



Supramolecular interactions in the 1:2 co-crystal of 4,4'-bipyridine and 3-chlorothiophene-2-carboxylic acid

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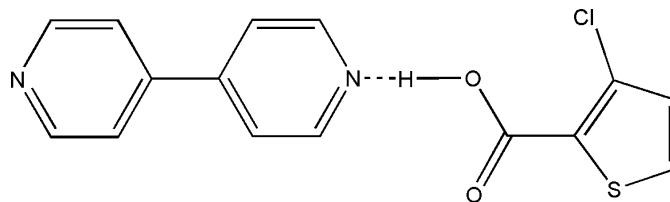
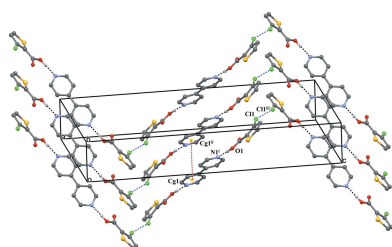
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Keywords: crystal structure; 3-chlorothiophene-2-carboxylic acid; 4,4'-bipyridine; O—H...N-based synthon; co-crystal.**CCDC reference:** 1501060**Supporting information:** this article has supporting information at journals.iucr.org/e

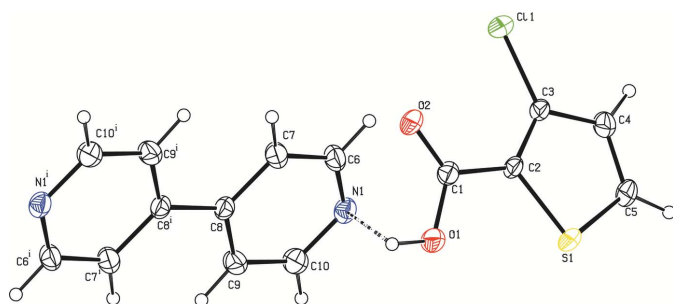
The asymmetric unit of the title compound, $2C_5H_3ClO_2S \cdot C_{10}H_8N_2$, is comprised of a molecule of 3-chlorothiophene-2-carboxylic acid (3TPC) and half of a molecule of 4,4'-bipyridine (BPY). A distinctive O—H...N-based synthon is present. Cl...Cl and π - π stacking interactions further stabilize the crystal structure, forming a two-dimensional network parallel to the *bc* plane.

1. Chemical context

Structurally homogeneous crystalline solids in well defined stoichiometry are called co-crystals. In recent years, the physicochemical properties of active pharmaceutical ingredients have been improved widely with the use of co-crystals (Lemmerer & Bernstein, 2010). Supramolecular synthons – modular representation of primary recognition between functional groups – are of great importance in providing an effective strategy for designing solids in crystal engineering. All geometrical and chemical information of molecular recognition is contained in the structural units called synthons. In the context of co-crystal formation, heterosynthons provide a predictive justification in terms of unique intermolecular interactions (Mukherjee *et al.*, 2011, 2013). There are many literature cases of O—H...N-bonded interactions between acid and pyridine-based systems (Shattock *et al.*, 2008; Lemmerer *et al.*, 2015). 4,4'-Bipyridine (BPY) is a weak bidentate base commonly used in crystal engineering on account of its bridging abilities. It also acts as the co-crystal former in the present study because it readily participates in hydrogen bonds with carboxyl-attached organic molecules (Pan *et al.*, 2008).



Intermolecular interactions involving halogen substituents, particularly chlorides, play an important role in molecular self-assembly in supra- and biomolecular systems to prepare highly stereoregular organic polymers. It has been observed that these interactions act as a tool in crystal engineering to


Figure 1

The asymmetric unit of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The dashed line represents the O—H···N hydrogen bond. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

enhance crystal formation and for the design of supramolecular aggregates (Cavallo *et al.*, 2016). In this context, the study of the effect of various halogens on the molecular packing and crystalline architecture of solids has attracted great attention (Csöregi *et al.*, 2001). The structure-forming ability of Cl···Cl interactions in assembling chains, ladders, two-dimensional sheets, *etc.* has been studied extensively (Navon *et al.*, 1997; Metrangolo & Resnati, 2014). It is based on the values of the two C—Hal···Hal angles, θ_1 and θ_2 (Vener *et al.*, 2013).

