Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Supramolecular interactions in 2,6-diamino-4-chloropyrimidin-1-ium 5-chlorosalicylate and bis(2,6-diamino-4-chloropyrimidin-1-ium) naphthalene-1,5-disulfonate

Robert Swinton Darious,[a] Packianathan Thomas Muthiah[a]* and Franc Perdih[b]

[a]School of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, Tamilnadu, India, and [b]Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna, pot 113, PO Box 537, SI-1000 Ljubljana, Slovenia. *Correspondence e-mail: tommtrichy@yahoo.co.in

Received 12 January 2018
Accepted 19 January 2018

Edited by M. Zeller, Purdue University, USA

Keywords: crystal structure; hydrogen bonding; supramolecular architecture; halogen–halogen interaction; quadruple array; homosynthon; heterosynthon.

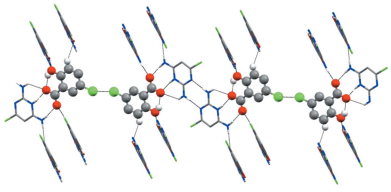
CCDC references: 1817972; 1817971

Supporting information: this article has supporting information at journals.iucr.org/e

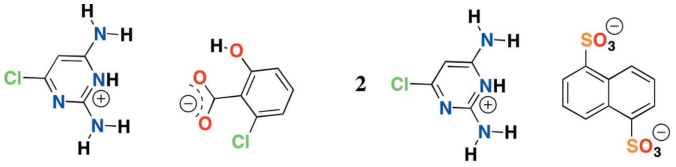
The crystals of two new salts, 2,6-diamino-4-chloropyrimidin-1-ium 5-chlorosalicylate, $C_4H_6ClN_4^+\cdot C_7H_4ClO_3^-$, (I), and bis(2,6-diamino-4-chloropyrimidin-1-ium) naphthalene-1,5-di-sulfonate, $2C_4H_6ClN_4^+\cdot C_{10}H_6O_6S_2^{2-}$, (II), have been synthesized and characterized by single-crystal X-ray diffraction. In both compounds, the N atom of the pyrimidine group in between the amino substituents is protonated and the pyrimidinium cation forms a pair of N—H···O hydrogen bonds with the carboxylate/sulfonate ion, leading to a robust $R_2^2(8)$ motif (supramolecular heterosynthon). In compound (I), a self-complementary base pairing involving the other pyrimidinium ring nitrogen atom and one of the amino groups *via* a pair of N—H···N hydrogen bonds [$R_2^2(8)$ homosynthon] is also present. In compound (II), the crystallographic inversion centre coincides with the inversion centre of the naphthalene-1,5-disulfonate ion and all the sulfonate O atoms are hydrogen-bond acceptors, generating fused-ring motifs and a quadruple *DDAA* array. A halogen-bond (Cl···Cl) interaction is present in (I) with a distance and angle of 3.3505 (12) Å and 151.37 (10)°, respectively. In addition, a C—Cl···π interaction and a π–π interaction in (I) and a π–π interaction in (II) further stabilize these crystal structures.

1. Chemical context

The study of supramolecular interactions in the crystals of pyrimidinium salts continues to be an active field since the pyrimidine fragment is a component of nucleobases and many drug molecules. The pyrimidine group offers two protonation sites (the two ring nitrogens) and the site of protonation depends on the nature of the substituents. Tautomerism of the pyrimidinium cation has also been reported recently (Rajam *et al.*, 2017). The pyrimidinium–carboxylate interaction is also of fundamental importance in biology since it is involved in protein–nucleic acid interactions and drug-receptor recognition (Hunt *et al.*, 1980; Baker & Santi, 1965). The molecules are often self-assembled by hydrogen bonding, halogen bonding, cation···π, anion···π and π–π stacking interactions. Among these interactions, halogen bonding is of particular current interest (Cavallo *et al.*, 2016). Various substituted pyrimidines and their interactions with different acids have been studied systematically in our laboratory. The variation in supramolecular architectures resulting from the different substituents in the base and the acid is being investigated, and



crystal structures of 2,6-diamino-4-chloropyrimidinium salts with carboxylate/sulfonate have been reported recently from our laboratory (Mohana *et al.*, 2017). The same pyrimidine derivative has been used to prepare the title compounds in order to further study the supramolecular architectures and the role of the halogen bond.



(I) (II)

2. Structural commentary

The salt of compound (I) crystallizes with one CDAPY (2,6-diamino-4-chloropyrimidinium) cation and one CSA (5-chlorosalicylate) anion in the asymmetric unit (Fig. 1). The pyrimidinium cation is protonated at the N1 position (see Fig. 1 for atom numbering) and this is confirmed by an increase in the internal bond angle. The C2—N3—C4 angle at the unprotonated N3 atom is 115.1 (2)°, while for the protonated N1 atom, the C2—N1—C6 angle is 121.8 (2)°. The ion-pair (CDAPY and CSA) is almost planar [dihedral angle = 4.22 (11)°]. The carboxylate group of CSA is twisted slightly with respect to the remainder of the anion [dihedral angle= 3.9 (3)°]. The salt of compound (II) crystallizes with one CDAPY (2,6-diamino-4-chloropyrimidinium) cation and half a molecule of NSA (naphthalene-1,5-disulfonate) anion in the asymmetric unit (Fig. 2), the other half of NSA being generated by an inversion centre. A crystallographic inversion centre coinciding with the inversion centre of the NSA ion has also been reported earlier (Liu, 2012; Xu, 2012; Liu & Chen, 2012). The pyrimidinium cation is again protonated at the N1 position (see Fig. 2 for atom numbering) and this is confirmed by an increase in the internal bond angle. The C2—N3—C4 angle at the unprotonated N3 atom is 115.40 (16)°, while the angle at the protonated N1 atom (C2—N1—C6) is 121.84 (16)°. All of the sulfonate oxygen atoms of the NSA anion are involved in hydrogen bonding. The S1—O1, S1—O2 and S1—O3 distances are similar [1.4550 (15), 1.4584 (15) and 1.4431 (16) Å respectively].

