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Crystal structure of ethyl 4-(2,4-dichlorophenyl)-2-methyl-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

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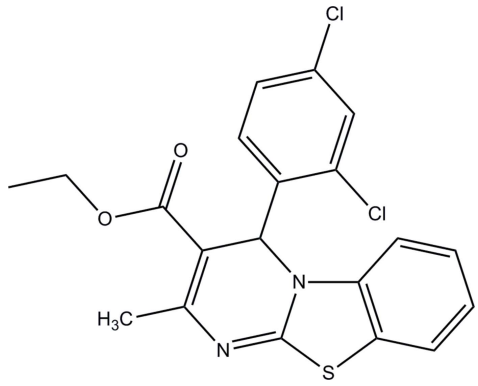
In the title compound, $C_{20}H_{16}Cl_2N_2O_2S$, the pyrimidine ring has a screw-boat conformation. The attached dichlorophenyl ring is twisted at an angle of 89.29 (13)° with respect to the pyrimidine ring mean plane. The benzothiazole group is approximately planar (r.m.s. deviation = 0.008 Å) and inclined to the pyrimidine ring mean plane by 3.04 (10)°. The carboxylate group assumes an extended conformation with respect to the pyrimidine ring, which can be seen from the O=C—O—C torsion angle of 3.2 (4) °. In the crystal, molecules are linked *via* C—H···O and C—H···N hydrogen bonds, forming slabs lying parallel to (100).

Keywords: crystal structure; pyrimidine; benzothiazole; C—H···O hydrogen bonds; C—H···N hydrogen bonds.

CCDC reference: 1056200

1. Related literature

For general background and literature on the biological properties of pyrimidine derivatives, see: Kumar *et al.* (2002); Baraldi *et al.* (2002); Nasr & Gineinah (2002).



2. Experimental

2.1. Crystal data

$C_{20}H_{16}Cl_2N_2O_2S$
M_r = 419.31
Monoclinic, $C2/c$
a = 38.654 (8) Å
b = 11.787 (3) Å
c = 8.774 (2) Å
β = 102.415 (14)°
V = 3904.1 (15) Å^3
Z = 8
Cu $K\alpha$ radiation
μ = 4.14 mm^{-1}
T = 296 K
0.30 × 0.27 × 0.25 mm

2.2. Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.370, T_{max} = 0.424
10089 measured reflections
3114 independent reflections
2519 reflections with $I > 2\sigma(I)$
R_{int} = 0.042

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.139
S = 1.04
3114 reflections
246 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···N1^{i}	0.93	2.59	3.515 (4)	176
C16—H16···O24^{ii}	0.93	2.53	3.180 (4)	128

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x, -y+2, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5114).

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supporting information

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Crystal structure of ethyl 4-(2,4-dichlorophenyl)-2-methyl-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

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S1. Structural commentary

Many pyrimidine derivatives are reported to have anti-bacterial, anti-tumor and anti-viral activities (Kumar *et al.*, 2012; Baraldi *et al.*, 2002; Nasr *et al.*, 2002). In view of their important properties we synthesized the title compound and report herein on its crystal structure.

The molecular structure of the title compound is shown in Fig. 1. The pyrimidine ring [N1/C13/C12/C11/N10/C2] has a screw-boat conformation and its mean plane is inclined to the planar benzothiazole group [S3/C2/N10/C4—C9; r.m.s. deviation = 0.008 Å] by 3.04 (10) °. The dichlorophenyl ring [C15—C20] is twisted at an angle of 89.29 (13) ° with respect to the pyrimidine ring mean plane. The carboxylate group assumes an extended conformation with respect to the pyrimidine ring, which can be seen from the torsion angle O24—C23—O25—C26 = 3.2 (4) °.

In the crystal, molecules are linked via C—H···O and C—H···N hydrogen bonds forming slabs lying parallel to (100); see Table 1 and Fig. 2.

