)	0.0285 (3)	0.0263 (3)	−0.0002 (2)	0.0052 (2)	0.0016 (2)
S6	0.0229 (3)	0.0303 (3)	0.0376 (4)	−0.0063 (2)	0.0053 (3)	−0.0021 (3)
O41	0.0474 (13)	0.0704 (16)	0.0770 (17)	0.0356 (12)	0.0251 (13)	0.0123 (13)
O42	0.0570 (13)	0.0305 (10)	0.0963 (18)	0.0005 (9)	0.0552 (13)	−0.0114 (11)
N1	0.0151 (8)	0.0274 (10)	0.0281 (10)	0.0005 (7)	0.0079 (8)	0.0013 (8)
N2	0.0201 (9)	0.0290 (10)	0.0322 (11)	−0.0019 (8)	0.0119 (8)	0.0018 (8)
N7	0.0165 (9)	0.0267 (10)	0.0244 (10)	0.0002 (7)	0.0050 (8)	−0.0012 (8)
N8	0.0155 (8)	0.0292 (10)	0.0222 (10)	0.0009 (7)	0.0070 (7)	0.0010 (8)
N44	0.0386 (13)	0.0280 (11)	0.0730 (18)	0.0075 (10)	0.0379 (13)	0.0064 (12)
C3	0.0193 (10)	0.0287 (12)	0.0268 (12)	−0.0021 (9)	0.0107 (9)	0.0014 (9)
C3A	0.0172 (10)	0.0297 (12)	0.0199 (11)	0.0007 (8)	0.0080 (9)	0.0028 (9)
C4	0.0166 (10)	0.0270 (11)	0.0182 (10)	0.0012 (8)	0.0071 (8)	0.0027 (8)
C4A	0.0139 (9)	0.0305 (12)	0.0177 (10)	0.0019 (8)	0.0048 (8)	0.0020 (8)
C6	0.0193 (10)	0.0298 (12)	0.0201 (11)	−0.0007 (9)	0.0045 (9)	−0.0005 (9)
C7A	0.0186 (10)	0.0270 (11)	0.0182 (10)	0.0015 (8)	0.0064 (8)	0.0009 (8)

C8A	0.0149 (9)	0.0293 (12)	0.0201 (11)	−0.0008 (8)	0.0073 (8)	0.0017 (9)
C11	0.0139 (9)	0.0353 (12)	0.0223 (11)	0.0011 (9)	0.0079 (8)	0.0037 (9)
C12	0.0189 (11)	0.0353 (13)	0.0334 (13)	−0.0019 (9)	0.0094 (10)	0.0028 (10)
C13	0.0154 (10)	0.0442 (15)	0.0317 (13)	−0.0025 (10)	0.0066 (10)	0.0015 (11)
C14	0.0158 (10)	0.0446 (14)	0.0258 (12)	0.0052 (9)	0.0066 (9)	0.0055 (10)
C15	0.0218 (11)	0.0352 (13)	0.0297 (13)	0.0031 (10)	0.0106 (10)	0.0041 (10)
C16	0.0179 (10)	0.0354 (13)	0.0284 (12)	−0.0008 (9)	0.0095 (9)	0.0020 (10)
C31	0.0243 (11)	0.0298 (13)	0.0423 (15)	−0.0012 (9)	0.0147 (11)	0.0047 (11)
C41	0.0166 (10)	0.0237 (11)	0.0257 (11)	−0.0010 (8)	0.0102 (9)	0.0019 (9)
C42	0.0249 (11)	0.0256 (11)	0.0265 (12)	0.0023 (9)	0.0082 (9)	−0.0019 (9)
C43	0.0225 (11)	0.0286 (12)	0.0370 (14)	0.0034 (9)	0.0079 (10)	0.0027 (10)
C44	0.0237 (11)	0.0219 (11)	0.0470 (15)	0.0015 (9)	0.0216 (11)	0.0028 (10)
C45	0.0368 (13)	0.0292 (12)	0.0383 (14)	−0.0047 (10)	0.0239 (12)	−0.0074 (10)
C46	0.0255 (11)	0.0322 (12)	0.0263 (12)	−0.0029 (9)	0.0115 (10)	−0.0031 (10)
O21	0.0623 (14)	0.0545 (14)	0.0632 (15)	0.0273 (11)	0.0280 (12)	−0.0024 (11)
N21	0.0391 (14)	0.0408 (14)	0.082 (2)	0.0051 (11)	0.0266 (14)	−0.0017 (13)
C22	0.072 (2)	0.0513 (19)	0.067 (2)	0.0275 (17)	0.0407 (19)	0.0256 (17)
C23A	0.059 (6)	0.044 (4)	0.101 (5)	0.012 (3)	0.062 (5)	0.026 (3)
C24A	0.040 (3)	0.069 (4)	0.064 (3)	0.010 (2)	−0.002 (2)	−0.008 (3)
C23B	0.059 (6)	0.044 (4)	0.101 (5)	0.012 (3)	0.062 (5)	0.026 (3)
C24B	0.040 (3)	0.069 (4)	0.064 (3)	0.010 (2)	−0.002 (2)	−0.008 (3)

