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# *N*-[4-(9-Chloroquino[3,2-*b*]benzo[1,4]-thiazin-6-yl)butyl]acetamide[1]

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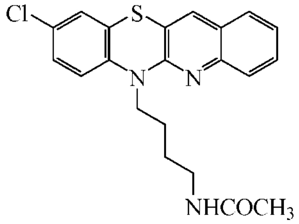
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.006 Å; $R$ factor = 0.067; $wR$ factor = 0.127; data-to-parameter ratio = 12.4.

In the title molecule, $C_{21}H_{20}ClN_3OS$, the tetracyclic system is close to planar [r.m.s. deviation = 0.110 (4) Å]. The dihedral angle between the quinoline ring system and the benzene ring is 178.3 (1)° and the angle between two (S—C=C—N) halves of the thiazine ring is 173.4 (1)°. In the crystal, molecules are arranged *via* $\pi$–$\pi$ interactions [centroid–centroid distances = 3.603 (2)–3.739 (2) Å] into slipped stacks extending along [010]. Intermolecular N—H$\cdots$O hydrogen bonds link the amide groups of neighbouring molecules along the stack, generating a $C$(4) motif. The title compound shows promising antiproliferative and anticancer activity.

## Related literature

For recent literature on biological activity of phenothiazines, see: Aaron *et al.* (2009); Pluta *et al.* (2011). For the synthesis and biological activity of 6-substituted quinobenzothiazines, see: Jeleń & Pluta (2009); Pluta *et al.* (2012). For the folded structures of similar tetracyclic systems, see: Jeleń *et al.* (2012); Luck *et al.* (2003); Yoshida *et al.* (1994). For crystal structures of phenothiazines, see: Chu (1988). For information on aza-phenothiazines, and their nomenclature and synthesis, see: Pluta *et al.* (2009).




[1] Part CXXXIII in the series of *Azinyl sulfides*.

## Experimental

### *Crystal data*

| | |
|---|---|
| $C_{21}H_{20}ClN_3OS$ | $V$ = 1805.3 (4) Å$^3$ |
| $M_r$ = 397.92 | $Z$ = 4 |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a$ = 12.7800 (4) Å | $\mu$ = 0.35 mm$^{-1}$ |
| $b$ = 4.9530 (11) Å | $T$ = 100 K |
| $c$ = 28.781 (2) Å | 0.60 × 0.10 × 0.05 mm |
| $\beta$ = 97.726 (5)° | |

### *Data collection*

| | |
|---|---|
| Nonius KappaCCD diffractometer upgraded with an APEXII detector | 3032 independent reflections |
| 17434 measured reflections | 1987 reflections with $I > 2\sigma(I)$ |
| | $R_{int}$ = 0.121 |

### *Refinement*

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.067 | 245 parameters |
| $wR(F^2)$ = 0.127 | H-atom parameters constrained |
| $S$ = 1.10 | $\Delta\rho_{max}$ = 0.32 e Å$^{-3}$ |
| 3032 reflections | $\Delta\rho_{min}$ = −0.29 e Å$^{-3}$ |

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

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N18—H18$\cdots$O21$^{i}$ | 0.88 | 1.97 | 2.819 (4) | 163 |

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2524).

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# supplementary materials

*Acta Cryst.* (2012). E**68**, o3324–o3325 [doi:10.1107/S1600536812045680]