S2. Synthesis and crystallization

A mixture of 2,4-dichloro benzaldehyde was treated with ethyl acetoacetate and 2-aminobenzothiazole in the presence of ammonium acetate in ethanol. The mixture was gently warmed in a water bath at 353 K until the colour changed and it was then kept aside overnight at room temperature. The completion of reaction was monitored by TLC. The solid obtained was separated and purified by means of column chromatography using hexane and ethyl acetate as eluent. The sample was recrystallized using a 1:1 mixture of ethanol and THF, yielding yellow block-like crystals.

S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geometrically and allowed to ride on their parent atoms: C—H = 0.93-0.98 Å with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for other H atoms.

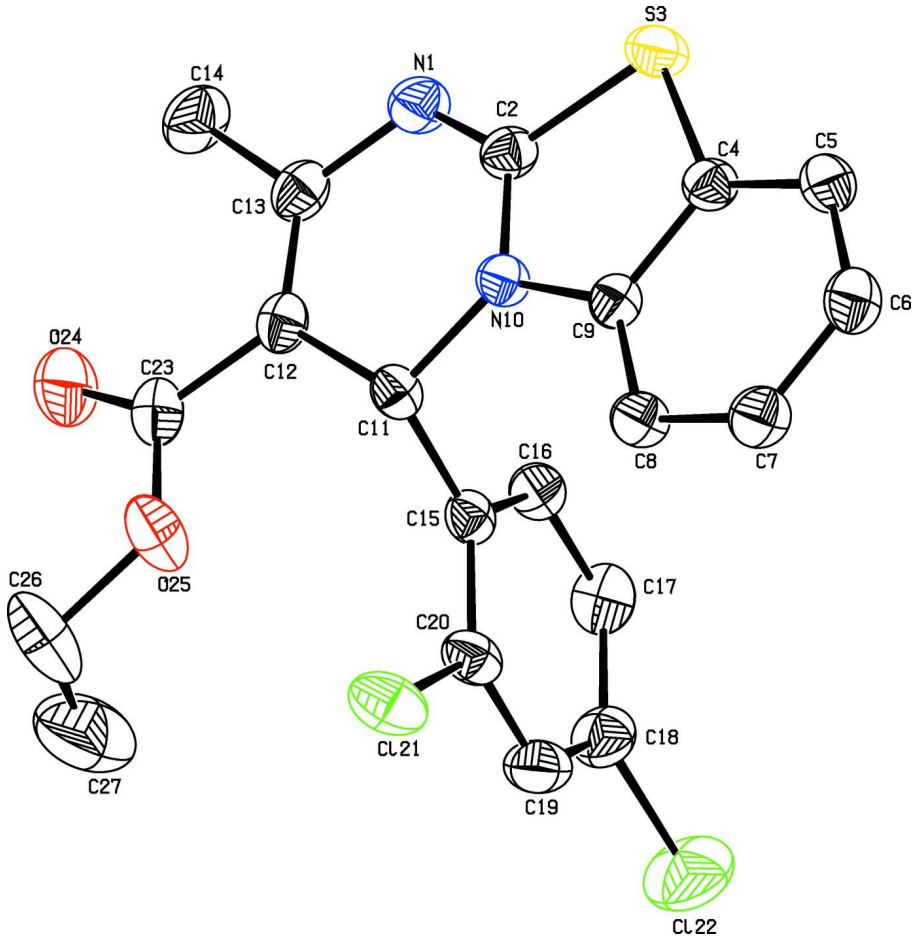

Figure 1

The molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

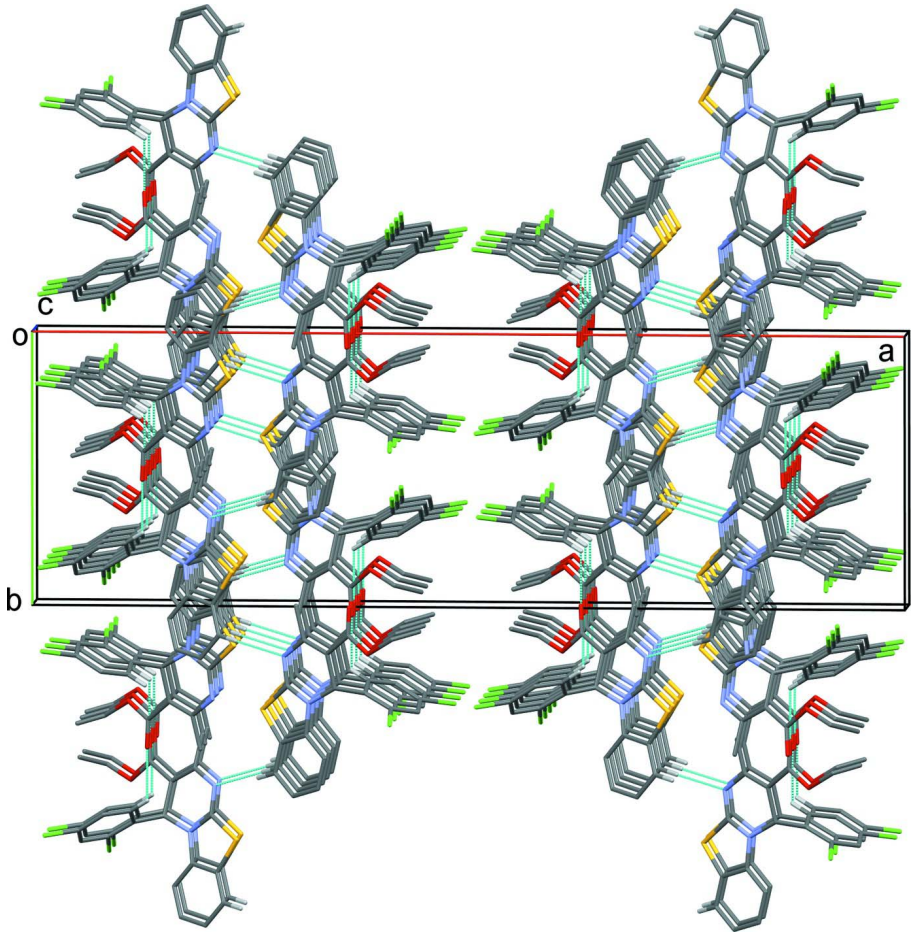

Figure 2

The crystal packing of the molecules viewed down the *c* axis.

Ethyl 4-(2,4-dichlorophenyl)-2-methyl-4*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate

Crystal data

$C_{20}H_{16}Cl_2N_2O_2S$
$M_r = 419.31$
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
$a = 38.654$ (8) Å
$b = 11.787$ (3) Å
$c = 8.774$ (2) Å
$\beta = 102.415$ (14)°
$V = 3904.1$ (15) Å^3
$Z = 8$
$F(000) = 1728$
$D_x = 1.427$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 3114 reflections
$\theta = 5.1$–$64.1°$
$\mu = 4.14$ mm^{-1}
$T = 296$ K
Block, yellow
0.30 × 0.27 × 0.25 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min} = 0.370$, $T_{max} = 0.424$
10089 measured reflections
3114 independent reflections
2519 reflections with $I > 2\sigma(I)$