Table 1

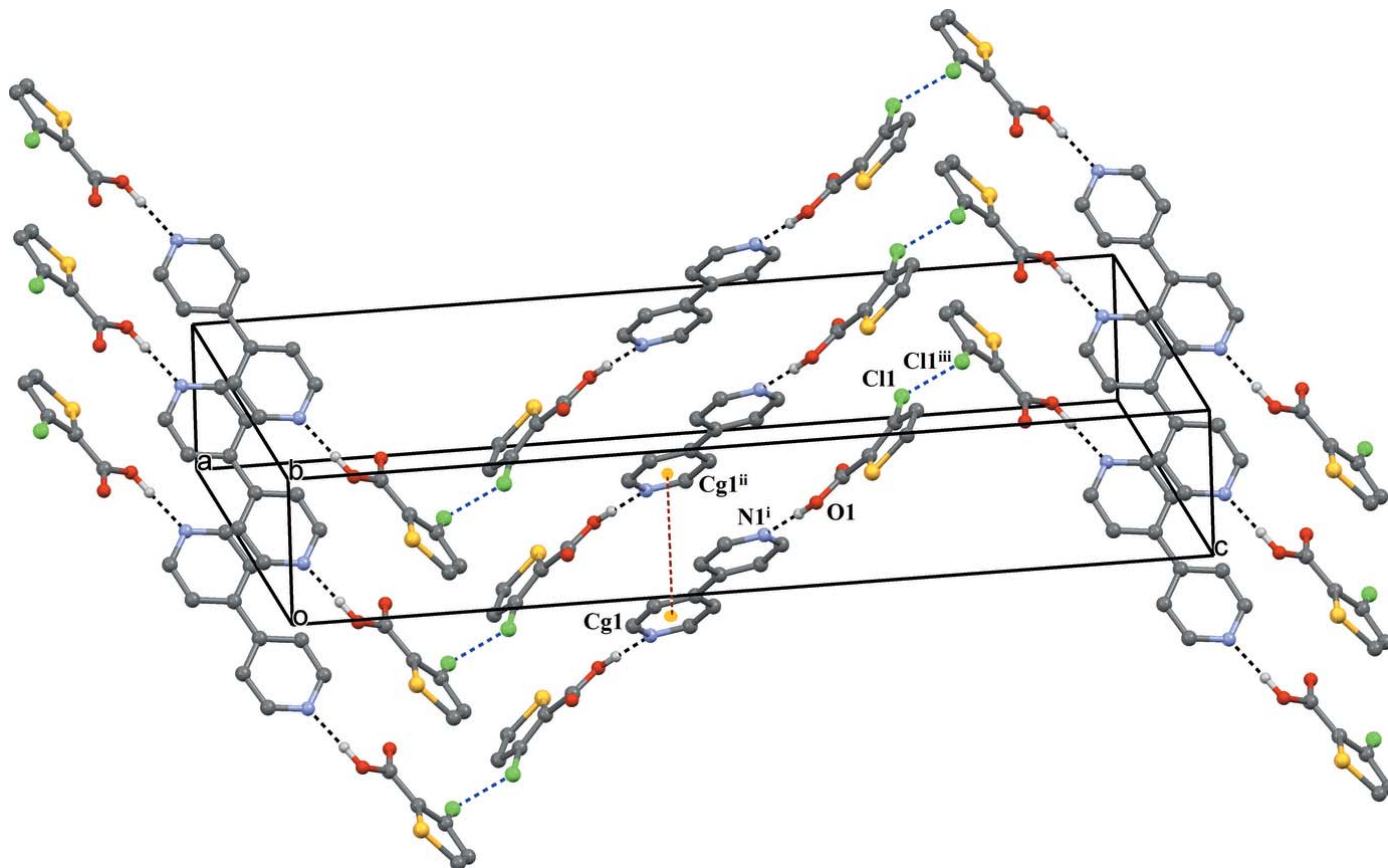
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1···N1 ⁱ	0.89 (5)	1.77 (5)	2.659 (4)	178 (5)