## *N*-[4-(9-Chloroquino[3,2-*b*]benzo[1,4]thiazin-6-yl)butyl]acetamide

**Małgorzata Jeleń, Kinga Suwińska, Krystian Pluta and Beata Morak-Młodawska**

### Comment

Classical phenothiazines are widely recognized as neuroleptic, antihistaminic and antitissive drugs. New phenothiazines are obtained by the introduction of new pharmacophoric substituents at the thiazine nitrogen atom and the substitution of the benzene ring with an azine ring (Pluta *et al.*, 2009, 2011). Both classical and newly synthesized phenothiazines exhibit valuable anticancer, antibacterial and reversal multidrug resistance (Aaron *et al.*, 2009; Pluta *et al.*, 2011). We modified the phenothiazine structure *via* the substitution of the benzene ring with the quinoline ring to form linear fused quinobenzothiazines. The title compound (Fig. 1) was obtained in a few step synthesis starting from the reaction of diquinodithiin or 2,2′-dichloro-3,3′-diquinolinyl disulfide with p-chloroaniline. The obtained 6H-9-chloroquinobenzothiazine *via* thiazine ring formation (Pluta *et al.*, 2009) was next alkylated with phthalimidobutyl bromide, hydrolyzed with hydrazine and acetylated with acetic anhydride (Pluta *et al.*, 2012). The structure elucidation was based on the $^{1}$H NMR spectrum which did not take all the doubts away. These reactions may lead to alternative products (II-V) (Fig. 1) as the results of other ring closure reaction, the Smiles rearrangement, tautomeric forms and competitive N-alkylation. The X-ray analysis fully confirmed the proposed structure as [3,2-*b*], the chlorine atom in position 9 and the acetylaminobutyl substituent at the thiazine nitrogen atom N6. The tetracyclic ring system (the plane from C1 atom up to C12A atom) in title molecule is unexpectedly almost planar [r.m.s. deviation 0.110 (4) Å]) with the dihedral angle between the quinoline and the benzene ring of 178.3 (1)° and the angle between two halves of the thiazine ring of 173.4 (1)°. All the classical neuroleptic phenothiazines are folded along theN–S axis with the angle of 134.0–153.6 ° (Chu, 1988) and the title molecule is the first example of planar azaphenothiazine with the aminoalkyl group at the thiazine nitrogen atom. Other similar tetracyclic compounds with the thiazine ring, 6-benzyl-10-trifluoromethylquinobenzothiazine (Pluta *et al.*, 2012), 6-methyldihydroquinobenzothiazine (Luck *et al.*, 2003) and 5H-naphthobenzothiazine (Yoshida *et al.*, 1994) were also folded. Close to planar structure was 6H-8-trifluoromethylquinobenzothiazine (Pluta *et al.*, 2012). The C10A–S11–C11A and C5A–N6–C6A bond angles are quite large, 102.2 (2)° and 123.8 (3)° and enable the thiazine ring to adopt the flat conformation. Both the thiazine N6 and the amide N18 nitrogen atoms do not show pyramidality as the sum of C–N–X bond angles (X = C or H) is 360.1 (5)° and 360°, repectively. The side chain is not coplanar with the tetracyclic system. The torsion angles involving the butyl group (C14–C17) show the antiperiplanar arrangement of the carbon chain. The torsion angle C16–C17–N18–C19 [135.2 (4)°] describes the anticlinal arrangement of these atoms. In the crystal, molecules are arranged into stacks *via* $\pi$–$\pi$ interactions with centroid-to-centroid distances in the range of 3.603 (2)–3.739 (2) Å and extending along the *b* crystallographic axis ( Fig. 3). N–H···O hydrogen bond (Table 1) connects adjacent molecules along the stacks via catemeric C(4) motif (Fig. 4). The significant antiproliferative and anticancer activities of the title molecule most probably result from intercalation of specific DNA by the planar azaphenothiazine system.

**Experimental**

The title compound was obtained in a few step synthesis starting from the reaction of diquinodithiin or 2,2′-dichloro-3,3′-diquinolinyl disulfide with p-chloroaniline (Jeleń *et al.*, 2009). The obtained 6H-9-chloroquinobenzothiazine was alkylated with phthalimidobutyl bromide in dry toluene in the presence of sodium hydride, hydrolyzed with hydrazine in ethanol and acetylated with acetican hydride in pyridine. The title compound has melting point 417-418 K (Pluta *et al.*, 2012). X-ray quality crystals were grown from chloroform-ethanol mixture by slow evaporation.