R_{int} = 0.042
θ_{max} = 64.1°, θ_{min} = 5.1°
h = −43→44
k = −12→12
l = −10→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.139
S = 1.04
3114 reflections
246 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
$w = 1/[\sigma^2(F_o^2) + (0.0772P)^2 + 2.6744P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
N1	0.29291 (6)	0.8365 (2)	0.6499 (3)	0.0540 (6)
C2	0.29669 (6)	0.7278 (2)	0.6518 (3)	0.0450 (6)
S3	0.267722 (17)	0.63964 (6)	0.72345 (9)	0.0552 (3)
C4	0.28999 (6)	0.5193 (2)	0.6806 (3)	0.0446 (6)
C5	0.28233 (7)	0.4079 (2)	0.7057 (3)	0.0520 (7)
H5	0.2631	0.3891	0.7488	0.062*
C6	0.30359 (8)	0.3250 (3)	0.6658 (4)	0.0561 (7)
H6	0.2990	0.2492	0.6832	0.067*
C7	0.33195 (8)	0.3533 (2)	0.5997 (4)	0.0560 (7)
H7	0.3460	0.2958	0.5730	0.067*
C8	0.33984 (7)	0.4649 (2)	0.5723 (3)	0.0484 (7)
H8	0.3589	0.4831	0.5276	0.058*
C9	0.31847 (6)	0.5488 (2)	0.6136 (3)	0.0406 (6)
N10	0.32157 (5)	0.66662 (18)	0.5982 (2)	0.0417 (5)
C11	0.35145 (6)	0.7226 (2)	0.5479 (3)	0.0411 (6)
H11	0.3537	0.6908	0.4474	0.049*
C12	0.34297 (7)	0.8489 (2)	0.5275 (3)	0.0463 (6)
C13	0.31608 (7)	0.8979 (2)	0.5811 (3)	0.0513 (7)
C14	0.30725 (9)	1.0217 (3)	0.5713 (4)	0.0694 (9)
H14A	0.3263	1.0638	0.6345	0.104*
H14B	0.2859	1.0344	0.6084	0.104*
H14C	0.3038	1.0464	0.4649	0.104*

C15	0.38581 (6)	0.7024 (2)	0.6676 (3)	0.0409 (6)
C16	0.38873 (7)	0.7454 (2)	0.8175 (3)	0.0472 (6)
H16	0.3695	0.7836	0.8417	0.057*
C17	0.41907 (8)	0.7332 (3)	0.9307 (4)	0.0608 (8)
H17	0.4205	0.7630	1.0300	0.073*
C18	0.44751 (8)	0.6758 (3)	0.8946 (4)	0.0627 (8)
C19	0.44582 (7)	0.6332 (3)	0.7486 (4)	0.0612 (8)
H19	0.4651	0.5953	0.7251	0.073*
C20	0.41531 (7)	0.6470 (2)	0.6369 (3)	0.0491 (7)
Cl21	0.41503 (2)	0.59197 (7)	0.45153 (10)	0.0706 (3)
Cl22	0.48585 (3)	0.65809 (11)	1.03772 (14)	0.1075 (4)
C23	0.36748 (8)	0.9170 (3)	0.4592 (3)	0.0556 (7)
O24	0.36870 (7)	1.0189 (2)	0.4524 (3)	0.0880 (8)
O25	0.39033 (6)	0.8507 (2)	0.4043 (3)	0.0734 (7)
C26	0.41805 (13)	0.9061 (4)	0.3433 (5)	0.1021 (15)
H26A	0.4088	0.9754	0.2903	0.122*