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.86	1.82	2.664 (3)	168
N2—H2A···O1	0.86	2.56	3.223 (3)	135
N2—H2B···N3^{i}	0.86	2.13	2.970 (3)	165
O3—H3···O1	0.82	1.83	2.557 (3)	146
N6—H6A···O2	0.86	1.97	2.824 (3)	172
N6—H6B···O2^{ii}	0.86	1.96	2.819 (3)	172
C10—H10···O3^{iii}	0.93	2.51	3.358 (4)	151

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

3. Supramolecular features

In salt (I), the protonated N1 atom and the amino hydrogen (N6) atom of CDAPY are hydrogen bonded *via* two N—H···O bonds (Table 1) forming a robust $R_2^2(8)$ ring motif (heterosynthon) involving the carboxylate group. The typical intramolecular hydrogen-bond $S(6)$ motif (involving the carboxyl group and the phenolic –OH) observed in salicylates/salicylic acid is also present (Bernstein *et al.*, 1995; Prabakaran *et al.*, 2001; Panneerselvam *et al.*, 2002) (Fig. 1). The 2-amino hydrogen atom of CDAPY interacts with the carboxylate oxygen O1 of CSA *via* an N—H···O hydrogen bond forming an $R_2^1(6)$ ring motif. Thus, the O1 oxygen atom acts as a trifurcated acceptor. A similar set of three fused rings was observed in the crystal structure of 2,6-diamino-4-chloropyrimidinium 2-carboxy-3-nitrobenzoate (Mohana *et al.*, 2017). However, in compound (I) the role of the 2-amino and 6-amino groups has been reversed. A self-complementary base pairing *via* a pair of N2—H···N3^{i} (homosynthon) hydrogen bonds forming an $R_2^2(8)$ ring motif is also been observed. This type of base pairing is also observed in the crystal structures of 2,6-diamino-4-chloropyridinium 4-carboxybutanoate (Edison *et al.*, 2014), 2,6-diamino-4-chloropyrimidine-benzoic acid (Thanigaimani *et al.*, 2012*a*) and bis(2,6-diamino-4-chloropyrimidin-1-ium) fumarate (Thanigaimani *et al.*, 2012*b*). The 2,6-diamino-4-chloropyrimidinium

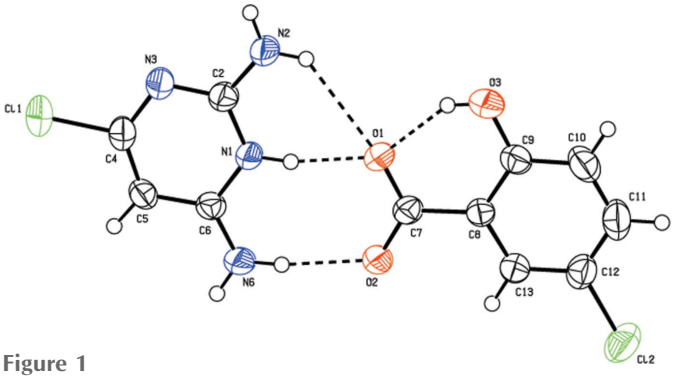


Figure 1
ORTEP view of compound (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level. Dashed lines represent hydrogen bonds.

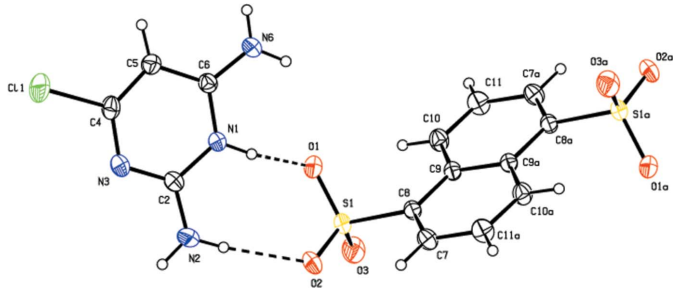


Figure 2
ORTEP view of compound (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level. Dashed lines represent hydrogen bonds.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.86	1.92	2.708 (2)	152
N2—H2A···O2^{i}	0.86	2.08	2.868 (3)	152
N2—H2B···O2	0.86	2.10	2.953 (2)	174
N6—H6A···N3^{ii}	0.86	2.25	2.943 (2)	138
N6—H6B···O3^{iii}	0.86	2.01	2.808 (2)	154

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

5-chlorosalicylate units are linked *via* a Cl···Cl interaction (a type I interaction; Cavallo *et al.*, 2016) with a distance and angle of 3.3505 (12) Å and 151.37 (10)°, respectively (Durka *et al.*, 2015) (Fig. 3). Furthermore, a weak C—H···O^{iii} hydrogen-bonding interaction is present in this crystal structure. In addition, a weak stacking interaction with *Cg*1···*Cg*2 [3.6624 (14) Å; symmetry code: $x, -1+y, z$; *Cg*1 and *Cg*2 are the centroids of the N1/C2/N3/C4/C5/C6 and C8–C13 rings, respectively] and C—Cl···π interactions [3.4469 (13) Å with an angle of 152.24 (9)°; symmetry code: $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$] (Muthukumaran *et al.*, 2011) further stabilize this crystal structure (Fig. 4).

In salt (II), the sulfonate group mimics the role of the carboxylate oxygen atoms in generating an $R_2^2(8)$ motif (heterosynthon) involving the aminopyrimidinium cation (CDAPY) (Bernstein *et al.*, 1995; Balasubramani *et al.*, 2007). All units of the CDAPY and NSA ions are hydrogen bonded (Table 2) to generate a quadruple DDAA array with fused ring motifs $R_2^2(8)$, $R_4^2(8)$ and $R_2^2(8)$ (Fig. 5). This type of array has also been reported earlier (Robert *et al.*, 2001; Umadevi *et al.*, 2002; Raj *et al.*, 2003; Subashini *et al.*, 2007; Thanigaimani *et al.*, 2007; Liu & Chen, 2012). In addition, the NSA anions also generate $R_3^2(10)$ and $R_3^3(21)$ ring motifs *via* N—H···O bonds. Weak π–π stacking interactions [*Cg*1···*Cg*4 = 3.4781 (11) Å; symmetry code: $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$ and *Cg*4···*Cg*2