**Refinement**

All H atoms were treated as riding atoms in geometrically calculated positions, with d(C–H) = 0.95, 0.99 and 0.98 Å for aromatic, methylene and methyl hydrogens, respectively, d(N–H) = 0.88 Å , and $U_{iso}$(H) = $kU_{eq}$(C,N), where $k$ = 1.5 for the methyl group and $k$ = 1.2 otherwise.

**Computing details**

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

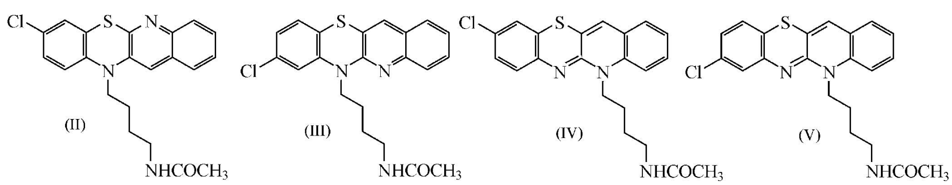


**Figure 1**

Alternative structures of the title compound.

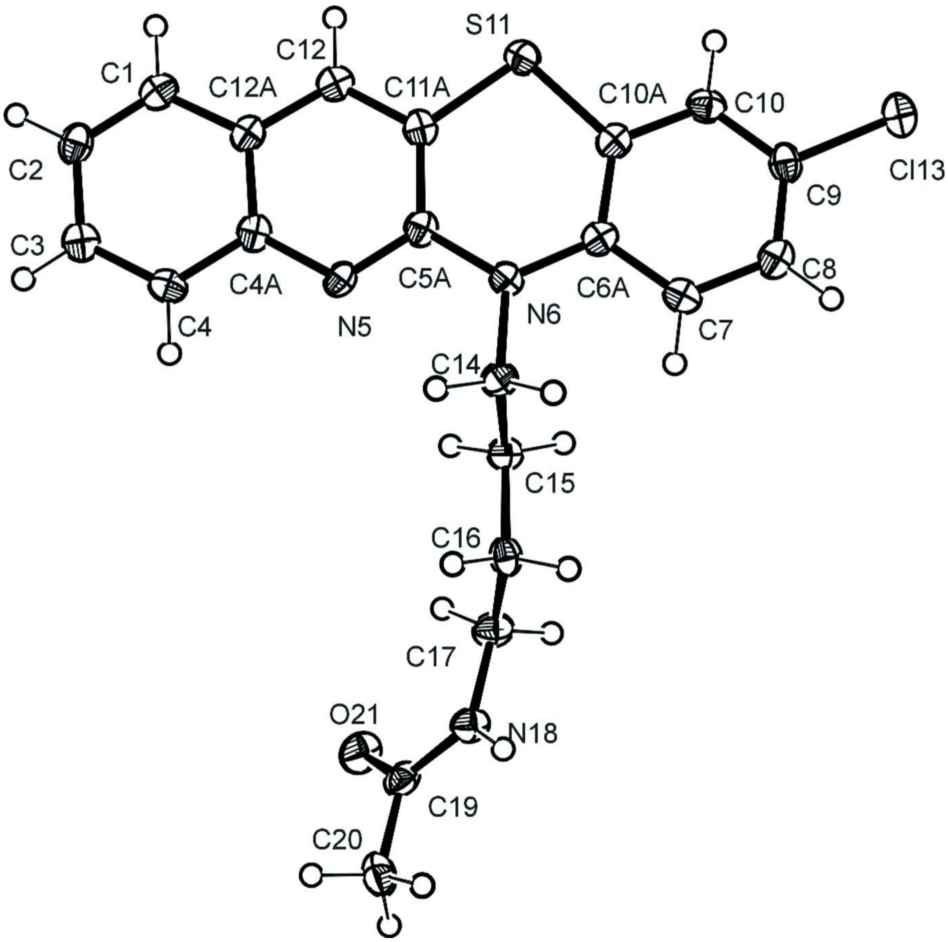


**Figure 2**

*ORTEP* drawing with displacement ellipsoids shown at the 50% probability level. SmilesCrystal packing shown along the *b* crystallographic axis.

