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Ethyl 6′-cyano-7′-(*p*-tolyl)-1′,6′,7′,7a′-tetrahydro-3′*H*-spiro[indeno[1,2-*b*]quinoxaline-11,5′-pyrrolo[1,2-*c*]thiazole]-6′-carboxylate

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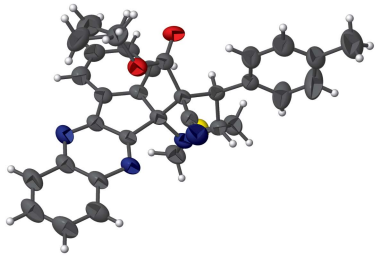
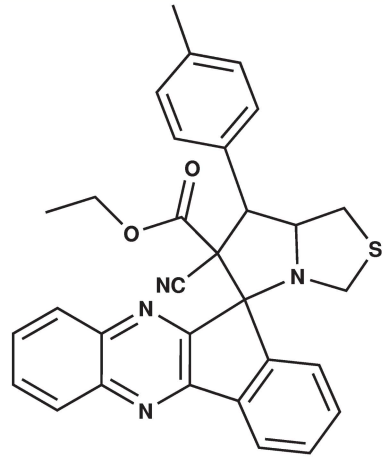
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{31}H_{26}N_4O_2S$, crystallizes in a triclinic centrosymmetric lattice with two molecules in the unit cell. The five-membered thiazole and pyrrolidine rings adopt twisted and envelope conformations, respectively. The methoxyphenyl and indenoquinoxaline planes are oriented with a dihedral angle of 88.1 (1)° to each other. The crystal structure features C—H···N, C—H···O and C—H···S intermolecular interactions forming two $R_2^2(16)$ ring motifs and a $C(11)$ and two $C_2^2(14)$ chain motifs. The –CH_3 group of the ethyl side chain is disordered over two positions with site occupancies of 0.55 and 0.45.

3D view



Chemical scheme



Structure description

The fusion of more heterocyclic rings, such as thiazoles, pyrrolidines and quinoxalines, in a single compound is being investigated by many researchers around the world due to the versatile applications of such compounds in the biological and pharmaceutical industries (He *et al.*, 2003; Swarnkar *et al.*, 2007; Verma & Saraf, 2008; Muralikrishnan *et al.*, 2013). When such a fused heterocyclic compound has attached donor and acceptor groups, it leads to intermolecular interactions which are normally weak hydrogen bonds. The introduction of a carboxylate or cyanide group is of our interest in the present investigation, which not only affects the conformation of the molecule but also the intermolecular interaction feasibility, along with a methoxyphenyl group. The new conformation of the structure and its packing specificity through hydrogen-bonding motifs is described. The biological and pharmaceutical applications of this type of mol-

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

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14···S1^{i}	0.93	3.01	3.881 (4)	156
C23—H23A···N2^{ii}	0.97	2.70	3.610 (4)	156
C4—H4···O1^{iii}	0.93	2.43	3.332 (3)	162

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

ecule have already been discussed in previous three recent related publications (Muthuselvi *et al.*, 2017, 2018*a*,*b*).

The structure of title compound is shown in Fig. 1. The five-membered thiazole ring adopts a twisted conformation with the puckering parameters of q_2 = 0.389 (3) Å and φ_2 = 165.3 (4)° on the C24—S1 bond. The five-membered pyrrolidine ring has puckering values of q_2 = 0.408 (3) Å and φ_2 = 109.3 (3)° and an envelope conformation on C16. The mean planes of the methoxyphenyl ring and the indenoquinoxaline ring system are inclined to one another at an angle of 88.1 (1)°.

The packing of the molecules in the centrosymmetric crystal lattice is shown in Fig. 2. As there is lack of classical hydrogen bonds, the crystal packing features C—H···S, C—H···O and C—H···N intermolecular interactions, Table 1. C—H···S interactions connect the molecules along the *ab* diagonal of the unit cell, leading to a $C(11)$ chain motif as depicted in Fig. 3. The molecules are further connected about the inversion centre of the unit cell through C—H···N and C—H···O intermolecular interactions, leading to two $R_2^2(16)$ ring motifs that are arranged adjacently, leading to two infinite $C_2^2(14)$ chain motifs running in opposite directions, as shown in Fig. 4.