H26B	0.4253	0.8568	0.2674	0.122*
C27	0.44862 (13)	0.9328 (5)	0.4666 (8)	0.134 (2)
H27A	0.4416	0.9836	0.5400	0.201*
H27B	0.4665	0.9682	0.4221	0.201*
H27C	0.4579	0.8642	0.5190	0.201*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0535 (13)	0.0408 (15)	0.0701 (16)	0.0048 (10)	0.0185 (12)	−0.0012 (11)
C2	0.0429 (13)	0.0401 (17)	0.0513 (15)	0.0021 (11)	0.0086 (11)	−0.0025 (12)
S3	0.0456 (4)	0.0476 (5)	0.0771 (5)	0.0017 (3)	0.0239 (3)	0.0002 (3)
C4	0.0394 (12)	0.0424 (17)	0.0512 (15)	−0.0019 (11)	0.0077 (11)	0.0004 (12)
C5	0.0495 (15)	0.0455 (18)	0.0619 (17)	−0.0077 (13)	0.0142 (13)	0.0038 (13)
C6	0.0656 (18)	0.0351 (16)	0.0682 (19)	−0.0063 (13)	0.0155 (15)	0.0017 (13)
C7	0.0608 (17)	0.0400 (18)	0.0682 (19)	0.0019 (13)	0.0163 (15)	−0.0035 (14)
C8	0.0491 (14)	0.0408 (17)	0.0574 (17)	−0.0014 (12)	0.0162 (12)	−0.0049 (13)
C9	0.0420 (13)	0.0351 (15)	0.0429 (14)	−0.0045 (11)	0.0050 (11)	−0.0022 (11)
N10	0.0421 (11)	0.0343 (13)	0.0502 (12)	−0.0013 (9)	0.0136 (10)	−0.0016 (9)
C11	0.0462 (13)	0.0366 (15)	0.0432 (14)	−0.0043 (11)	0.0154 (11)	−0.0037 (11)
C12	0.0538 (15)	0.0379 (16)	0.0450 (15)	−0.0023 (11)	0.0058 (12)	0.0034 (11)
C13	0.0560 (16)	0.0381 (16)	0.0563 (17)	0.0024 (12)	0.0044 (13)	0.0004 (12)
C14	0.075 (2)	0.0404 (19)	0.092 (2)	0.0083 (15)	0.0153 (18)	0.0044 (16)
C15	0.0456 (13)	0.0315 (14)	0.0479 (14)	−0.0041 (11)	0.0152 (11)	−0.0003 (11)
C16	0.0526 (14)	0.0401 (16)	0.0513 (15)	0.0009 (12)	0.0165 (12)	−0.0034 (12)
C17	0.0724 (19)	0.057 (2)	0.0495 (17)	−0.0046 (16)	0.0048 (15)	−0.0073 (14)
C18	0.0493 (16)	0.063 (2)	0.070 (2)	−0.0035 (15)	0.0002 (14)	0.0069 (16)
C19	0.0433 (15)	0.057 (2)	0.085 (2)	0.0012 (13)	0.0171 (15)	0.0003 (17)
C20	0.0490 (14)	0.0414 (16)	0.0623 (17)	−0.0040 (12)	0.0241 (13)	−0.0068 (13)
Cl21	0.0700 (5)	0.0747 (6)	0.0771 (5)	−0.0009 (4)	0.0375 (4)	−0.0252 (4)
Cl22	0.0677 (6)	0.1307 (10)	0.1058 (8)	0.0037 (6)	−0.0221 (5)	0.0064 (7)
C23	0.0678 (18)	0.048 (2)	0.0501 (17)	−0.0049 (14)	0.0103 (14)	0.0078 (13)