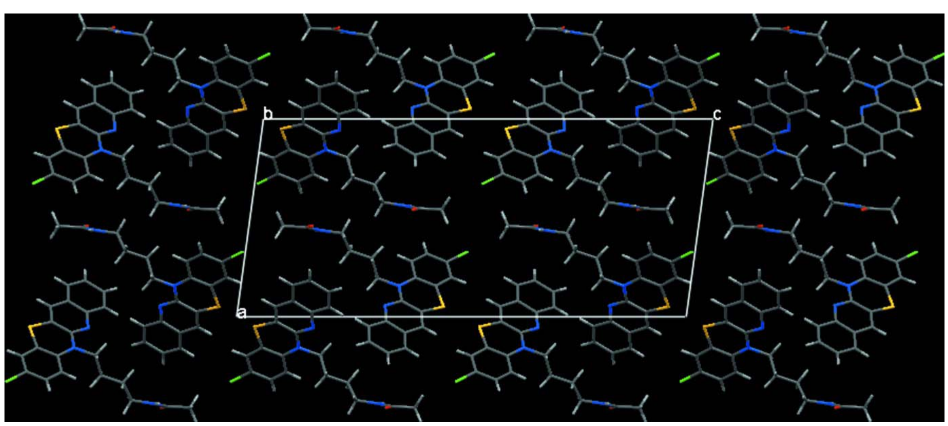


**Figure 3**

$\pi$–$\pi$ stacking of the aromatic rings and one dimensional hydrogen-bond network.

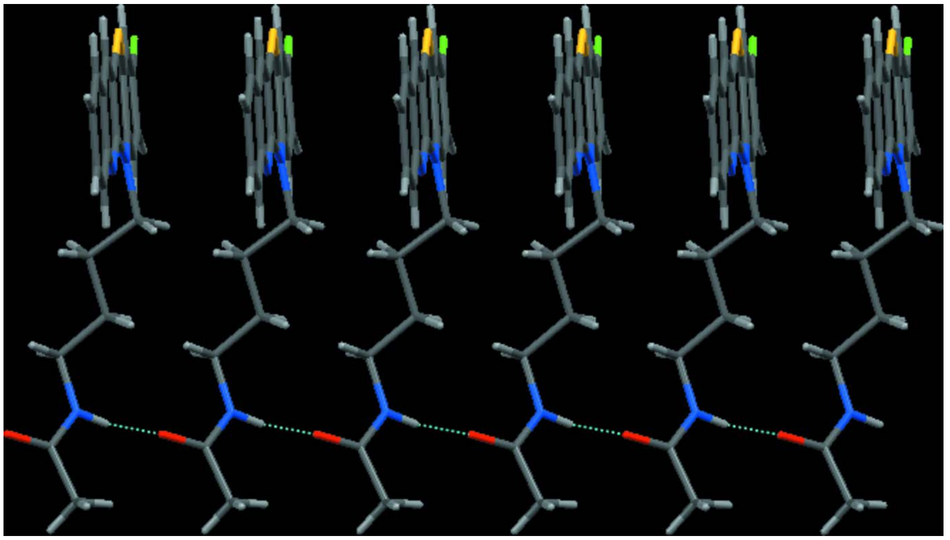

**Figure 4**

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**N-[4-(9-Chloroquino[3,2-b]benzo[1,4]thiazin-6-yl)butyl]acetamide**

*Crystal data*

$C_{21}H_{20}ClN_3OS$
$M_r$ = 397.92
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a$ = 12.7800 (4) Å
$b$ = 4.9530 (11) Å
$c$ = 28.781 (2) Å
$\beta$ = 97.726 (5)°
$V$ = 1805.3 (4) Å$^3$
$Z$ = 4
$F(000)$ = 832
$D_x$ = 1.464 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 5229 reflections
$\theta$ = 2.9–24.7°
$\mu$ = 0.35 mm$^{-1}$
$T$ = 100 K
Needle, yellow
0.60 × 0.10 × 0.05 mm