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

2. Structural commentary

The asymmetric unit of the title compound (I) consists of a molecule of 3-chlorothiophene-2-carboxylic acid, 3TPC, and a half of a molecule of 4,4'-bipyridine, BPY, which is located on a crystallographic inversion center. The internal angle at N1 in BPY is $117.1(3)^\circ$ and bond lengths [N1—C6 = $1.336(5)$ Å and N1—C10 = $1.329(5)$ Å] agree with those reported for neutral BPY structures (see for example Jennifer & Muthiah, 2014; Atria *et al.*, 2014; Moon & Park, 2012; Qin, 2011; Najafpour *et al.*, 2008). The two external bond angles at the carbon of the carboxyl group are $123.7(3)^\circ$ and $112.4(3)^\circ$. The high discrepancy between these two angles is typical of an unionized carboxyl group, as are the C=O distance of $1.219(4)$ Å and C—OH distance of $1.3254(5)$ Å (see for example Prajina *et al.*, 2016; Atria *et al.*, 2014; Jennifer & Muthiah, 2014; Qin, 2011). The bond distances and angles of the thiophene ring agree with those in structures reported earlier (Zhang *et al.*, 2014).


Figure 2

A view of the O—H···N hydrogen bonds (black dashed lines), π – π stacking (brown dashed lines) and Cl···Cl interactions (blue dashed lines). Symmetry codes: (i) $x, y - 1, z$; (ii) $1 - x, 2 - y, 1 - z$; (iii) $1 - x, y, \frac{1}{2} - z$.

3. Supramolecular features

3TPC and BPY are interconnected *via* O—H...N hydrogen-bonding interactions between (O1—H1) of the carboxyl group and the nitrogen (N1) of BPY (Table 1 and Fig. 1). This O—H...N hydrogen bond is a frequently observed supramolecular synthon in crystal engineering involving a carboxylic acid and a pyridine system (Dubey & Desiraju, 2015; Lemmerer & Bernstein, 2010; Mukherjee *et al.*, 2011, 2013; Prajina *et al.*, 2016; Seaton, 2014; Thomas *et al.*, 2010). This supramolecular synthon is also present in the co-crystal of 5-chlorothiophene-2-carboxylic acid with BPY (5TPC44BIPY) and in the co-crystal of thiophene-2-carboxylic acid with BPY reported from our laboratory (Jennifer & Muthiah, 2014). The co-crystal 5TPC44BIPY and the title co-crystal differ only in the position of chlorine in the thiophene ring with the same base. A chloro derivative was chosen as co-molecule with the expectation that the presence of a Cl atom would result in halogen–halogen interactions. As expected, a Cl...Cl interaction plays the key role in connecting the O—H...N hydrogen-bonded units to form an infinite zigzag chain, *i.e.*, the three-molecule aggregates are further linked to similar neighbouring aggregates through Cl...Cl interactions [$3.3925(12)$ Å, C3—Cl1...Cl1ⁱⁱⁱ = $151.71(1)^\circ$; symmetry code: (iii) $1 - x, y, \frac{1}{2} - z$] (Vener *et al.*, 2013; Sarma & Desiraju, 1986; Capdevila-Cortada *et al.*, 2014). The hydrogen-bonded units are stabilized *via* π – π stacking interactions between the aromatic systems of BPY molecules [$Cg1 \cdots Cg1^{ii}$ = $3.794(2)$ Å; Cg1 is the centroid of the N1/C6/C7/C8/C9/C10 ring; symmetry code: (ii) $1 - x, 2 - y, 1 - z$]. The perpendicular distance between two parallel molecules is $3.4812(15)$ Å. This weak interaction holds the hydrogen-bonded chains together, supporting a two-dimensional supramolecular network parallel to the *bc* plane, as seen in Fig. 2.