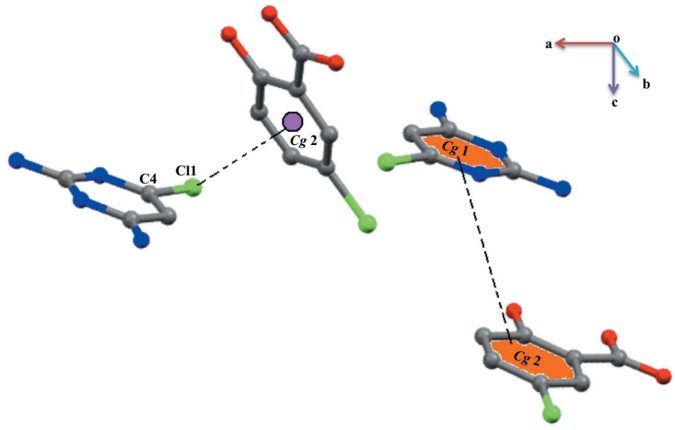


Figure 4
A weak C—Cl···π interaction and π–π stacking interactions.

=3.4781 (11) Å; symmetry code: $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$; *Cg*1, *Cg*2 and *Cg*4 are the centroids of the C7/C8/C9/C9′/C10′/C11′, C9/C10/C11/C7′/C8′/C9′ and N1/C2/N3/C4/C5/C6 rings, respectively] is also present (Fig. 6).

4. Database survey

Various salts of 5-chlorosalicylate have been reported: 2-methylquinolinium 5-chloro-2-hydroxybenzoate (Zhang *et al.*, 2014), 4-amino-5-chloro-2,6-dimethylpyrimidinium 5-chloro-2-hydroxybenzoate (Rajam *et al.*, 2017) and 2-amino-4,6-dimethylpyrimidinium 5-chlorosalicylate (Ebenezer & Muthiah, 2012). Similarly, various salts of half a molecule of naphthalene-1,5-disulfonate have been reported: bis(2-trifluoromethyl-1*H*-benzimidazole-3-ium) naphthalene-1,5-disulfonate (Liu, 2012), bis(3-methylanilinium) naphthalene-1,5-disulfonate (Liu & Chen, 2012) and bis(2-methylpiperidinium) naphthalene-1,5-disulfonate (Xu, 2012).

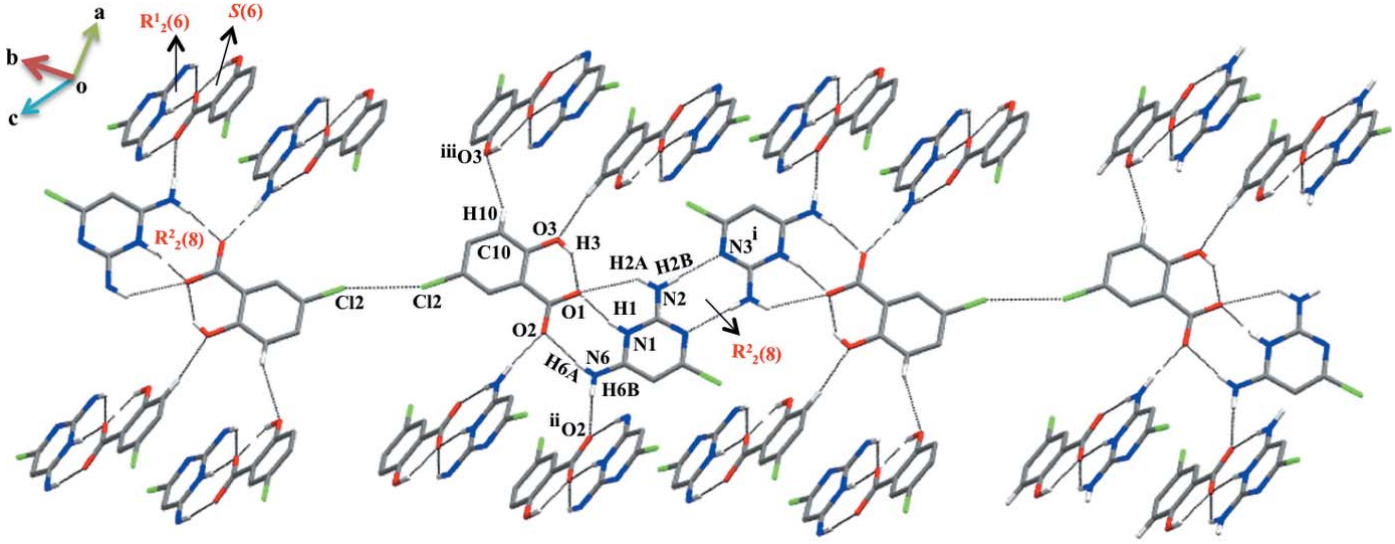


Figure 3
Supramolecular layered structure extended as a chain *via* Cl···Cl interactions in (I).

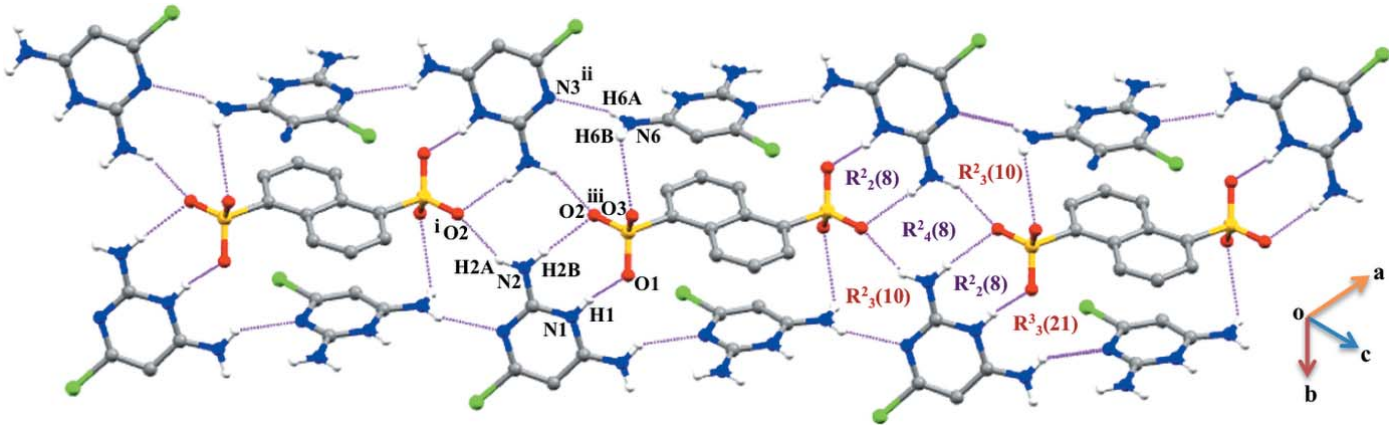


Figure 5
Formation of a quadruple *DDAA* array in (II) *via* N—H···O hydrogen bonds.