*Data collection*

Nonius KappaCCD diffractometer upgraded with an APEXII detector
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3 pixels mm$^{-1}$
$\omega$ scan
17434 measured reflections
3032 independent reflections
1987 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.121
$\theta_{max}$ = 24.7°, $\theta_{min}$ = 3.1°
$h = -15 \rightarrow 15$
$k = -5 \rightarrow 5$
$l = -32 \rightarrow 33$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.127
$S$ = 1.10
3032 reflections
245 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

$w = 1/[\sigma^2(F_o^2) + (0.016P)^2 + 1.5516P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å$^{-3}$
$\Delta\rho_{min} = -0.29$ 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 $F^2 > 2\sigma(F^2)$ 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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 1.1591 (3) | 0.0335 (8) | 0.38503 (15) | 0.0286 (11) |
| H1 | 1.1969 | 0.0022 | 0.4153 | 0.034* |
| C2 | 1.1827 (3) | −0.1165 (8) | 0.34779 (14) | 0.0298 (11) |
| H2 | 1.2360 | −0.2513 | 0.3520 | 0.036* |
| C3 | 1.1264 (3) | −0.0669 (8) | 0.30318 (15) | 0.0285 (11) |
| H3 | 1.1426 | −0.1689 | 0.2771 | 0.034* |
| C4 | 1.0484 (3) | 0.1260 (8) | 0.29646 (14) | 0.0252 (10) |
| H4 | 1.0116 | 0.1557 | 0.2660 | 0.030* |
| C4A | 1.0226 (3) | 0.2802 (8) | 0.33455 (14) | 0.0240 (10) |
| C5A | 0.9204 (3) | 0.6158 (8) | 0.36259 (14) | 0.0249 (10) |
| C6A | 0.8031 (3) | 0.9780 (8) | 0.38605 (14) | 0.0249 (10) |
| C7 | 0.7205 (3) | 1.1593 (8) | 0.37258 (14) | 0.0251 (10) |
| H7 | 0.6895 | 1.1630 | 0.3407 | 0.030* |
| C8 | 0.6820 (3) | 1.3348 (8) | 0.40429 (14) | 0.0281 (11) |
| H8 | 0.6289 | 1.4636 | 0.3939 | 0.034* |
| C9 | 0.7229 (3) | 1.3170 (8) | 0.45101 (14) | 0.0278 (11) |
| C10 | 0.8017 (3) | 1.1362 (8) | 0.46564 (14) | 0.0283 (11) |
| H10 | 0.8280 | 1.1239 | 0.4980 | 0.034* |
| C10A | 0.8439 (3) | 0.9705 (8) | 0.43379 (14) | 0.0258 (10) |
| C11A | 0.9741 (3) | 0.5778 (8) | 0.40921 (14) | 0.0244 (10) |
| C12 | 1.0516 (3) | 0.3889 (8) | 0.41680 (14) | 0.0246 (10) |
| H12 | 1.0871 | 0.3616 | 0.4476 | 0.030* |
| C12A | 1.0802 (3) | 0.2326 (8) | 0.37939 (14) | 0.0243 (10) |
| C14 | 0.8053 (3) | 0.8667 (8) | 0.30219 (13) | 0.0257 (10) |
| H14A | 0.8611 | 0.8131 | 0.2833 | 0.031* |
| H14B | 0.7936 | 1.0632 | 0.2978 | 0.031* |
| C15 | 0.7036 (3) | 0.7195 (8) | 0.28324 (13) | 0.0252 (10) |
| H15A | 0.6482 | 0.7613 | 0.3031 | 0.030* |
| H15B | 0.7160 | 0.5222 | 0.2843 | 0.030* |
| C16 | 0.6666 (3) | 0.8062 (8) | 0.23276 (13) | 0.0272 (11) |
| H16A | 0.6422 | 0.9960 | 0.2327 | 0.033* |
| H16B | 0.7271 | 0.7982 | 0.2147 | 0.033* |
| C17 | 0.5779 (3) | 0.6321 (9) | 0.20864 (14) | 0.0316 (11) |