4. Database survey

In the title compound, the most dominant interaction is the O—H...N hydrogen bond formed between a carboxyl group and a pyridine N atom (Fig. 1). The length of this hydrogen bond [O...N = $2.659(4)$ Å] is very close to those of O—H...N bonds found in similar reported co-crystals, such as in the adduct of 2,5-dihydroxy-1,4-benzoquinone and BPY (Cowan *et al.*, 2001) and in the co-crystal of BPY with *N,N'*-dioxide-3-hydroxy-2-naphthoic acid (1/2) (Lou & Huang, 2007) and in a series of nine co-crystals involving acridine and benzoic acids (Kowalska *et al.*, 2015). The angle of the hydrogen bond formed between the 3CTPC and BPY molecules is $178(5)^\circ$. A similar value is found in the co-crystal of BPY with 3,5-dinitrobenzoic acid for which the O...N distance is $2.547(2)$ Å (Thomas *et al.*, 2010). In the crystal structure of the co-crystal of adamantane-1,3-dicarboxylic acid and 4,4'-bipyridine, π – π interactions connect the O—H...N hydrogen-bonded zigzag chains, supporting a two-dimensional network (Pan *et al.*, 2008).

Table 2

Experimental details.

Crystal data	
Chemical formula	$2C_5H_3ClO_2S \cdot C_{10}H_8N_2$
M_r	481.35
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	200
a, b, c (Å)	13.538 (4), 5.1230 (18), 30.167 (10)
β ($^\circ$)	95.968 (9)
V (Å ³)	2080.8 (12)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.54
Crystal size (mm)	$0.50 \times 0.50 \times 0.10$
Data collection	
Diffractometer	Bruker SMART X2S benchtop
Absorption correction	Multi-scan (SADABS; Bruker, 2013)
T_{\min}, T_{\max}	0.69, 0.95
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10427, 1907, 1563
R_{int}	0.078
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.607
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.055, 0.136, 1.19
No. of reflections	1907
No. of parameters	140
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.37, -0.32

Computer programs: APEX2 (Bruker, 2013), SAINT (Bruker, 2013), SHELXS97 (Sheldrick, 2008), SHELXL2014 (Sheldrick, 2015), PLATON (Spek, 2009), Mercury (Macrae *et al.*, 2008) and publCIF (Westrip, 2010).

5. Synthesis and crystallization

To 10 ml of a hot methanol solution of 3TPC (40.6 mg, 25 mmol), 10 ml of a hot methanolic solution of BPY (39.0 mg, 25 mmol) was added. The resulting solution was warmed over a water bath for half an hour and then kept at room temperature for crystallization. After a week, clear yellow plates were obtained. The crystal used for X-ray diffraction data collection was cut from a larger crystal.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were located in difference Fourier maps. The hydrogen atoms bonded to carbon were refined using a riding model with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The carboxylic acid hydrogen atom was freely refined, including its isotropic displacement parameter.

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supporting information

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Supramolecular interactions in the 1:2 co-crystal of 4,4'-bipyridine and 3-chlorothiophene-2-carboxylic acid

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Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINTE* (Bruker, 2013); data reduction: *SAINTE* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

bis(3-Chlorothiophene-2-carboxylic acid); 4,4'-bipyridine

Crystal data

$2\text{C}_5\text{H}_3\text{ClO}_2\text{S} \cdot \text{C}_{10}\text{H}_8\text{N}_2$

$M_r = 481.35$

Monoclinic, *C2/c*

$a = 13.538$ (4) Å

$b = 5.1230$ (18) Å

$c = 30.167$ (10) Å

$\beta = 95.968$ (9)°

$V = 2080.8$ (12) Å³

$Z = 4$

$F(000) = 984$

$D_x = 1.537$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3438 reflections

$\theta = 2.7\text{--}24.8^\circ$

$\mu = 0.54$ mm⁻¹

$T = 200$ K

Plate, clear colourless

$0.50 \times 0.50 \times 0.10$ mm

Data collection

Bruker SMART X2S benchtop
diffractometer

Radiation source: sealed microfocus tube

ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2013)