5. Synthesis and crystallization

Compounds (I) and (II) were synthesized by mixing hot ethanolic solutions (1:1) of 2,6-diamino-4-chloropyrimidine (36 mg) with 5-chlorosalicylic acid (43 mg) (I)/naphthalene-1,5-disulfonic acid (72 mg) (II). These mixtures were warmed to 333 K for 25 min. Colourless crystals separated out from the mother liquor at room temperature after a week.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were initially located readily in difference-Fourier maps and were treated as riding atoms with C—H = 0.93 Å (aromatic), N—H = 0.86 Å and O—H = 0.82 Å with $U_{iso}(H) = kU_{eq}(C,N,O)$, where k = 1.5 for hydroxy and 1.2 for all other H atoms.

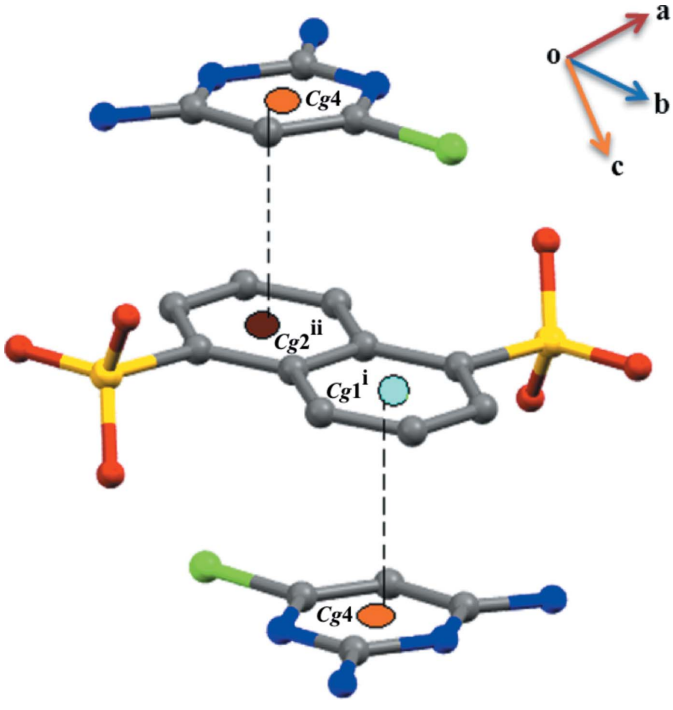


Figure 6
A view of the π–π stacking interactions between the pyrimidinium cation and the anion.

Acknowledgements

The EN–FIST Centre of Excellence, Ljubljana, Slovenia, is thanked for the use of the SuperNova diffractometer.

Funding information

RSD thanks the UGC–BSR India for the award of an RFSMS. PTM thanks UGC, New Delhi, for a UGC Emeritus fellowship. FP thanks the Slovenian Research Agency for financial support (PI-0230–0175).

References

Agilent. (2013). *CrysAlis PRO*. Agilent Technologies UK Ltd, Yarnton, England.
Baker, B. R. & Santi, D. V. (1965). *J. Pharm. Sci.* **54**, 1252–1257.
Balasubramani, K., Thomas Muthiah, P. & Lynch, D. E. (2007). *Chem. Cent. J.* **1**, 28.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Cavallo, G., Metrangolo, P., Milani, R., Pilati, T., Priimagi, A., Resnati, G. & Terraneo, G. (2016). *Chem. Rev.* **116**, 2478–2601.
Durka, K., Kliś, T. & Serwatowski, J. (2015). *Acta Cryst.* E**71**, 1471–1474.
Ebenezer, S. & Muthiah, P. T. (2012). *Cryst. Growth Des.* **12**, 3766–3785.
Edison, B., Balasubramani, K., Thanigaimani, K., Khalib, N. C., Arshad, S. & Razak, I. A. (2014). *Acta Cryst.* E**70**, o857–o858.
Hunt, W. E., Schwalbe, C. H., Bird, K. & Mallinson, P. D. (1980). *Biochem. J.* **187**, 533–536.
Liu, M.-L. (2012). *Acta Cryst.* E**68**, o342.
Liu, M.-L. & Chen, Z.-Q. (2012). *Acta Cryst.* E**68**, o1745.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Mohana, M., Thomas Muthiah, P. & Butcher, R. J. (2017). *Acta Cryst.* C**73**, 536–540.
Muthukumaran, J., Parthiban, A., Kannan, M., Rao, H. S. P. & Krishna, R. (2011). *Acta Cryst.* E**67**, o898–o899.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_4H_6ClN_4^+\cdot C_7H_4ClO_3^-$	$2C_4H_6ClN_4^+\cdot C_{10}H_6O_6S_2^{2-}$
M_r	317.13	577.42
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	293	293
a, b, c (Å)	13.9203 (14), 7.0285 (6), 15.4294 (14)	9.1696 (4), 13.0848 (7), 9.9663 (5)
β (°)	114.544 (12)	90.526 (5)
V (Å^3)	1373.2 (3)	1195.73 (10)
Z	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.49	0.50
Crystal size (mm)	0.40 × 0.10 × 0.03	0.40 × 0.40 × 0.06
Data collection		
Diffractometer	Agilent SuperNova Dual Source diffractometer with an Atlas detector	Agilent SuperNova Dual Source diffractometer with an Atlas detector
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2013)	Multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min}, T_{max}	0.644, 1.000	0.527, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7906, 3144, 2137	10382, 2735, 2274
R_{int}	0.027	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649	0.649
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.128, 1.04	0.038, 0.102, 1.05
No. of reflections	3144	2735
No. of parameters	182	163
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.40	0.49, −0.59

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008).