| | | | | |
|---|---|---|---|---|
| H17A | 0.5948 | 0.4398 | 0.2154 | 0.038* |
| H17B | 0.5119 | 0.6750 | 0.2215 | 0.038* |
| C19 | 0.5476 (3) | 0.4691 (9) | 0.12731 (15) | 0.0290 (11) |
| C20 | 0.5415 (3) | 0.5422 (9) | 0.07638 (14) | 0.0362 (12) |
| H20A | 0.5999 | 0.4565 | 0.0631 | 0.054* |
| H20B | 0.5463 | 0.7387 | 0.0733 | 0.054* |
| H20C | 0.4742 | 0.4791 | 0.0595 | 0.054* |
| N5 | 0.9431 (2) | 0.4684 (6) | 0.32683 (11) | 0.0227 (8) |
| N6 | 0.8438 (3) | 0.8161 (6) | 0.35178 (11) | 0.0237 (8) |
| N18 | 0.5615 (3) | 0.6734 (7) | 0.15804 (11) | 0.0279 (9) |
| H18 | 0.5607 | 0.8396 | 0.1472 | 0.033* |
| O21 | 0.5405 (2) | 0.2316 (6) | 0.14005 (10) | 0.0400 (8) |
| S11 | 0.94961 (9) | 0.7684 (2) | 0.45749 (4) | 0.0304 (3) |
| Cl13 | 0.67276 (9) | 1.5212 (2) | 0.49241 (4) | 0.0364 (3) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.025 (3) | 0.028 (3) | 0.032 (3) | −0.002 (2) | 0.003 (2) | 0.005 (2) |
| C2 | 0.025 (3) | 0.026 (3) | 0.040 (3) | 0.000 (2) | 0.008 (2) | 0.002 (2) |
| C3 | 0.030 (3) | 0.022 (3) | 0.035 (3) | −0.006 (2) | 0.007 (2) | 0.000 (2) |
| C4 | 0.027 (3) | 0.023 (2) | 0.026 (2) | −0.009 (2) | 0.002 (2) | −0.001 (2) |
| C4A | 0.025 (2) | 0.016 (2) | 0.032 (2) | −0.004 (2) | 0.007 (2) | 0.003 (2) |
| C5A | 0.026 (3) | 0.019 (2) | 0.030 (2) | −0.002 (2) | 0.005 (2) | 0.002 (2) |
| C6A | 0.023 (2) | 0.023 (2) | 0.029 (2) | −0.004 (2) | 0.003 (2) | 0.003 (2) |
| C7 | 0.027 (3) | 0.024 (3) | 0.025 (2) | −0.009 (2) | 0.005 (2) | 0.001 (2) |
| C8 | 0.026 (3) | 0.022 (3) | 0.037 (3) | −0.003 (2) | 0.006 (2) | 0.005 (2) |
| C9 | 0.030 (3) | 0.021 (3) | 0.034 (3) | −0.002 (2) | 0.008 (2) | −0.003 (2) |
| C10 | 0.031 (3) | 0.027 (3) | 0.027 (2) | −0.005 (2) | 0.001 (2) | 0.001 (2) |
| C10A | 0.024 (2) | 0.024 (2) | 0.029 (2) | −0.002 (2) | 0.004 (2) | 0.002 (2) |
| C11A | 0.027 (3) | 0.019 (2) | 0.028 (2) | −0.004 (2) | 0.007 (2) | 0.0015 (19) |
| C12 | 0.024 (2) | 0.021 (2) | 0.029 (2) | −0.006 (2) | 0.004 (2) | 0.005 (2) |
| C12A | 0.021 (2) | 0.021 (2) | 0.031 (2) | −0.003 (2) | 0.005 (2) | 0.003 (2) |
| C14 | 0.033 (3) | 0.021 (2) | 0.023 (2) | 0.002 (2) | 0.003 (2) | 0.0061 (19) |
| C15 | 0.028 (3) | 0.021 (2) | 0.026 (2) | −0.003 (2) | 0.001 (2) | 0.0018 (19) |
| C16 | 0.032 (3) | 0.020 (2) | 0.032 (2) | 0.000 (2) | 0.009 (2) | −0.0005 (19) |
| C17 | 0.037 (3) | 0.028 (3) | 0.029 (2) | −0.002 (2) | 0.001 (2) | 0.008 (2) |
| C19 | 0.022 (2) | 0.029 (3) | 0.034 (3) | 0.002 (2) | −0.003 (2) | 0.000 (2) |
| C20 | 0.037 (3) | 0.033 (3) | 0.040 (3) | 0.002 (2) | 0.009 (2) | −0.011 (2) |
| N5 | 0.0211 (19) | 0.018 (2) | 0.029 (2) | 0.0004 (17) | 0.0033 (16) | 0.0048 (16) |
| N6 | 0.027 (2) | 0.021 (2) | 0.0228 (19) | −0.0017 (17) | 0.0043 (16) | 0.0008 (16) |
| N18 | 0.035 (2) | 0.018 (2) | 0.029 (2) | −0.0034 (17) | −0.0004 (17) | 0.0051 (16) |
| O21 | 0.050 (2) | 0.0159 (18) | 0.050 (2) | −0.0015 (16) | −0.0054 (16) | −0.0007 (15) |
| S11 | 0.0343 (7) | 0.0290 (7) | 0.0271 (6) | 0.0036 (6) | 0.0006 (5) | −0.0018 (5) |
| Cl13 | 0.0404 (7) | 0.0309 (7) | 0.0391 (7) | 0.0040 (6) | 0.0105 (6) | −0.0054 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.371 (5) | C10A—S11 | 1.745 (4) |
| C1—C12A | 1.405 (5) | C11A—C12 | 1.359 (5) |