Geometric parameters (Å, º)

N1—N2	1.383 (3)	C44—N44	1.470 (3)
N2—C3	1.322 (3)	N44—O41	1.215 (3)
C3—C3A	1.433 (3)	N44—O42	1.231 (3)
C3A—C4	1.408 (3)	C45—C46	1.387 (3)
C4—C4A	1.387 (3)	C45—H45	0.95
C4A—S5	1.745 (2)	C46—H46	0.95
S5—C6	1.749 (2)	N7—H7	0.88
C6—N7	1.350 (3)	O21—C22	1.198 (4)
N7—C7A	1.380 (3)	N21—C22	1.323 (4)
C7A—N8	1.328 (3)	N21—C24A	1.415 (4)
N8—C8A	1.339 (3)	N21—C23B	1.454 (5)
C8A—N1	1.373 (3)	N21—C23A	1.464 (4)
C3A—C8A	1.412 (3)	N21—C24B	1.492 (5)
C4A—C7A	1.414 (3)	C22—H22	0.95
C6—S6	1.656 (2)	C23A—H23A	0.98
N1—C11	1.427 (3)	C23A—H23B	0.98
C11—C16	1.384 (3)	C23A—H23C	0.98
C11—C12	1.396 (3)	C23A—H23D	0.98
C12—C13	1.382 (3)	C23A—H23E	0.98
C12—H12	0.95	C23A—H23F	0.98
C13—C14	1.383 (4)	C24A—H24A	0.98
C13—H13	0.95	C24A—H24B	0.98
C14—C15	1.389 (3)	C24A—H24C	0.98
C14—H14	0.95	C24A—H24D	0.98

C15—C16	1.389 (3)	C24A—H24E	0.98
C15—H15	0.95	C24A—H24F	0.98
C16—H16	0.95	C23B—H23G	0.98
C3—C31	1.486 (3)	C23B—H23H	0.98
C31—H31A	0.98	C23B—H23I	0.98
C31—H31B	0.98	C23B—H23J	0.98
C31—H31C	0.98	C23B—H23K	0.98
C4—C41	1.484 (3)	C23B—H23L	0.98
C41—C46	1.392 (3)	C24B—H24G	0.98
C41—C42	1.393 (3)	C24B—H24H	0.98
C42—C43	1.390 (3)	C24B—H24I	0.98
C42—H42	0.95	C24B—H24J	0.98
C43—C44	1.371 (4)	C24B—H24K	0.98
C43—H43	0.95	C24B—H24L	0.98
C44—C45	1.381 (4)		

C8A—N1—N2	110.42 (17)	N21—C23A—H23A	109.5
C8A—N1—C11	130.41 (19)	N21—C23A—H23B	109.5
N2—N1—C11	119.14 (17)	H23A—C23A—H23B	109.5
C16—C11—C12	120.1 (2)	N21—C23A—H23C	109.5
C16—C11—N1	121.87 (19)	H23A—C23A—H23C	109.5
C12—C11—N1	118.0 (2)	H23B—C23A—H23C	109.5
C13—C12—C11	119.7 (2)	N21—C23A—H23D	109.5
C13—C12—H12	120.2	H23A—C23A—H23D	141.1
C11—C12—H12	120.2	H23B—C23A—H23D	56.3
C12—C13—C14	120.9 (2)	H23C—C23A—H23D	56.3
C12—C13—H13	119.6	N21—C23A—H23E	109.5
C14—C13—H13	119.6	H23A—C23A—H23E	56.3
C13—C14—C15	119.0 (2)	H23B—C23A—H23E	141.1
C13—C14—H14	120.5	H23C—C23A—H23E	56.3
C15—C14—H14	120.5	H23D—C23A—H23E	109.5
C16—C15—C14	121.0 (2)	N21—C23A—H23F	109.5
C16—C15—H15	119.5	H23A—C23A—H23F	56.3
C14—C15—H15	119.5	H23B—C23A—H23F	56.3
C11—C16—C15	119.4 (2)	H23C—C23A—H23F	141.1
C11—C16—H16	120.3	H23D—C23A—H23F	109.5
C15—C16—H16	120.3	H23E—C23A—H23F	109.5
C3—N2—N1	107.43 (18)	N21—C24A—H24A	109.5
N2—C3—C3A	110.3 (2)	N21—C24A—H24B	109.5
N2—C3—C31	120.6 (2)	H24A—C24A—H24B	109.5
C3A—C3—C31	129.0 (2)	N21—C24A—H24C	109.5
C3—C31—H31A	109.5	H24A—C24A—H24C	109.5
C3—C31—H31B	109.5	H24B—C24A—H24C	109.5
H31A—C31—H31B	109.5	N21—C24A—H24D	109.5
C3—C31—H31C	109.5	H24A—C24A—H24D	141.1
H31A—C31—H31C	109.5	H24B—C24A—H24D	56.3
H31B—C31—H31C	109.5	H24C—C24A—H24D	56.3
C4—C3A—C8A	118.9 (2)	N21—C24A—H24E	109.5