Panneerselvam, P., Stanley, N. & Muthiah, P. T. (2002). *Acta Cryst.* E**58**, o180–o182.
Prabakaran, P., Murugesan, S., Muthiah, P. T., Bocelli, G. & Righi, L. (2001). *Acta Cryst.* E**57**, o933–o936.
Raj, S. B., Muthiah, P. T., Rychlewska, U. & Warzajtis, B. (2003). *CrystEngComm*, **5**, 48–53.
Rajam, A., Muthiah, P. T., Butcher, R. J., Jasinski, J. P. & Glidewell, C. (2017). *Acta Cryst.* C**73**, 862–868.
Robert, J. J., Raj, S. B. & Muthiah, P. T. (2001). *Acta Cryst.* E**57**, o1206–o1208.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Subashini, A., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2007). *Acta Cryst.* E**63**, o3775.
Thanigaimani, K., Khalib, N. C., Arshad, S. & Razak, I. A. (2012*a*). *Acta Cryst.* E**68**, o3442–o3443.
Thanigaimani, K., Khalib, N. C., Farhadikoutenaei, A., Arshad, S. & Razak, I. A. (2012*b*). *Acta Cryst.* E**68**, o3321–o3322.
Thanigaimani, K., Muthiah, P. T. & Lynch, D. E. (2007). *Acta Cryst.* E**63**, o4555–o4556.
Umadevi, B., Prabakaran, P. & Muthiah, P. T. (2002). *Acta Cryst.* C**58**, o510–o512.
Xu, Q. (2012). *Acta Cryst.* E**68**, o1733.
Zhang, J., Jin, S., Tao, L., Liu, B. & Wang, D. (2014). *J. Mol. Struct.* **1072**, 208–220.

supporting information

Acta Cryst. (2018). E**74**, 237-241 [https://doi.org/10.1107/S2056989018001196]

Supramolecular interactions in 2,6-diamino-4-chloropyrimidin-1-ium 5-chloro-salicylate and bis(2,6-diamino-4-chloropyrimidin-1-ium) naphthalene-1,5-di-sulfonate

Robert Swinton Darious, Packianathan Thomas Muthiah and Franc Perdih

Computing details

For both structures, data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009).

2,6-Diamino-4-chloropyrimidin-1-ium 2-chloro-6-hydroxybenzoate (I)

Crystal data

$C_4H_6ClN_4^+·C_7H_4ClO_3^-$
M_r = 317.13
Monoclinic, $P2_1/n$
a = 13.9203 (14) Å
b = 7.0285 (6) Å
c = 15.4294 (14) Å
β = 114.544 (12)°
V = 1373.2 (3) Å^3
Z = 4
$F(000)$ = 648
D_x = 1.534 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1734 reflections
θ = 3.9–27.5°
μ = 0.49 mm^{-1}
T = 293 K
Needle, colorless
0.40 × 0.10 × 0.03 mm

Data collection

Agilent SuperNova Dual Source diffractometer with an Atlas detector
Radiation source: SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 10.4933 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO); Agilent, 2013)
T_{min} = 0.644, T_{max} = 1.000
7906 measured reflections
3144 independent reflections
2137 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 27.5°, θ_{min} = 2.9°
h = −18→17
k = −7→9
l = −20→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.128
S = 1.04
3144 reflections
182 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.5033P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.25461 (6)	−0.27636 (11)	−0.00641 (5)	0.0674 (2)
N1	0.38557 (14)	0.2707 (3)	0.12207 (13)	0.0386 (4)
H1	0.4128	0.3792	0.1450	0.046*
N2	0.50448 (17)	0.2485 (3)	0.05504 (16)	0.0566 (6)
H2B	0.5313	0.1895	0.0215	0.068*
H2A	0.5293	0.3573	0.0796	0.068*
N3	0.38700 (15)	0.0032 (3)	0.03064 (13)	0.0442 (5)
N6	0.27205 (16)	0.3072 (3)	0.19347 (15)	0.0503 (5)
H6A	0.3023	0.4141	0.2157	0.060*
H6B	0.2207	0.2687	0.2063	0.060*
C2	0.42485 (18)	0.1715 (3)	0.06889 (16)	0.0404 (5)
C4	0.30522 (17)	−0.0606 (3)	0.04713 (16)	0.0414 (5)
C5	0.26096 (16)	0.0273 (3)	0.09993 (15)	0.0398 (5)
H5	0.2048	−0.0266	0.1089	0.048*
C6	0.30401 (16)	0.2033 (3)	0.14025 (15)	0.0368 (5)
Cl2	0.50995 (6)	1.29096 (12)	0.45221 (5)	0.0745 (3)
O1	0.49261 (13)	0.5917 (2)	0.18881 (13)	0.0534 (5)
O2	0.38734 (12)	0.6467 (2)	0.26174 (12)	0.0501 (4)
O3	0.62982 (14)	0.8382 (3)	0.19368 (15)	0.0617 (5)
H3	0.5981	0.7365	0.1805	0.093*
C7	0.46259 (17)	0.6930 (3)	0.24184 (16)	0.0393 (5)
C8	0.51962 (15)	0.8751 (3)	0.27862 (15)	0.0362 (5)
C9	0.60003 (17)	0.9377 (4)	0.25339 (17)	0.0437 (6)
C10	0.65092 (19)	1.1105 (4)	0.28915 (19)	0.0563 (7)
H10	0.7038	1.1527	0.2718	0.068*
C11	0.6235 (2)	1.2181 (4)	0.34943 (19)	0.0580 (7)
H11	0.6576	1.3330	0.3729	0.070*
C12	0.54500 (19)	1.1548 (4)	0.37507 (17)	0.0488 (6)
C13	0.49410 (17)	0.9865 (3)	0.34066 (16)	0.0412 (5)
H13	0.4417	0.9458	0.3590	0.049*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0648 (4)	0.0561 (5)	0.0783 (5)	−0.0240 (3)	0.0267 (4)	−0.0292 (4)
N1	0.0432 (10)	0.0303 (10)	0.0503 (10)	−0.0045 (8)	0.0274 (9)	−0.0059 (9)