| | | | |
|---|---|---|---|
| C1—H1 | 0.9500 | C11A—S11 | 1.743 (4) |
| C2—C3 | 1.406 (5) | C12—C12A | 1.413 (5) |
| C2—H2 | 0.9500 | C12—H12 | 0.9500 |
| C3—C4 | 1.376 (5) | C14—N6 | 1.468 (4) |
| C3—H3 | 0.9500 | C14—C15 | 1.526 (5) |
| C4—C4A | 1.411 (5) | C14—H14A | 0.9900 |
| C4—H4 | 0.9500 | C14—H14B | 0.9900 |
| C4A—N5 | 1.374 (5) | C15—C16 | 1.528 (5) |
| C4A—C12A | 1.417 (5) | C15—H15A | 0.9900 |
| C5A—N5 | 1.325 (5) | C15—H15B | 0.9900 |
| C5A—N6 | 1.399 (5) | C16—C17 | 1.515 (5) |
| C5A—C11A | 1.435 (5) | C16—H16A | 0.9900 |
| C6A—C7 | 1.400 (5) | C16—H16B | 0.9900 |
| C6A—C10A | 1.403 (5) | C17—N18 | 1.458 (5) |
| C6A—N6 | 1.423 (5) | C17—H17A | 0.9900 |
| C7—C8 | 1.397 (5) | C17—H17B | 0.9900 |
| C7—H7 | 0.9500 | C19—O21 | 1.239 (5) |
| C8—C9 | 1.378 (5) | C19—N18 | 1.340 (5) |
| C8—H8 | 0.9500 | C19—C20 | 1.502 (5) |
| C9—C10 | 1.371 (5) | C20—H20A | 0.9800 |
| C9—Cl13 | 1.749 (4) | C20—H20B | 0.9800 |
| C10—C10A | 1.392 (5) | C20—H20C | 0.9800 |
| C10—H10 | 0.9500 | N18—H18 | 0.8800 |