$T_{\min} = 0.69$, $T_{\max} = 0.95$

10427 measured reflections

1907 independent reflections

1563 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.078$

$\theta_{\max} = 25.6^\circ$, $\theta_{\min} = 1.4^\circ$

$h = -16 \rightarrow 16$

$k = -6 \rightarrow 6$

$l = -36 \rightarrow 36$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.055$

$wR(F^2) = 0.136$

$S = 1.19$

1907 reflections

140 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 4.3057P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.37$ e Å⁻³

$\Delta\rho_{\min} = -0.32$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.3544 (2)	0.9782 (6)	0.54889 (10)	0.0363 (7)
C8	0.4696 (2)	0.6000 (7)	0.51024 (11)	0.0312 (8)
C7	0.4776 (3)	0.6415 (8)	0.55606 (12)	0.0406 (9)
H7	0.5227	0.5401	0.5752	0.049*
C6	0.4200 (3)	0.8304 (8)	0.57370 (11)	0.0385 (9)
H6	0.4275	0.8563	0.6051	0.046*
C10	0.3468 (3)	0.9421 (8)	0.50506 (12)	0.0423 (9)
H10	0.3016	1.0481	0.4868	0.051*
C9	0.4017 (3)	0.7571 (7)	0.48451 (12)	0.0386 (9)
H9	0.3931	0.7377	0.4530	0.046*
S1	0.12214 (6)	0.6112 (2)	0.64475 (3)	0.0420 (3)
Cl1	0.40721 (6)	0.8001 (2)	0.70764 (3)	0.0447 (3)
O1	0.24836 (19)	0.2918 (6)	0.59585 (9)	0.0462 (7)
O2	0.39160 (18)	0.3397 (5)	0.63983 (8)	0.0411 (6)
C2	0.2498 (2)	0.5841 (7)	0.65494 (11)	0.0304 (7)
C5	0.1177 (3)	0.8526 (8)	0.68316 (12)	0.0454 (10)
H5	0.0579	0.9341	0.6899	0.054*
C4	0.2091 (3)	0.9160 (8)	0.70321 (12)	0.0414 (9)
H4	0.2210	1.0482	0.7252	0.050*
C3	0.2846 (2)	0.7602 (7)	0.68722 (10)	0.0312 (8)
C1	0.3043 (3)	0.3936 (7)	0.63023 (11)	0.0325 (8)
H1	0.283 (4)	0.184 (10)	0.5800 (16)	0.072 (15)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0315 (16)	0.0350 (17)	0.0435 (17)	−0.0014 (13)	0.0097 (13)	−0.0083 (13)
C8	0.0258 (18)	0.0349 (19)	0.0340 (17)	−0.0042 (15)	0.0083 (14)	−0.0031 (14)
C7	0.041 (2)	0.049 (2)	0.0321 (18)	0.0065 (18)	0.0083 (16)	−0.0011 (16)
C6	0.042 (2)	0.042 (2)	0.0330 (18)	−0.0001 (17)	0.0108 (15)	−0.0080 (15)
C10	0.040 (2)	0.046 (2)	0.041 (2)	0.0100 (18)	0.0024 (16)	−0.0040 (17)
C9	0.041 (2)	0.042 (2)	0.0331 (18)	0.0043 (17)	0.0029 (15)	−0.0075 (15)
S1	0.0207 (5)	0.0602 (7)	0.0448 (5)	0.0069 (4)	0.0021 (4)	−0.0076 (4)
Cl1	0.0261 (5)	0.0630 (7)	0.0440 (5)	0.0012 (4)	−0.0013 (4)	−0.0081 (4)
O1	0.0313 (14)	0.0611 (19)	0.0459 (15)	0.0083 (13)	0.0023 (12)	−0.0207 (14)
O2	0.0254 (13)	0.0515 (17)	0.0466 (14)	0.0130 (12)	0.0047 (11)	−0.0053 (12)
C2	0.0196 (16)	0.040 (2)	0.0316 (17)	0.0064 (14)	0.0048 (13)	0.0036 (14)
C5	0.031 (2)	0.061 (3)	0.045 (2)	0.0188 (19)	0.0092 (16)	−0.0057 (18)
C4	0.038 (2)	0.051 (2)	0.0357 (19)	0.0114 (18)	0.0063 (16)	−0.0071 (16)