N2	0.0670 (13)	0.0480 (13)	0.0795 (15)	−0.0198 (11)	0.0551 (12)	−0.0247 (12)
N3	0.0479 (11)	0.0401 (11)	0.0490 (11)	−0.0089 (9)	0.0245 (9)	−0.0100 (10)
N6	0.0527 (11)	0.0418 (12)	0.0747 (14)	−0.0065 (10)	0.0448 (11)	−0.0087 (11)
C2	0.0460 (12)	0.0383 (13)	0.0442 (12)	−0.0032 (11)	0.0258 (10)	−0.0027 (11)
C4	0.0403 (12)	0.0346 (13)	0.0421 (11)	−0.0045 (10)	0.0099 (10)	−0.0031 (11)
C5	0.0337 (11)	0.0385 (13)	0.0477 (12)	−0.0050 (10)	0.0176 (10)	0.0007 (11)
C6	0.0354 (11)	0.0341 (12)	0.0433 (11)	0.0029 (9)	0.0187 (10)	0.0030 (10)
Cl2	0.0751 (5)	0.0685 (5)	0.0735 (5)	0.0006 (4)	0.0245 (4)	−0.0334 (4)
O1	0.0566 (10)	0.0395 (10)	0.0798 (12)	−0.0057 (8)	0.0439 (9)	−0.0171 (9)
O2	0.0519 (10)	0.0380 (9)	0.0762 (11)	−0.0081 (8)	0.0425 (9)	−0.0081 (9)
O3	0.0555 (11)	0.0592 (13)	0.0892 (13)	−0.0074 (9)	0.0487 (10)	−0.0126 (11)
C7	0.0401 (12)	0.0314 (12)	0.0494 (12)	0.0037 (10)	0.0216 (10)	0.0012 (10)
C8	0.0315 (10)	0.0326 (12)	0.0427 (11)	0.0022 (9)	0.0136 (9)	0.0001 (10)
C9	0.0351 (11)	0.0427 (14)	0.0539 (13)	0.0011 (10)	0.0192 (10)	0.0002 (12)
C10	0.0436 (13)	0.0566 (17)	0.0695 (16)	−0.0126 (13)	0.0242 (13)	−0.0008 (15)
C11	0.0517 (15)	0.0456 (15)	0.0638 (16)	−0.0121 (13)	0.0112 (13)	−0.0105 (14)
C12	0.0451 (13)	0.0436 (14)	0.0485 (13)	0.0009 (11)	0.0102 (11)	−0.0088 (12)
C13	0.0356 (11)	0.0399 (13)	0.0466 (12)	0.0005 (10)	0.0156 (10)	−0.0032 (11)

Geometric parameters (Å, º)

Cl1—C4	1.731 (2)	Cl2—C12	1.747 (3)
N1—C2	1.353 (3)	O1—C7	1.279 (3)
N1—C6	1.362 (3)	O2—C7	1.251 (3)
N1—H1	0.8600	O3—C9	1.352 (3)
N2—C2	1.328 (3)	O3—H3	0.8200
N2—H2B	0.8600	C7—C8	1.488 (3)
N2—H2A	0.8600	C8—C13	1.392 (3)
N3—C2	1.329 (3)	C8—C9	1.400 (3)
N3—C4	1.342 (3)	C9—C10	1.399 (4)
N6—C6	1.307 (3)	C10—C11	1.370 (4)
N6—H6A	0.8600	C10—H10	0.9300
N6—H6B	0.8600	C11—C12	1.382 (4)
C4—C5	1.357 (3)	C11—H11	0.9300
C5—C6	1.402 (3)	C12—C13	1.368 (3)
C5—H5	0.9300	C13—H13	0.9300
C2—N1—C6	121.80 (19)	C9—O3—H3	109.5
C2—N1—H1	119.1	O2—C7—O1	122.8 (2)
C6—N1—H1	119.1	O2—C7—C8	119.9 (2)
C2—N2—H2B	120.0	O1—C7—C8	117.29 (19)
C2—N2—H2A	120.0	C13—C8—C9	118.4 (2)
H2B—N2—H2A	120.0	C13—C8—C7	119.85 (19)
C2—N3—C4	115.1 (2)	C9—C8—C7	121.7 (2)
C6—N6—H6A	120.0	O3—C9—C10	118.0 (2)
C6—N6—H6B	120.0	O3—C9—C8	122.3 (2)
H6A—N6—H6B	120.0	C10—C9—C8	119.7 (2)
N2—C2—N3	119.6 (2)	C11—C10—C9	120.6 (2)