Synthesis and crystallization

Equimolar amounts of 1*H*-indeno[1,2-*b*]quinoxalin-11-one and thiazolidine-4-carboxylic acid were added to 20 ml of methanol and refluxed under a water bath for two minutes. An equimolar amount of propyl-(*E*)-2-cyano-3-(*p*-tolyl) acrylate was added to the reaction mixture and refluxing was continued

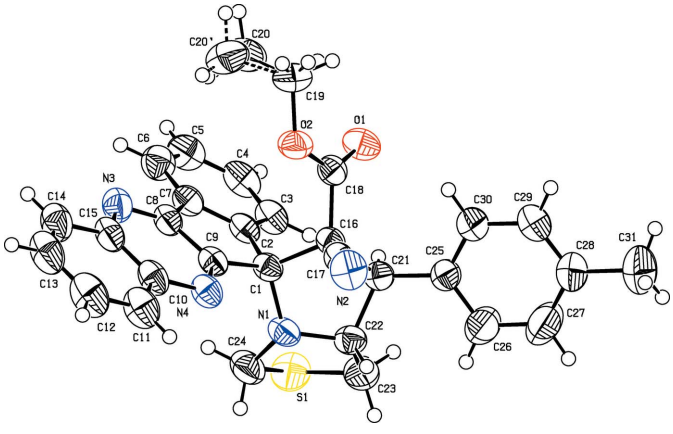


Figure 1
The asymmetric unit of the title compound with atom-numbering scheme and 50% probability displacement ellipsoids. The –CH_3 group (C20) is disordered over two positions with site occupancies of 0.55 and 0.45.

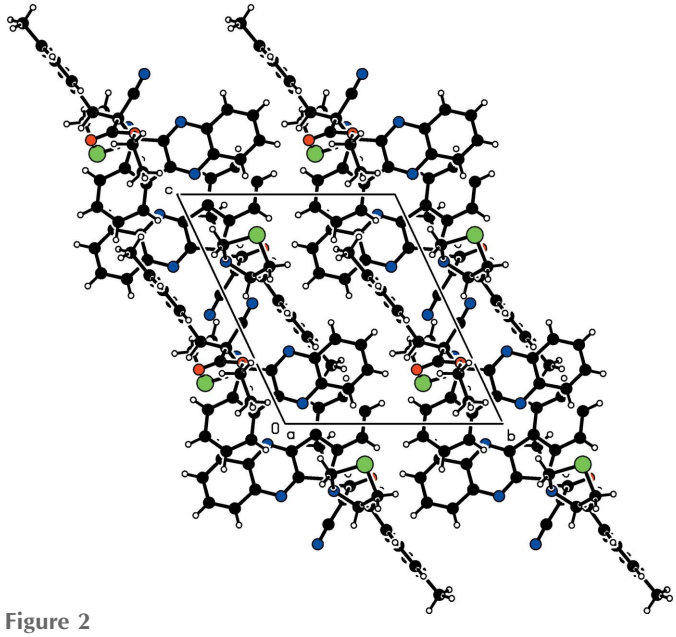


Figure 2
Packing diagram of the title compound viewed down the *a* axis. Hydrogen bonds are shown as dashed lines. The minor component of the disordered –CH_3 group (C20 atom) is omitted for clarity.

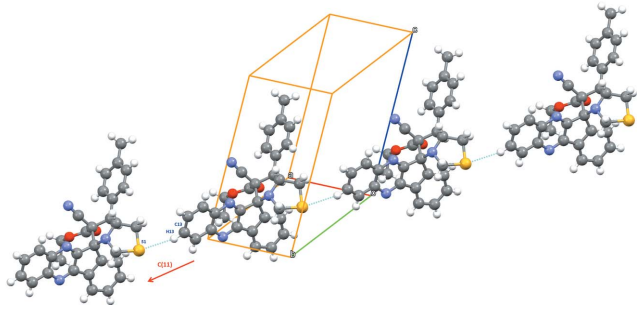


Figure 3
$C(11)$ chain motif extending along the *ab*-axis of the unit cell formed by a C—H···S interaction. Hydrogen bonds are shown as dashed lines. The minor component of the disordered –CH_3 group (C20 atom) is omitted for clarity.

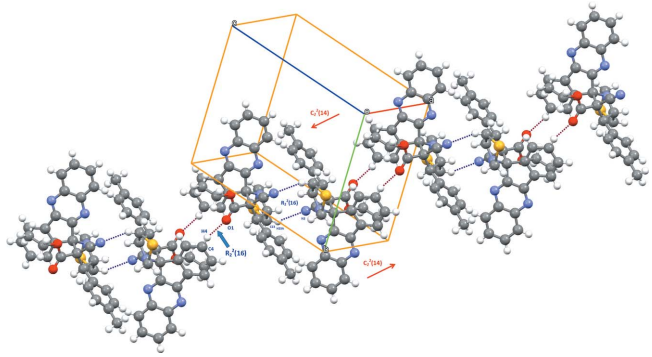


Figure 4
Two centrosymmetrically related $R_2^2(16)$ ring motifs and two $C_2^2(14)$ chain motifs running in opposite directions formed by C—H···N and C—H···O interactions. Hydrogen bonds are shown as dashed lines. The minor component of the disordered –CH_3 group (C20 atom) is omitted for clarity.