O24	0.0960 (18)	0.0479 (16)	0.127 (2)	−0.0077 (12)	0.0385 (16)	0.0245 (14)
O25	0.0905 (16)	0.0654 (16)	0.0767 (15)	−0.0168 (12)	0.0455 (13)	−0.0005 (11)
C26	0.126 (3)	0.104 (3)	0.098 (3)	−0.039 (3)	0.071 (3)	−0.006 (2)
C27	0.088 (3)	0.143 (5)	0.182 (6)	−0.025 (3)	0.050 (4)	−0.008 (4)

Geometric parameters (Å, º)

N1—C2	1.290 (4)	C14—H14A	0.9600
N1—C13	1.387 (4)	C14—H14B	0.9600
C2—N10	1.364 (3)	C14—H14C	0.9600
C2—S3	1.741 (3)	C15—C20	1.390 (3)
S3—C4	1.741 (3)	C15—C16	1.392 (4)
C4—C5	1.375 (4)	C16—C17	1.372 (4)
C4—C9	1.399 (3)	C16—H16	0.9300
C5—C6	1.369 (4)	C17—C18	1.384 (4)
C5—H5	0.9300	C17—H17	0.9300
C6—C7	1.387 (4)	C18—C19	1.365 (5)
C6—H6	0.9300	C18—Cl22	1.737 (3)
C7—C8	1.383 (4)	C19—C20	1.371 (4)
C7—H7	0.9300	C19—H19	0.9300
C8—C9	1.385 (4)	C20—Cl21	1.748 (3)
C8—H8	0.9300	C23—O24	1.204 (4)
C9—N10	1.403 (3)	C23—O25	1.343 (4)
N10—C11	1.478 (3)	O25—C26	1.452 (4)
C11—C15	1.524 (3)	C26—C27	1.455 (7)
C11—C12	1.527 (4)	C26—H26A	0.9700
C11—H11	0.9800	C26—H26B	0.9700
C12—C13	1.358 (4)	C27—H27A	0.9600
C12—C23	1.465 (4)	C27—H27B	0.9600
C13—C14	1.497 (4)	C27—H27C	0.9600
C2—N1—C13	116.2 (2)	C13—C14—H14B	109.5
N1—C2—N10	127.4 (2)	H14A—C14—H14B	109.5
N1—C2—S3	121.2 (2)	C13—C14—H14C	109.5
N10—C2—S3	111.4 (2)	H14A—C14—H14C	109.5
C4—S3—C2	91.26 (12)	H14B—C14—H14C	109.5
C5—C4—C9	121.3 (2)	C20—C15—C16	116.8 (2)
C5—C4—S3	127.6 (2)	C20—C15—C11	124.7 (2)
C9—C4—S3	111.0 (2)	C16—C15—C11	118.4 (2)
C6—C5—C4	118.6 (3)	C17—C16—C15	121.9 (3)
C6—C5—H5	120.7	C17—C16—H16	119.0
C4—C5—H5	120.7	C15—C16—H16	119.0
C5—C6—C7	120.5 (3)	C16—C17—C18	118.9 (3)
C5—C6—H6	119.8	C16—C17—H17	120.6
C7—C6—H6	119.7	C18—C17—H17	120.6
C8—C7—C6	121.6 (3)	C19—C18—C17	121.0 (3)
C8—C7—H7	119.2	C19—C18—Cl22	119.7 (3)
C6—C7—H7	119.2	C17—C18—Cl22	119.3 (3)

C7—C8—C9	117.9 (3)	C18—C19—C20	119.2 (3)
C7—C8—H8	121.1	C18—C19—H19	120.4
C9—C8—H8	121.1	C20—C19—H19	120.4
C8—C9—C4	120.0 (2)	C19—C20—C15	122.2 (3)
C8—C9—N10	127.8 (2)	C19—C20—Cl21	117.0 (2)
C4—C9—N10	112.2 (2)	C15—C20—Cl21	120.9 (2)
C2—N10—C9	114.1 (2)	O24—C23—O25	121.8 (3)
C2—N10—C11	121.4 (2)	O24—C23—C12	127.0 (3)
C9—N10—C11	124.0 (2)	O25—C23—C12	111.2 (3)
N10—C11—C15	110.2 (2)	C23—O25—C26	117.7 (3)
N10—C11—C12	108.0 (2)	O25—C26—C27	111.6 (4)
C15—C11—C12	111.5 (2)	O25—C26—H26A	109.3
N10—C11—H11	109.0	C27—C26—H26A	109.3
C15—C11—H11	109.0	O25—C26—H26B	109.3
C12—C11—H11	109.0	C27—C26—H26B	109.3
C13—C12—C23	121.3 (3)	H26A—C26—H26B	108.0
C13—C12—C11	122.4 (2)	C26—C27—H27A	109.5
C23—C12—C11	116.1 (2)	C26—C27—H27B	109.5
C12—C13—N1	122.9 (3)	H27A—C27—H27B	109.5
C12—C13—C14	125.2 (3)	C26—C27—H27C	109.5
N1—C13—C14	111.9 (3)	H27A—C27—H27C	109.5
C13—C14—H14A	109.5	H27B—C27—H27C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···N1^{i}	0.93	2.59	3.515 (4)	176
C16—H16···O24^{ii}	0.93	2.53	3.180 (4)	128

Symmetry codes: (i) −*x*+1/2, *y*−1/2, −*z*+3/2; (ii) *x*, −*y*+2, *z*+1/2.