N2—C2—N1	117.5 (2)	C11—C10—H10	119.7
N3—C2—N1	122.8 (2)	C9—C10—H10	119.7
N3—C4—C5	126.4 (2)	C10—C11—C12	119.5 (2)
N3—C4—Cl1	114.28 (18)	C10—C11—H11	120.2
C5—C4—Cl1	119.28 (18)	C12—C11—H11	120.2
C4—C5—C6	116.8 (2)	C13—C12—C11	120.7 (2)
C4—C5—H5	121.6	C13—C12—Cl2	119.5 (2)
C6—C5—H5	121.6	C11—C12—Cl2	119.8 (2)
N6—C6—N1	117.7 (2)	C12—C13—C8	121.0 (2)
N6—C6—C5	125.3 (2)	C12—C13—H13	119.5
N1—C6—C5	117.0 (2)	C8—C13—H13	119.5
C4—N3—C2—N2	−178.7 (2)	O1—C7—C8—C9	2.6 (3)
C4—N3—C2—N1	1.2 (3)	C13—C8—C9—O3	179.9 (2)
C6—N1—C2—N2	−180.0 (2)	C7—C8—C9—O3	0.7 (3)
C6—N1—C2—N3	0.2 (3)	C13—C8—C9—C10	−1.2 (3)
C2—N3—C4—C5	−1.7 (3)	C7—C8—C9—C10	179.5 (2)
C2—N3—C4—Cl1	178.08 (16)	O3—C9—C10—C11	179.5 (2)
N3—C4—C5—C6	0.9 (3)	C8—C9—C10—C11	0.7 (4)
Cl1—C4—C5—C6	−178.93 (16)	C9—C10—C11—C12	0.1 (4)
C2—N1—C6—N6	179.0 (2)	C10—C11—C12—C13	−0.2 (4)
C2—N1—C6—C5	−1.1 (3)	C10—C11—C12—Cl2	179.8 (2)
C4—C5—C6—N6	−179.5 (2)	C11—C12—C13—C8	−0.3 (4)
C4—C5—C6—N1	0.6 (3)	Cl2—C12—C13—C8	179.61 (17)
O2—C7—C8—C13	4.7 (3)	C9—C8—C13—C12	1.1 (3)
O1—C7—C8—C13	−176.68 (19)	C7—C8—C13—C12	−179.7 (2)
O2—C7—C8—C9	−176.1 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.86	1.82	2.664 (3)	168
N2—H2*A*···O1	0.86	2.56	3.223 (3)	135
N2—H2*B*···N3^{i}	0.86	2.13	2.970 (3)	165
O3—H3···O1	0.82	1.83	2.557 (3)	146
N6—H6*A*···O2	0.86	1.97	2.824 (3)	172
N6—H6*B*···O2^{ii}	0.86	1.96	2.819 (3)	172
C10—H10···O3^{iii}	0.93	2.51	3.358 (4)	151

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

Bis(2,6-diamino-4-chloropyrimidin-1-ium) naphthalene-1,5-disulfonate (II)

Crystal data

$2C_4H_6ClN_4^+·C_{10}H_6O_6S_2^{2-}$
M_r = 577.42
Monoclinic, $P2_1/n$
a = 9.1696 (4) Å
b = 13.0848 (7) Å
c = 9.9663 (5) Å
β = 90.526 (5)°
V = 1195.73 (10) Å^3
Z = 2
F(000) = 592
D_x = 1.604 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å

Cell parameters from 3749 reflections
θ = 3.7–30.1°
μ = 0.50 mm^{-1}

T = 293 K
Prism, colorless
0.40 × 0.40 × 0.06 mm

Data collection

Agilent SuperNova Dual Source diffractometer with an Atlas detector
Radiation source: SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 10.4933 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2013)

T_{min} = 0.527, T_{max} = 1.000
10382 measured reflections
2735 independent reflections
2274 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −8→11
k = −16→15
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.102
S = 1.05
2735 reflections
163 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 0.5881P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.10474 (6)	0.91005 (5)	0.13497 (8)	0.0693 (2)
N1	0.47951 (17)	0.72194 (12)	0.24106 (15)	0.0379 (4)
H1	0.5541	0.6839	0.2572	0.045*
N2	0.4259 (2)	0.61789 (16)	0.0635 (2)	0.0675 (7)
H2A	0.3734	0.6006	−0.0047	0.081*
H2B	0.5013	0.5823	0.0853	0.081*
N3	0.27559 (18)	0.75496 (14)	0.10314 (17)	0.0437 (4)
N6	0.54208 (19)	0.81915 (14)	0.42350 (17)	0.0444 (4)
H6A	0.6148	0.7789	0.4376	0.053*
H6B	0.5275	0.8701	0.4761	0.053*
C2	0.3908 (2)	0.69909 (16)	0.1347 (2)	0.0420 (5)
C4	0.2528 (2)	0.83590 (15)	0.1817 (2)	0.0393 (4)
C5	0.3328 (2)	0.86453 (15)	0.2911 (2)	0.0377 (4)
H5	0.3089	0.9215	0.3422	0.045*
C6	0.45350 (19)	0.80277 (14)	0.32183 (18)	0.0333 (4)
S1	0.80386 (5)	0.55638 (4)	0.21480 (4)	0.03723 (15)
O1	0.75993 (16)	0.65802 (11)	0.25770 (15)	0.0491 (4)
O2	0.68017 (17)	0.49952 (12)	0.15999 (15)	0.0517 (4)

O3	0.92854 (18)	0.55687 (13)	0.12748 (14)	0.0541 (4)
C7	0.7936 (2)	0.40041 (15)	0.39206 (19)	0.0379 (4)
H7	0.7184	0.3761	0.3375	0.045*
C8	0.86088 (18)	0.49007 (14)	0.36151 (17)	0.0307 (4)
C9	0.97829 (18)	0.52894 (13)	0.44251 (17)	0.0293 (4)
C10	1.0523 (2)	0.62150 (15)	0.41375 (19)	0.0385 (4)
H10	1.0250	0.6595	0.3388	0.046*
C11	1.1626 (2)	0.65540 (16)	0.4944 (2)	0.0427 (5)
H11	1.2097	0.7163	0.4739	0.051*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0446 (3)	0.0740 (4)	0.0888 (5)	0.0223 (3)	−0.0221 (3)	−0.0052 (4)
N1	0.0362 (8)	0.0366 (8)	0.0405 (8)	0.0056 (7)	−0.0128 (7)	−0.0061 (7)
N2	0.0709 (13)	0.0633 (13)	0.0676 (13)	0.0230 (11)	−0.0364 (11)	−0.0346 (11)
N3	0.0371 (9)	0.0485 (10)	0.0454 (9)	0.0019 (7)	−0.0144 (7)	−0.0041 (8)
N6	0.0459 (10)	0.0451 (9)	0.0420 (9)	0.0073 (8)	−0.0150 (8)	−0.0107 (7)
C2	0.0415 (11)	0.0420 (11)	0.0424 (10)	0.0010 (8)	−0.0122 (9)	−0.0066 (8)
C4	0.0275 (9)	0.0429 (11)	0.0474 (11)	0.0012 (8)	−0.0047 (8)	0.0052 (9)
C5	0.0347 (9)	0.0367 (10)	0.0416 (10)	0.0032 (8)	−0.0022 (8)	−0.0028 (8)
C6	0.0327 (9)	0.0338 (9)	0.0333 (9)	−0.0023 (7)	−0.0023 (7)	0.0000 (7)
S1	0.0411 (3)	0.0401 (3)	0.0303 (2)	0.0063 (2)	−0.00909 (19)	0.00095 (18)
O1	0.0499 (8)	0.0425 (8)	0.0545 (9)	0.0128 (7)	−0.0185 (7)	−0.0033 (7)
O2	0.0563 (9)	0.0532 (9)	0.0451 (8)	0.0030 (7)	−0.0252 (7)	−0.0052 (7)
O3	0.0625 (10)	0.0643 (10)	0.0356 (8)	0.0090 (8)	0.0075 (7)	0.0121 (7)
C7	0.0326 (9)	0.0426 (11)	0.0382 (10)	−0.0054 (8)	−0.0048 (8)	−0.0017 (8)
C8	0.0295 (8)	0.0349 (9)	0.0276 (8)	0.0026 (7)	−0.0017 (7)	0.0004 (7)
C9	0.0279 (8)	0.0325 (9)	0.0276 (8)	0.0019 (7)	−0.0002 (6)	0.0012 (7)
C10	0.0415 (10)	0.0380 (10)	0.0361 (9)	−0.0029 (8)	−0.0033 (8)	0.0086 (8)
C11	0.0437 (11)	0.0387 (10)	0.0456 (11)	−0.0133 (8)	−0.0023 (9)	0.0073 (8)