| | | | |
|---|---|---|---|
| C2—C1—C12A | 121.4 (4) | C1—C12A—C4A | 119.9 (4) |
| C2—C1—H1 | 119.3 | C12—C12A—C4A | 116.6 (4) |
| C12A—C1—H1 | 119.3 | N6—C14—C15 | 115.1 (3) |
| C1—C2—C3 | 118.7 (4) | N6—C14—H14A | 108.5 |
| C1—C2—H2 | 120.7 | C15—C14—H14A | 108.5 |
| C3—C2—H2 | 120.7 | N6—C14—H14B | 108.5 |
| C4—C3—C2 | 121.4 (4) | C15—C14—H14B | 108.5 |
| C4—C3—H3 | 119.3 | H14A—C14—H14B | 107.5 |
| C2—C3—H3 | 119.3 | C14—C15—C16 | 110.2 (3) |
| C3—C4—C4A | 120.5 (4) | C14—C15—H15A | 109.6 |
| C3—C4—H4 | 119.8 | C16—C15—H15A | 109.6 |
| C4A—C4—H4 | 119.8 | C14—C15—H15B | 109.6 |
| N5—C4A—C4 | 119.1 (4) | C16—C15—H15B | 109.6 |
| N5—C4A—C12A | 122.8 (4) | H15A—C15—H15B | 108.1 |
| C4—C4A—C12A | 118.1 (4) | C17—C16—C15 | 113.1 (3) |
| N5—C5A—N6 | 115.9 (4) | C17—C16—H16A | 109.0 |
| N5—C5A—C11A | 121.8 (4) | C15—C16—H16A | 109.0 |
| N6—C5A—C11A | 122.2 (4) | C17—C16—H16B | 109.0 |
| C7—C6A—C10A | 117.1 (4) | C15—C16—H16B | 109.0 |
| C7—C6A—N6 | 120.1 (4) | H16A—C16—H16B | 107.8 |
| C10A—C6A—N6 | 122.8 (4) | N18—C17—C16 | 112.1 (3) |
| C8—C7—C6A | 122.5 (4) | N18—C17—H17A | 109.2 |
| C8—C7—H7 | 118.8 | C16—C17—H17A | 109.2 |
| C6A—C7—H7 | 118.8 | N18—C17—H17B | 109.2 |
| C9—C8—C7 | 118.5 (4) | C16—C17—H17B | 109.2 |

| | | | |
|---|---|---|---|
| C9—C8—H8 | 120.8 | H17A—C17—H17B | 107.9 |
| C7—C8—H8 | 120.8 | O21—C19—N18 | 122.0 (4) |
| C10—C9—C8 | 120.5 (4) | O21—C19—C20 | 121.4 (4) |
| C10—C9—Cl13 | 119.3 (3) | N18—C19—C20 | 116.5 (4) |
| C8—C9—Cl13 | 120.1 (3) | C19—C20—H20A | 109.5 |
| C9—C10—C10A | 121.1 (4) | C19—C20—H20B | 109.5 |
| C9—C10—H10 | 119.5 | H20A—C20—H20B | 109.5 |
| C10A—C10—H10 | 119.5 | C19—C20—H20C | 109.5 |
| C10—C10A—C6A | 120.3 (4) | H20A—C20—H20C | 109.5 |
| C10—C10A—S11 | 115.4 (3) | H20B—C20—H20C | 109.5 |
| C6A—C10A—S11 | 124.3 (3) | C5A—N5—C4A | 118.8 (3) |
| C12—C11A—C5A | 119.2 (4) | C5A—N6—C6A | 123.8 (3) |
| C12—C11A—S11 | 116.7 (3) | C5A—N6—C14 | 118.1 (3) |
| C5A—C11A—S11 | 124.1 (3) | C6A—N6—C14 | 118.2 (3) |
| C11A—C12—C12A | 120.8 (4) | C19—N18—C17 | 122.8 (3) |
| C11A—C12—H12 | 119.6 | C19—N18—H18 | 118.6 |
| C12A—C12—H12 | 119.6 | C17—N18—H18 | 118.6 |
| C1—C12A—C12 | 123.5 (4) | C11A—S11—C10A | 102.2 (2) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N18—H18···O21$^{i}$ | 0.88 | 1.97 | 2.819 (4) | 163 |

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