until the TLC analysis indicated that the reaction was completed (continued for 4 h). The precipitated solid was filtered and washed with methanol to obtain the title compound in good yield (94–98%). Colourless block-shaped crystals were obtained by slow evaporation after recrystallization from chloroform solution.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The $-CH_3$ group of the ethyl side chain (atom C20) is disordered over two positions with site occupancies of 0.55 and 0.45. The C—C distances involving the disordered methyl group were restrained to 1.500 (5) Å. The displacement parameters of the disordered atoms were restrained to be similar to those of the atom to which they are bonded.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{31}H_{26}N_4O_2S$
M_r	518.62
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	293
a, b, c (Å)	10.5467 (17), 11.6469 (19), 12.942 (2)
α, β, γ (°)	108.321 (3), 102.108 (3), 110.887 (3)
V (Å^3)	1313.9 (4)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.16
Crystal size (mm)	0.21 × 0.18 × 0.16
Data collection	
Diffractometer	Bruker SMART APEX CCD area-detector
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12753, 4622, 3771
R_{int}	0.023
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.061, 0.151, 1.07
No. of reflections	4622
No. of parameters	355
No. of restraints	22
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.26

Computer programs: *SMART* and *SAINT* (Bruker, 2001), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

Acknowledgements

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full crystallographic data

IUCrData (2019). **4**, x190010 [https://doi.org/10.1107/S2414314619000105]

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Crystal data

$C_{31}H_{26}N_4O_2S$
M_r = 518.62
Triclinic, $P\overline{1}$
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c = 12.942 (2) Å
α = 108.321 (3)°
β = 102.108 (3)°
γ = 110.887 (3)°
V = 1313.9 (4) Å^3
Z = 2
$F(000)$ = 544
D_x = 1.311 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2425 reflections
θ = 2.2–24.7°
μ = 0.16 mm^{-1}
T = 293 K
Block, colourless
0.21 × 0.18 × 0.16 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
ω scans
12753 measured reflections
4622 independent reflections
3771 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 25.0°, θ_{min} = 2.1°
h = −12→12
k = −13→13
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.151
S = 1.07
4622 reflections
355 parameters
22 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0638P)^2 + 0.7519P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Special details

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

Refinement. All the H atoms were constrained and refined in the riding model approximation with C—H = 0.93–0.98 Å and U_{iso}(H) = 1.2–1.5 U_{eq}(parent carbon atom). The –CH_3 group of the ethyl side chain (atom C20) is disordered two positions with site occupancies of 0.55 and 0.45. The C—C distances involving the disordered methyl group were restrained to 1.500 (5) Å. The displacement parameters of the disordered atoms were restrained to be similar as the one of the atom to which they are bonded.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.5961 (2)	0.9197 (2)	0.2416 (2)	0.0408 (6)	
C2	0.5481 (3)	0.8168 (2)	0.1140 (2)	0.0427 (6)	
C3	0.4668 (3)	0.6764 (2)	0.0615 (2)	0.0499 (6)	
H3	0.4307	0.6306	0.1043	0.060*	
C4	0.4402 (3)	0.6057 (3)	−0.0548 (3)	0.0574 (7)	
H4	0.3862	0.5116	−0.0899	0.069*	
C5	0.4918 (3)	0.6713 (3)	−0.1198 (3)	0.0621 (8)	
H5	0.4720	0.6214	−0.1982	0.075*	
C6	0.5729 (3)	0.8109 (3)	−0.0695 (2)	0.0591 (7)	
H6	0.6081	0.8559	−0.1131	0.071*	
C7	0.6005 (3)	0.8823 (3)	0.0474 (2)	0.0457 (6)	
C8	0.6789 (3)	1.0287 (2)	0.1196 (2)	0.0446 (6)	
C9	0.6725 (2)	1.0533 (2)	0.2330 (2)	0.0410 (6)	
C10	0.7864 (3)	1.2786 (2)	0.2866 (2)	0.0500 (6)	
C11	0.8413 (3)	1.4131 (3)	0.3690 (3)	0.0665 (8)	
H11	0.8322	1.4301	0.4415	0.080*	
C12	0.9078 (3)	1.5189 (3)	0.3436 (3)	0.0737 (10)	
H12	0.9449	1.6076	0.3992	0.088*	
C13	0.9205 (3)	1.4948 (3)	0.2353 (4)	0.0720 (10)	
H13	0.9654	1.5680	0.2188	0.086*	
C14	0.8685 (3)	1.3663 (3)	0.1527 (3)	0.0642 (8)	
H14	0.8789	1.3524	0.0808	0.077*	
C15	0.7989 (3)	1.2542 (3)	0.1755 (3)	0.0508 (7)	
C16	0.6976 (2)	0.8932 (2)	0.3302 (2)	0.0389 (5)	
C17	0.7946 (3)	1.0183 (2)	0.4386 (2)	0.0430 (6)	
C18	0.7898 (3)	0.8377 (3)	0.2721 (2)	0.0425 (6)	
C21	0.5848 (3)	0.7902 (2)	0.3579 (2)	0.0413 (6)	
H21	0.5381	0.7027	0.2891	0.050*	
C22	0.4708 (3)	0.8422 (3)	0.3620 (2)	0.0471 (6)	
H22	0.4956	0.9036	0.4431	0.057*	
C23	0.3105 (3)	0.7322 (3)	0.3151 (3)	0.0647 (8)	
H23A	0.2636	0.7565	0.3695	0.078*	
H23B	0.3072	0.6452	0.3063	0.078*	
C24	0.3470 (3)	0.8973 (3)	0.2200 (3)	0.0662 (8)	
H24A	0.3550	0.9121	0.1514	0.079*	
H24B	0.3143	0.9586	0.2625	0.079*	
C25	0.6408 (3)	0.7648 (2)	0.4626 (2)	0.0457 (6)	
C26	0.5612 (4)	0.7430 (5)	0.5313 (3)	0.0890 (12)	
H26	0.4753	0.7511	0.5177	0.107*	