C3	0.0233 (17)	0.042 (2)	0.0282 (16)	0.0065 (15)	0.0034 (13)	0.0029 (14)
C1	0.0294 (19)	0.0352 (19)	0.0335 (17)	0.0025 (15)	0.0056 (14)	0.0019 (14)

Geometric parameters (Å, °)

N1—C10	1.329 (5)	S1—C2	1.729 (3)
N1—C6	1.336 (5)	Cl1—C3	1.721 (3)
C8—C7	1.391 (5)	O1—C1	1.325 (4)
C8—C9	1.395 (5)	O1—H1	0.89 (5)
C8—C8 ⁱ	1.489 (7)	O2—C1	1.219 (4)
C7—C6	1.384 (5)	C2—C3	1.374 (5)
C7—H7	0.9500	C2—C1	1.472 (5)
C6—H6	0.9500	C5—C4	1.359 (6)
C10—C9	1.389 (5)	C5—H5	0.9500
C10—H10	0.9500	C4—C3	1.421 (5)
C9—H9	0.9500	C4—H4	0.9500
S1—C5	1.700 (4)		
C10—N1—C6	117.1 (3)	C1—O1—H1	112 (3)
C7—C8—C9	116.3 (3)	C3—C2—C1	129.8 (3)
C7—C8—C8 ⁱ	121.8 (4)	C3—C2—S1	109.7 (3)
C9—C8—C8 ⁱ	121.8 (4)	C1—C2—S1	120.5 (3)
C6—C7—C8	120.0 (3)	C4—C5—S1	112.4 (3)
C6—C7—H7	120.0	C4—C5—H5	123.8
C8—C7—H7	120.0	S1—C5—H5	123.8
N1—C6—C7	123.4 (3)	C5—C4—C3	111.7 (3)
N1—C6—H6	118.3	C5—C4—H4	124.2
C7—C6—H6	118.3	C3—C4—H4	124.2
N1—C10—C9	123.4 (3)	C2—C3—C4	113.8 (3)
N1—C10—H10	118.3	C2—C3—Cl1	125.4 (3)
C9—C10—H10	118.3	C4—C3—Cl1	120.9 (3)
C10—C9—C8	119.8 (3)	O2—C1—O1	123.9 (3)
C10—C9—H9	120.1	O2—C1—C2	123.7 (3)
C8—C9—H9	120.1	O1—C1—C2	112.4 (3)
C5—S1—C2	92.46 (18)		
C9—C8—C7—C6	0.0 (5)	S1—C5—C4—C3	-0.9 (5)
C8 ⁱ —C8—C7—C6	179.7 (4)	C1—C2—C3—C4	179.3 (3)
C10—N1—C6—C7	-1.4 (6)	S1—C2—C3—C4	-0.4 (4)
C8—C7—C6—N1	0.8 (6)	C1—C2—C3—Cl1	-0.3 (6)
C6—N1—C10—C9	1.4 (6)	S1—C2—C3—Cl1	180.0 (2)
N1—C10—C9—C8	-0.7 (6)	C5—C4—C3—C2	0.9 (5)
C7—C8—C9—C10	-0.1 (5)	C5—C4—C3—Cl1	-179.5 (3)
C8 ⁱ —C8—C9—C10	-179.7 (4)	C3—C2—C1—O2	10.6 (6)
C5—S1—C2—C3	-0.1 (3)	S1—C2—C1—O2	-169.7 (3)

C5—S1—C2—C1	-179.8 (3)	C3—C2—C1—O1	-168.0 (4)
C2—S1—C5—C4	0.6 (3)	S1—C2—C1—O1	11.7 (4)

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

Hydrogen-bond geometry (Å, °)

<i>D—H</i> ⋯ <i>A</i>	<i>D—H</i>	<i>H</i> ⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D—H</i> ⋯ <i>A</i>
O1—H1⋯N1 ⁱⁱ	0.89 (5)	1.77 (5)	2.659 (4)	178 (5)

Symmetry code: (ii) $x, y-1, z$.