C4—C3A—C3	136.0 (2)	H24A—C24A—H24E	56.3
C8A—C3A—C3	105.07 (18)	H24B—C24A—H24E	141.1
C4A—C4—C3A	114.8 (2)	H24C—C24A—H24E	56.3
C4A—C4—C41	120.13 (19)	H24D—C24A—H24E	109.5
C3A—C4—C41	125.0 (2)	N21—C24A—H24F	109.5
C46—C41—C42	119.9 (2)	H24A—C24A—H24F	56.3
C46—C41—C4	119.4 (2)	H24B—C24A—H24F	56.3
C42—C41—C4	120.5 (2)	H24C—C24A—H24F	141.1
C43—C42—C41	120.2 (2)	H24D—C24A—H24F	109.5
C43—C42—H42	119.9	H24E—C24A—H24F	109.5
C41—C42—H42	119.9	N21—C23B—H23G	109.5
C44—C43—C42	118.4 (2)	N21—C23B—H23H	109.5
C44—C43—H43	120.8	H23G—C23B—H23H	109.5
C42—C43—H43	120.8	N21—C23B—H23I	109.5
C43—C44—C45	122.8 (2)	H23G—C23B—H23I	109.5
C43—C44—N44	119.5 (2)	H23H—C23B—H23I	109.5
C45—C44—N44	117.6 (2)	N21—C23B—H23J	109.5
O41—N44—O42	123.7 (2)	H23G—C23B—H23J	141.1
O41—N44—C44	118.4 (2)	H23H—C23B—H23J	56.3
O42—N44—C44	117.9 (3)	H23I—C23B—H23J	56.3
C44—C45—C46	118.5 (2)	N21—C23B—H23K	109.5
C44—C45—H45	120.8	H23G—C23B—H23K	56.3
C46—C45—H45	120.8	H23H—C23B—H23K	141.1
C45—C46—C41	120.1 (2)	H23I—C23B—H23K	56.3
C45—C46—H46	119.9	H23J—C23B—H23K	109.5
C41—C46—H46	119.9	N21—C23B—H23L	109.5
C4—C4A—C7A	120.46 (19)	H23G—C23B—H23L	56.3
C4—C4A—S5	129.67 (17)	H23H—C23B—H23L	56.3
C7A—C4A—S5	109.67 (16)	H23I—C23B—H23L	141.1
C4A—S5—C6	91.77 (10)	H23J—C23B—H23L	109.5
N7—C6—S6	126.22 (18)	H23K—C23B—H23L	109.5
N7—C6—S5	110.28 (16)	N21—C24B—H24G	109.5
S6—C6—S5	123.47 (13)	N21—C24B—H24H	109.5
C6—N7—C7A	115.86 (19)	H24G—C24B—H24H	109.5
C6—N7—H7	121.2	N21—C24B—H24I	109.5
C7A—N7—H7	122.8	H24G—C24B—H24I	109.5
N8—C7A—N7	121.15 (19)	H24H—C24B—H24I	109.5
N8—C7A—C4A	126.4 (2)	N21—C24B—H24J	109.5
N7—C7A—C4A	112.37 (18)	H24G—C24B—H24J	141.1
C7A—N8—C8A	112.04 (18)	H24H—C24B—H24J	56.3
N8—C8A—N1	126.0 (2)	H24I—C24B—H24J	56.3
N8—C8A—C3A	127.33 (19)	N21—C24B—H24K	109.5
N1—C8A—C3A	106.72 (19)	H24G—C24B—H24K	56.3
C22—N21—C24A	119.3 (4)	H24H—C24B—H24K	141.1
C22—N21—C23B	129.9 (8)	H24I—C24B—H24K	56.3
C22—N21—C23A	118.8 (5)	H24J—C24B—H24K	109.5
C24A—N21—C23A	120.7 (5)	N21—C24B—H24L	109.5
C22—N21—C24B	118.1 (4)	H24G—C24B—H24L	56.3