C27	0.6058 (5)	0.7094 (5)	0.6206 (4)	0.1080 (15)	
H27	0.5477	0.6937	0.6647	0.130*	
C28	0.7324 (4)	0.6982 (4)	0.6471 (3)	0.0708 (9)	
C29	0.8159 (4)	0.7278 (4)	0.5832 (3)	0.0775 (10)	
H29	0.9051	0.7259	0.6008	0.093*	
C30	0.7719 (4)	0.7604 (4)	0.4930 (3)	0.0724 (9)	
H30	0.8323	0.7801	0.4514	0.087*	
C31	0.7813 (5)	0.6613 (5)	0.7454 (4)	0.1092 (15)	
H31A	0.8405	0.7426	0.8164	0.164*	
H31B	0.8369	0.6134	0.7266	0.164*	
H31C	0.6976	0.6045	0.7555	0.164*	
N1	0.4856 (2)	0.9211 (2)	0.2931 (2)	0.0479 (5)	
N2	0.8697 (3)	1.1096 (2)	0.5250 (2)	0.0624 (6)	
N3	0.7420 (2)	1.1249 (2)	0.0893 (2)	0.0533 (6)	
N4	0.7208 (2)	1.1737 (2)	0.31545 (19)	0.0483 (5)	
O1	0.7654 (2)	0.72191 (18)	0.23620 (16)	0.0570 (5)	
O2	0.8942 (2)	0.93702 (19)	0.26587 (18)	0.0579 (5)	
C19	0.9941 (4)	0.9032 (4)	0.2154 (3)	0.0799 (10)	
H19A	1.0083	0.8336	0.2347	0.096*	0.55
H19B	1.0878	0.9830	0.2486	0.096*	0.55
H19C	0.9644	0.8067	0.1887	0.096*	0.45
H19D	1.0915	0.9521	0.2741	0.096*	0.45
S1	0.21886 (8)	0.72141 (9)	0.17723 (8)	0.0703 (3)	
C20	0.9376 (12)	0.8542 (10)	0.0874 (5)	0.094 (3)	0.55
H20A	0.8556	0.7658	0.0531	0.141*	0.55
H20B	1.0126	0.8489	0.0579	0.141*	0.55
H20C	0.9078	0.9159	0.0679	0.141*	0.55
C20′	0.9945 (16)	0.9404 (12)	0.1157 (8)	0.096 (4)	0.45
H20D	0.8991	0.8883	0.0559	0.144*	0.45
H20E	1.0636	0.9214	0.0847	0.144*	0.45
H20F	1.0210	1.0354	0.1419	0.144*	0.45