Geometric parameters (Å, º)

Cl1—C4	1.7290 (19)	S1—O3	1.4431 (16)
N1—C6	1.352 (2)	S1—O1	1.4550 (15)
N1—C2	1.363 (2)	S1—O2	1.4584 (15)
N1—H1	0.8600	S1—C8	1.7749 (17)
N2—C2	1.319 (3)	C7—C8	1.361 (3)
N2—H2A	0.8600	C7—C11^{i}	1.403 (3)
N2—H2B	0.8600	C7—H7	0.9300
N3—C2	1.321 (3)	C8—C9	1.433 (2)
N3—C4	1.335 (3)	C9—C10	1.419 (3)
N6—C6	1.311 (2)	C9—C9^{i}	1.427 (3)
N6—H6A	0.8600	C10—C11	1.361 (3)
N6—H6B	0.8600	C10—H10	0.9300
C4—C5	1.361 (3)	C11—C7^{i}	1.403 (3)
C5—C6	1.402 (3)	C11—H11	0.9300

C5—H5	0.9300		
C6—N1—C2	121.84 (16)	O3—S1—O1	113.34 (10)
C6—N1—H1	119.1	O3—S1—O2	113.21 (10)
C2—N1—H1	119.1	O1—S1—O2	111.10 (9)
C2—N2—H2A	120.0	O3—S1—C8	105.66 (8)
C2—N2—H2B	120.0	O1—S1—C8	106.56 (8)
H2A—N2—H2B	120.0	O2—S1—C8	106.34 (9)
C2—N3—C4	115.40 (16)	C8—C7—C11^{i}	120.15 (17)
C6—N6—H6A	120.0	C8—C7—H7	119.9
C6—N6—H6B	120.0	C11^{i}—C7—H7	119.9
H6A—N6—H6B	120.0	C7—C8—C9	121.31 (16)
N2—C2—N3	121.08 (18)	C7—C8—S1	118.35 (13)
N2—C2—N1	116.65 (18)	C9—C8—S1	120.31 (13)
N3—C2—N1	122.27 (18)	C10—C9—C9^{i}	119.00 (19)
N3—C4—C5	127.02 (18)	C10—C9—C8	123.19 (15)
N3—C4—Cl1	114.47 (14)	C9^{i}—C9—C8	117.8 (2)
C5—C4—Cl1	118.51 (16)	C11—C10—C9	120.90 (17)
C4—C5—C6	115.80 (18)	C11—C10—H10	119.6
C4—C5—H5	122.1	C9—C10—H10	119.6
C6—C5—H5	122.1	C10—C11—C7^{i}	120.83 (18)
N6—C6—N1	118.48 (17)	C10—C11—H11	119.6
N6—C6—C5	123.87 (18)	C7^{i}—C11—H11	119.6
N1—C6—C5	117.64 (16)		
C4—N3—C2—N2	−179.1 (2)	O3—S1—C8—C7	−116.17 (16)
C4—N3—C2—N1	0.7 (3)	O1—S1—C8—C7	122.99 (16)
C6—N1—C2—N2	−179.4 (2)	O2—S1—C8—C7	4.41 (18)
C6—N1—C2—N3	0.8 (3)	O3—S1—C8—C9	61.75 (17)
C2—N3—C4—C5	−1.8 (3)	O1—S1—C8—C9	−59.08 (16)
C2—N3—C4—Cl1	178.00 (16)	O2—S1—C8—C9	−177.67 (14)
N3—C4—C5—C6	1.3 (3)	C7—C8—C9—C10	179.44 (18)
Cl1—C4—C5—C6	−178.48 (14)	S1—C8—C9—C10	1.6 (2)
C2—N1—C6—N6	178.92 (19)	C7—C8—C9—C9^{i}	−0.6 (3)
C2—N1—C6—C5	−1.3 (3)	S1—C8—C9—C9^{i}	−178.50 (17)
C4—C5—C6—N6	−179.95 (19)	C9^{i}—C9—C10—C11	−0.3 (3)
C4—C5—C6—N1	0.3 (3)	C8—C9—C10—C11	179.62 (19)
C11^{i}—C7—C8—C9	0.8 (3)	C9—C10—C11—C7^{i}	0.1 (3)
C11^{i}—C7—C8—S1	178.73 (16)		

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.86	1.92	2.708 (2)	152
N2—H2*A*···O2^{ii}	0.86	2.08	2.868 (3)	152
N2—H2*B*···O2	0.86	2.10	2.953 (2)	174

N6—H6*A*···N3^{iii}	0.86	2.25	2.943 (2)	138
N6—H6*B*···O3^{iv}	0.86	2.01	2.808 (2)	154

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