C23B—N21—C24B	110.9 (8)	H24H—C24B—H24L	56.3
O21—C22—N21	128.4 (4)	H24I—C24B—H24L	141.1
O21—C22—H22	115.8	H24J—C24B—H24L	109.5
N21—C22—H22	115.8	H24K—C24B—H24L	109.5
N2—N1—C11—C12	3.8 (3)	C43—C44—C45—C46	−1.7 (4)
C8A—N1—C11—C12	−174.1 (2)	N44—C44—C45—C46	178.8 (2)
N2—N1—C11—C16	−177.4 (2)	C44—C45—C46—C41	0.1 (3)
C8A—N1—C11—C16	4.8 (4)	C42—C41—C46—C45	1.6 (3)
C16—C11—C12—C13	−0.9 (4)	C4—C41—C46—C45	−173.7 (2)
N1—C11—C12—C13	178.0 (2)	C3A—C4—C4A—C7A	2.8 (3)
C11—C12—C13—C14	0.1 (4)	C41—C4—C4A—C7A	−173.28 (19)
C12—C13—C14—C15	0.5 (4)	C3A—C4—C4A—S5	177.18 (17)
C13—C14—C15—C16	−0.4 (4)	C41—C4—C4A—S5	1.1 (3)
C12—C11—C16—C15	1.0 (3)	C4—C4A—S5—C6	−174.6 (2)
N1—C11—C16—C15	−177.8 (2)	C7A—C4A—S5—C6	0.21 (17)
C14—C15—C16—C11	−0.3 (4)	C4A—S5—C6—N7	−1.54 (18)
C8A—N1—N2—C3	1.2 (2)	C4A—S5—C6—S6	176.62 (16)
C11—N1—N2—C3	−177.02 (19)	S6—C6—N7—C7A	−175.52 (17)
N1—N2—C3—C3A	−0.2 (3)	S5—C6—N7—C7A	2.6 (2)
N1—N2—C3—C31	−179.3 (2)	C6—N7—C7A—N8	175.0 (2)
N2—C3—C3A—C4	−179.4 (2)	C6—N7—C7A—C4A	−2.5 (3)
C31—C3—C3A—C4	−0.5 (4)	C4—C4A—C7A—N8	−0.8 (3)
N2—C3—C3A—C8A	−0.8 (3)	S5—C4A—C7A—N8	−176.17 (18)
C31—C3—C3A—C8A	178.1 (2)	C4—C4A—C7A—N7	176.54 (19)
C8A—C3A—C4—C4A	−2.5 (3)	S5—C4A—C7A—N7	1.1 (2)
C3—C3A—C4—C4A	176.0 (2)	N7—C7A—N8—C8A	−178.76 (19)
C8A—C3A—C4—C41	173.4 (2)	C4A—C7A—N8—C8A	−1.7 (3)
C3—C3A—C4—C41	−8.1 (4)	C7A—N8—C8A—N1	−178.4 (2)
C3A—C4—C41—C42	128.2 (2)	C7A—N8—C8A—C3A	2.1 (3)
C4A—C4—C41—C42	−56.1 (3)	N2—N1—C8A—N8	178.7 (2)
C3A—C4—C41—C46	−56.6 (3)	C11—N1—C8A—N8	−3.3 (4)
C4A—C4—C41—C46	119.1 (2)	N2—N1—C8A—C3A	−1.8 (2)
C46—C41—C42—C43	−1.7 (3)	C11—N1—C8A—C3A	176.3 (2)
C4—C41—C42—C43	173.5 (2)	C4—C3A—C8A—N8	0.0 (3)
C41—C42—C43—C44	0.2 (3)	C3—C3A—C8A—N8	−178.9 (2)
C42—C43—C44—C45	1.5 (4)	C4—C3A—C8A—N1	−179.59 (19)
C42—C43—C44—N44	−178.9 (2)	C3—C3A—C8A—N1	1.5 (2)
C43—C44—N44—O41	1.6 (4)	C24A—N21—C22—O21	−24.7 (6)
C45—C44—N44—O41	−178.9 (2)	C23B—N21—C22—O21	−168.1 (6)
C43—C44—N44—O42	−178.2 (2)	C23A—N21—C22—O21	167.7 (4)
C45—C44—N44—O42	1.3 (3)	C24B—N21—C22—O21	25.6 (7)

Hydrogen-bond geometry (Å, º)

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) $x+1/2, -y+1/2, z+1/2$.