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0386 (13)	0.0321 (12)	0.0492 (14)	0.0161 (10)	0.0146 (11)	0.0155 (11)
C2	0.0356 (12)	0.0390 (13)	0.0489 (14)	0.0191 (11)	0.0073 (11)	0.0158 (11)
C3	0.0458 (14)	0.0377 (14)	0.0531 (16)	0.0168 (12)	0.0067 (12)	0.0137 (12)
C4	0.0505 (16)	0.0403 (14)	0.0597 (18)	0.0202 (12)	0.0016 (13)	0.0078 (13)
C5	0.0635 (18)	0.0623 (19)	0.0468 (16)	0.0320 (15)	0.0090 (14)	0.0100 (14)
C6	0.0608 (17)	0.0638 (19)	0.0512 (17)	0.0312 (15)	0.0154 (14)	0.0226 (15)
C7	0.0402 (13)	0.0455 (14)	0.0480 (15)	0.0213 (11)	0.0100 (11)	0.0179 (12)
C8	0.0396 (13)	0.0438 (14)	0.0535 (15)	0.0209 (11)	0.0130 (11)	0.0247 (12)
C9	0.0349 (12)	0.0346 (13)	0.0517 (15)	0.0161 (10)	0.0119 (11)	0.0185 (11)
C10	0.0416 (14)	0.0368 (14)	0.0659 (18)	0.0155 (11)	0.0098 (12)	0.0242 (13)
C11	0.0645 (19)	0.0407 (16)	0.078 (2)	0.0171 (14)	0.0130 (16)	0.0221 (15)
C12	0.0626 (19)	0.0362 (16)	0.099 (3)	0.0111 (14)	0.0108 (18)	0.0257 (16)
C13	0.0464 (16)	0.0534 (19)	0.116 (3)	0.0134 (14)	0.0198 (18)	0.053 (2)

C14	0.0520 (16)	0.0614 (19)	0.090 (2)	0.0234 (15)	0.0243 (16)	0.0482 (18)
C15	0.0381 (13)	0.0467 (15)	0.0700 (18)	0.0183 (12)	0.0129 (12)	0.0332 (14)
C16	0.0380 (12)	0.0318 (12)	0.0446 (13)	0.0158 (10)	0.0138 (10)	0.0146 (10)
C17	0.0418 (13)	0.0365 (13)	0.0477 (15)	0.0157 (11)	0.0146 (12)	0.0178 (12)
C18	0.0397 (13)	0.0427 (15)	0.0412 (13)	0.0188 (11)	0.0098 (11)	0.0162 (11)
C21	0.0421 (13)	0.0328 (12)	0.0456 (13)	0.0149 (10)	0.0171 (11)	0.0144 (10)
C22	0.0478 (14)	0.0428 (14)	0.0521 (15)	0.0219 (12)	0.0219 (12)	0.0179 (12)
C23	0.0496 (16)	0.0700 (19)	0.089 (2)	0.0272 (15)	0.0326 (16)	0.0456 (18)
C24	0.0500 (16)	0.070 (2)	0.101 (2)	0.0348 (15)	0.0330 (16)	0.0515 (19)
C25	0.0498 (15)	0.0369 (13)	0.0495 (15)	0.0179 (11)	0.0195 (12)	0.0184 (11)
C26	0.073 (2)	0.154 (4)	0.089 (2)	0.066 (2)	0.045 (2)	0.082 (3)
C27	0.096 (3)	0.189 (5)	0.100 (3)	0.078 (3)	0.059 (2)	0.103 (3)
C28	0.084 (2)	0.083 (2)	0.0649 (19)	0.0458 (19)	0.0302 (18)	0.0444 (18)
C29	0.083 (2)	0.105 (3)	0.083 (2)	0.064 (2)	0.0364 (19)	0.058 (2)
C30	0.075 (2)	0.103 (3)	0.084 (2)	0.059 (2)	0.0445 (18)	0.063 (2)
C31	0.128 (4)	0.151 (4)	0.099 (3)	0.083 (3)	0.046 (3)	0.087 (3)
N1	0.0409 (11)	0.0403 (11)	0.0696 (14)	0.0215 (9)	0.0232 (10)	0.0265 (11)
N2	0.0628 (15)	0.0466 (14)	0.0539 (15)	0.0163 (12)	0.0083 (12)	0.0115 (12)
N3	0.0512 (13)	0.0526 (14)	0.0619 (14)	0.0235 (11)	0.0195 (11)	0.0322 (12)
N4	0.0470 (12)	0.0355 (11)	0.0569 (13)	0.0172 (10)	0.0131 (10)	0.0185 (10)
O1	0.0612 (12)	0.0411 (11)	0.0619 (12)	0.0269 (9)	0.0211 (9)	0.0107 (9)
O2	0.0519 (11)	0.0607 (12)	0.0831 (14)	0.0326 (10)	0.0390 (10)	0.0394 (11)
C19	0.078 (2)	0.107 (3)	0.104 (3)	0.063 (2)	0.062 (2)	0.062 (2)
S1	0.0417 (4)	0.0768 (6)	0.0791 (6)	0.0151 (4)	0.0168 (4)	0.0345 (5)
C20	0.100 (8)	0.143 (9)	0.089 (5)	0.091 (7)	0.048 (5)	0.059 (6)
C20′	0.112 (10)	0.141 (11)	0.082 (6)	0.084 (10)	0.062 (6)	0.056 (7)

Geometric parameters (Å, º)

C1—N1	1.461 (3)	C21—H21	0.9800
C1—C9	1.528 (3)	C22—N1	1.461 (3)
C1—C2	1.546 (3)	C22—C23	1.550 (4)
C1—C16	1.581 (3)	C22—H22	0.9800
C2—C3	1.389 (3)	C23—S1	1.784 (3)
C2—C7	1.393 (4)	C23—H23A	0.9700
C3—C4	1.378 (4)	C23—H23B	0.9700
C3—H3	0.9300	C24—N1	1.440 (3)
C4—C5	1.375 (4)	C24—S1	1.825 (3)
C4—H4	0.9300	C24—H24A	0.9700
C5—C6	1.381 (4)	C24—H24B	0.9700
C5—H5	0.9300	C25—C26	1.366 (4)
C6—C7	1.385 (4)	C25—C30	1.379 (4)
C6—H6	0.9300	C26—C27	1.378 (5)
C7—C8	1.461 (3)	C26—H26	0.9300
C8—N3	1.306 (3)	C27—C28	1.370 (5)
C8—C9	1.425 (4)	C27—H27	0.9300
C9—N4	1.299 (3)	C28—C29	1.359 (5)
C10—N4	1.379 (3)	C28—C31	1.516 (5)

C10—C11	1.404 (4)	C29—C30	1.379 (4)
C10—C15	1.420 (4)	C29—H29	0.9300
C11—C12	1.361 (4)	C30—H30	0.9300
C11—H11	0.9300	C31—H31A	0.9600
C12—C13	1.386 (5)	C31—H31B	0.9600
C12—H12	0.9300	C31—H31C	0.9600
C13—C14	1.359 (5)	O2—C19	1.454 (3)
C13—H13	0.9300	C19—C20	1.474 (5)
C14—C15	1.408 (4)	C19—C20′	1.484 (5)
C14—H14	0.9300	C19—H19A	0.9700
C15—N3	1.374 (3)	C19—H19B	0.9700
C16—C17	1.479 (3)	C19—H19C	0.9700
C16—C18	1.542 (3)	C19—H19D	0.9700
C16—C21	1.553 (3)	C20—H20A	0.9600
C17—N2	1.135 (3)	C20—H20B	0.9600
C18—O1	1.188 (3)	C20—H20C	0.9600
C18—O2	1.320 (3)	C20′—H20D	0.9600
C21—C25	1.521 (3)	C20′—H20E	0.9600
C21—C22	1.531 (3)	C20′—H20F	0.9600

N1—C1—C9	111.29 (18)	C23—C22—H22	108.4
N1—C1—C2	119.08 (19)	C22—C23—S1	108.18 (19)
C9—C1—C2	100.51 (19)	C22—C23—H23A	110.1
N1—C1—C16	100.80 (19)	S1—C23—H23A	110.1
C9—C1—C16	114.22 (18)	C22—C23—H23B	110.1
C2—C1—C16	111.61 (18)	S1—C23—H23B	110.1
C3—C2—C7	119.0 (2)	H23A—C23—H23B	108.4
C3—C2—C1	130.0 (2)	N1—C24—S1	107.03 (19)
C7—C2—C1	111.0 (2)	N1—C24—H24A	110.3
C4—C3—C2	119.2 (3)	S1—C24—H24A	110.3
C4—C3—H3	120.4	N1—C24—H24B	110.3
C2—C3—H3	120.4	S1—C24—H24B	110.3
C5—C4—C3	121.4 (3)	H24A—C24—H24B	108.6
C5—C4—H4	119.3	C26—C25—C30	116.2 (3)
C3—C4—H4	119.3	C26—C25—C21	121.0 (3)
C4—C5—C6	120.5 (3)	C30—C25—C21	122.8 (2)
C4—C5—H5	119.8	C25—C26—C27	121.2 (3)
C6—C5—H5	119.8	C25—C26—H26	119.4
C5—C6—C7	118.4 (3)	C27—C26—H26	119.4
C5—C6—H6	120.8	C28—C27—C26	122.5 (3)
C7—C6—H6	120.8	C28—C27—H27	118.7
C6—C7—C2	121.6 (2)	C26—C27—H27	118.7
C6—C7—C8	129.1 (3)	C29—C28—C27	116.2 (3)
C2—C7—C8	109.3 (2)	C29—C28—C31	121.3 (3)
N3—C8—C9	123.7 (2)	C27—C28—C31	122.4 (3)
N3—C8—C7	128.1 (2)	C28—C29—C30	121.7 (3)
C9—C8—C7	108.1 (2)	C28—C29—H29	119.1
N4—C9—C8	123.8 (2)	C30—C29—H29	119.1

N4—C9—C1	125.3 (2)	C29—C30—C25	121.9 (3)
C8—C9—C1	110.8 (2)	C29—C30—H30	119.1
N4—C10—C11	119.1 (3)	C25—C30—H30	119.1
N4—C10—C15	121.8 (2)	C28—C31—H31A	109.5
C11—C10—C15	119.1 (3)	C28—C31—H31B	109.5
C12—C11—C10	120.6 (3)	H31A—C31—H31B	109.5
C12—C11—H11	119.7	C28—C31—H31C	109.5
C10—C11—H11	119.7	H31A—C31—H31C	109.5
C11—C12—C13	120.2 (3)	H31B—C31—H31C	109.5
C11—C12—H12	119.9	C24—N1—C22	112.6 (2)
C13—C12—H12	119.9	C24—N1—C1	118.3 (2)
C14—C13—C12	121.2 (3)	C22—N1—C1	112.25 (18)
C14—C13—H13	119.4	C8—N3—C15	114.3 (2)
C12—C13—H13	119.4	C9—N4—C10	114.4 (2)
C13—C14—C15	120.3 (3)	C18—O2—C19	117.1 (2)
C13—C14—H14	119.8	O2—C19—C20	111.1 (5)
C15—C14—H14	119.8	O2—C19—C20′	109.8 (6)
N3—C15—C14	119.5 (3)	O2—C19—H19A	109.4
N3—C15—C10	121.9 (2)	C20—C19—H19A	109.4
C14—C15—C10	118.6 (3)	O2—C19—H19B	109.4
C17—C16—C18	109.64 (19)	C20—C19—H19B	109.4
C17—C16—C21	109.5 (2)	H19A—C19—H19B	108.0
C18—C16—C21	114.19 (19)	O2—C19—H19C	109.7
C17—C16—C1	111.59 (18)	C20′—C19—H19C	109.7
C18—C16—C1	109.77 (19)	O2—C19—H19D	109.7
C21—C16—C1	101.94 (18)	C20′—C19—H19D	109.7
N2—C17—C16	176.0 (3)	H19C—C19—H19D	108.2
O1—C18—O2	126.5 (2)	C23—S1—C24	90.07 (14)
O1—C18—C16	123.8 (2)	C19—C20—H20A	109.5
O2—C18—C16	109.7 (2)	C19—C20—H20B	109.5
C25—C21—C22	115.2 (2)	H20A—C20—H20B	109.5
C25—C21—C16	117.8 (2)	C19—C20—H20C	109.5
C22—C21—C16	102.65 (19)	H20A—C20—H20C	109.5
C25—C21—H21	106.8	H20B—C20—H20C	109.5
C22—C21—H21	106.8	C19—C20′—H20D	109.5
C16—C21—H21	106.8	C19—C20′—H20E	109.5
N1—C22—C21	105.81 (19)	H20D—C20′—H20E	109.5
N1—C22—C23	109.4 (2)	C19—C20′—H20F	109.5
C21—C22—C23	116.1 (2)	H20D—C20′—H20F	109.5
N1—C22—H22	108.4	H20E—C20′—H20F	109.5
C21—C22—H22	108.4		

N1—C1—C2—C3	−55.0 (3)	C21—C16—C18—O2	−171.9 (2)
C9—C1—C2—C3	−176.7 (2)	C1—C16—C18—O2	74.3 (2)
C16—C1—C2—C3	61.8 (3)	C17—C16—C21—C25	−47.3 (3)
N1—C1—C2—C7	126.1 (2)	C18—C16—C21—C25	76.1 (3)
C9—C1—C2—C7	4.4 (2)	C1—C16—C21—C25	−165.60 (19)
C16—C1—C2—C7	−117.1 (2)	C17—C16—C21—C22	80.4 (2)

C7—C2—C3—C4	0.1 (4)	C18—C16—C21—C22	−156.2 (2)
C1—C2—C3—C4	−178.7 (2)	C1—C16—C21—C22	−37.9 (2)
C2—C3—C4—C5	−0.4 (4)	C25—C21—C22—N1	152.5 (2)
C3—C4—C5—C6	0.3 (4)	C16—C21—C22—N1	23.1 (2)
C4—C5—C6—C7	0.0 (4)	C25—C21—C22—C23	−86.0 (3)
C5—C6—C7—C2	−0.3 (4)	C16—C21—C22—C23	144.7 (2)
C5—C6—C7—C8	−178.2 (3)	N1—C22—C23—S1	12.8 (3)
C3—C2—C7—C6	0.2 (4)	C21—C22—C23—S1	−106.8 (2)
C1—C2—C7—C6	179.3 (2)	C22—C21—C25—C26	22.1 (4)
C3—C2—C7—C8	178.5 (2)	C16—C21—C25—C26	143.6 (3)
C1—C2—C7—C8	−2.5 (3)	C22—C21—C25—C30	−158.7 (3)
C6—C7—C8—N3	−0.8 (4)	C16—C21—C25—C30	−37.3 (4)
C2—C7—C8—N3	−178.9 (2)	C30—C25—C26—C27	−4.4 (6)
C6—C7—C8—C9	177.3 (3)	C21—C25—C26—C27	174.8 (4)
C2—C7—C8—C9	−0.8 (3)	C25—C26—C27—C28	1.2 (7)
N3—C8—C9—N4	4.4 (4)	C26—C27—C28—C29	2.7 (7)
C7—C8—C9—N4	−173.8 (2)	C26—C27—C28—C31	179.9 (4)
N3—C8—C9—C1	−178.0 (2)	C27—C28—C29—C30	−3.2 (6)
C7—C8—C9—C1	3.8 (3)	C31—C28—C29—C30	179.5 (4)
N1—C1—C9—N4	45.6 (3)	C28—C29—C30—C25	−0.1 (6)
C2—C1—C9—N4	172.7 (2)	C26—C25—C30—C29	3.9 (5)
C16—C1—C9—N4	−67.7 (3)	C21—C25—C30—C29	−175.3 (3)
N1—C1—C9—C8	−131.9 (2)	S1—C24—N1—C22	−32.2 (3)
C2—C1—C9—C8	−4.9 (2)	S1—C24—N1—C1	101.5 (2)
C16—C1—C9—C8	114.8 (2)	C21—C22—N1—C24	138.6 (2)
N4—C10—C11—C12	179.4 (3)	C23—C22—N1—C24	12.8 (3)
C15—C10—C11—C12	−1.0 (4)	C21—C22—N1—C1	2.1 (3)
C10—C11—C12—C13	0.8 (5)	C23—C22—N1—C1	−123.7 (2)
C11—C12—C13—C14	−0.6 (5)	C9—C1—N1—C24	79.0 (3)
C12—C13—C14—C15	0.6 (5)	C2—C1—N1—C24	−37.2 (3)
C13—C14—C15—N3	177.5 (3)	C16—C1—N1—C24	−159.5 (2)
C13—C14—C15—C10	−0.8 (4)	C9—C1—N1—C22	−147.2 (2)
N4—C10—C15—N3	2.4 (4)	C2—C1—N1—C22	96.6 (3)
C11—C10—C15—N3	−177.2 (2)	C16—C1—N1—C22	−25.7 (2)
N4—C10—C15—C14	−179.4 (2)	C9—C8—N3—C15	−1.9 (3)
C11—C10—C15—C14	1.0 (4)	C7—C8—N3—C15	175.9 (2)
N1—C1—C16—C17	−78.2 (2)	C14—C15—N3—C8	−179.4 (2)
C9—C1—C16—C17	41.2 (3)	C10—C15—N3—C8	−1.2 (3)
C2—C1—C16—C17	154.3 (2)	C8—C9—N4—C10	−3.0 (3)
N1—C1—C16—C18	160.00 (18)	C1—C9—N4—C10	179.8 (2)
C9—C1—C16—C18	−80.6 (2)	C11—C10—N4—C9	179.4 (2)
C2—C1—C16—C18	32.6 (3)	C15—C10—N4—C9	−0.2 (3)
N1—C1—C16—C21	38.6 (2)	O1—C18—O2—C19	−3.3 (4)
C9—C1—C16—C21	158.01 (19)	C16—C18—O2—C19	178.7 (2)
C2—C1—C16—C21	−88.8 (2)	C18—O2—C19—C20	87.4 (5)
C17—C16—C18—O1	133.3 (2)	C18—O2—C19—C20′	123.8 (6)
C21—C16—C18—O1	10.0 (3)	C22—C23—S1—C24	−26.2 (2)
C1—C16—C18—O1	−103.7 (3)	N1—C24—S1—C23	33.7 (2)

C17—C16—C18—O2	−48.6 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···S1^{i}	0.93	3.01	3.881 (4)	156
C23—H23*A*···N2^{ii}	0.97	2.70	3.610 (4)	156
C4—H4···O1^{iii}	0.93	2.43	3.332 (3)	162

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*; (ii) −*x*+1, −*y*+2, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*.