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Lamotrigine is a drug used in the treatment of epilepsy and related convulsive diseases. The drug in its free form is rather inadequate for pharmacological use due to poor absorption by the patient, which limits its bioavailability. On the other hand, the lamotrigine molecule is an excellent hydrogen-bonding agent and this has been exploited intensively in the search for better formulations. The formulation presently commercialized (under the brand name Lamictal) is rather complex and includes a number of anions in addition to the active pharmaceutical ingredient (API). The title salts of lamotrigine, namely 3,5-diamino-6-(2,3-dichlorophenyl)-1,2,4-triazin-2-ium 2-[(2-carboxyphenyl)disulfanyl]benzoate monohydrate, $C_9H_8Cl_2N_5^+ \cdot C_{14}H_9O_4S_2^- \cdot H_2O$, (I), and the anhydrate, $C_9H_8Cl_2N_5^+ \cdot C_{14}H_9O_4S_2^-$, (II), contain a lamotriginium cation (L), a hydrogen dithiodibenzoate monoanion (D) and, in the case of (I), a disordered solvent water molecule. Both L and D present their usual configurations severely twisted around their central C—C and S—S bonds, respectively. The supramolecular structure generated by the many available donor and acceptor sites is characterized by a planar antisymmetric motif of the form D–L–L–D, i.e. the structural building block. Although this characteristic motif is extremely similar in both structures, its conformation involves different donors and acceptors in its $R_2^2(8)$ central L–L homosynthon. The lateral $R_2^2(8)$ D–L heterosynthons are, on the other hand, identical. These substructures are further connected by strong hydrogen bonds into broad two-dimensional structures, in turn weakly linked to each other. Even if the homo- and heterosynthons in (I) and (II) are rather frequent in lamotrigine structural chemistry, the composite tetrameric synthon appears to be much less common. The occurrence of these motifs among lamotrigine salts and cocrystals is analyzed.

1. Introduction

6-(2,3-Dichlorophenyl)-1,2,4-triazine-3,5-diamine (best known as lamotrigine) is an anti-epileptic drug used in the treatment of epilepsy and related convulsive diseases. In spite of its excellent therapeutic performance, the drug in its free form is rather inadequate for pharmacological use due to poor absorption by the patient, as a result of low water solubility and dissolution rates (Parmer et al., 2009; Chadha et al., 2013) which limit its bioavailability. On the other hand, the lamotrigine molecule is an excellent hydrogen-bonding agent, presenting a number of donor and acceptor sites, which make it a potential target for both salt and cocrystal formation. This fact has been exploited intensively in the search for better formulations from a pharmacological point of view, and an impressive number of salts and cocrystals have been reported,

-C-S-S-C- torsion angle
(about 1000 entries)
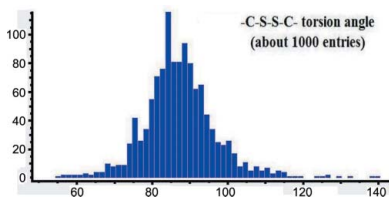
Table 1
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_9H_8Cl_2N_5^+\cdot C_{14}H_9O_4S_2^-\cdot H_2O$	$C_9H_8Cl_2N_5^+\cdot C_{14}H_9O_4S_2^-$
M_r	580.45	562.44
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Temperature (K)	294	294
a, b, c (Å)	8.0598 (7), 12.3474 (13), 13.4484 (10)	8.5368 (4), 12.3100 (8), 12.9348 (8)
α, β, γ (°)	100.996 (7), 98.101 (7), 103.659 (8)	64.689 (6), 86.474 (5), 77.230 (5)
V (Å^3)	1252.1 (2)	1197.56 (14)
Z	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.47	0.49
Crystal size (mm)	$0.50 \times 0.25 \times 0.15$	$0.44 \times 0.26 \times 0.16$
Data collection		
Diffractometer	Oxford Diffraction Gemini CCD S Ultra	Oxford Diffraction Gemini CCD S Ultra
Absorption correction	Multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	Multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min}, T_{max}	0.84, 0.95	0.82, 0.90
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11193, 5794, 3744	10448, 5165, 3784
R_{int}	0.035	0.028
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.689	0.679
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.166, 1.00	0.045, 0.118, 1.03
No. of reflections	5794	5165
No. of parameters	356	343
No. of restraints	8	8
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.78, −0.42	0.69, −0.40

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

as shown by a search in the Cambridge Structural Database (CSD, Version 5.37 and updates; Groom *et al.*, 2016), which lists 52 salts and 19 cocrystals. In fact, the formulation presently commercialized (under the brand name Lamictal) is rather complex and includes a number of anions in addition to the active pharmaceutical ingredient (API).

(I) · **H₂O**
(II) **anhydrous**
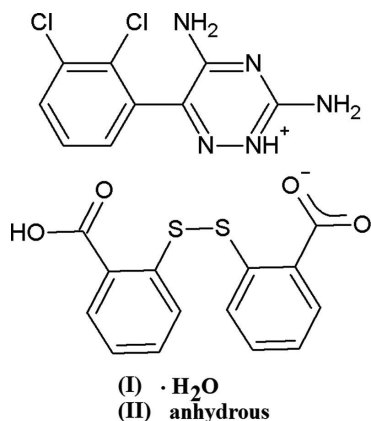
We present herein two different crystal structures of a new member of the vast universe of lamotrigine salts, *viz.* lamotrigine dithiodibenzoate, obtained under slightly different synthetic conditions (see below and §2.1), *viz.* the mono-hydrate form (I) and the anhydrate form (II), in both of which the extremely interactive 2,2′-dithiodibenzoic acid molecule (in its monoanionic form) crystallizes with a counter-ion also

extremely active in hydrogen bonding. As expected, this gives rise to a complex hydrogen-bonding behaviour which we study in detail. In addition, we analyze the preferences which the lamotrigine molecule shows regarding hydrogen-bonding synthons in its many appearances in the literature.

Both title lamotrigine dithiobenzoate solvatomorphs, namely 3,5-diamino-6-(2,3-dichlorophenyl)-1,2,4-triazin-2-ium 2-[(2-carboxyphenyl)disulfanyl]benzoate monohydrate, (I), and the anhydrate, (II), were unwittingly obtained while trying to synthesize lamotrigine thiosalicilate, starting from different media and at different reaction/crystallization temperatures. This indicates a surprising tendency of thiosalicilic acid to dimerize towards dithiobenzoate. The reasons for this behaviour are not clear yet and, while reporting these unexpected though extremely interesting products, we continue to strive for the elusive thiosalicilate.

2. Experimental

2.1. Synthesis and crystallization

The title salts were obtained by similar methods, but at different temperatures [296 K for (I) and 328 K for (II)] from different solvents [methanol for (I) and ethanol for (II)] and with different amounts of reactant [lamotrigine: 25 mg for (I) and 50 mg for (II); thiosalicilic acid: 15 mg for (I) and 30 mg for (II); solvent: 5 ml for (I) and 10 ml for (II)].
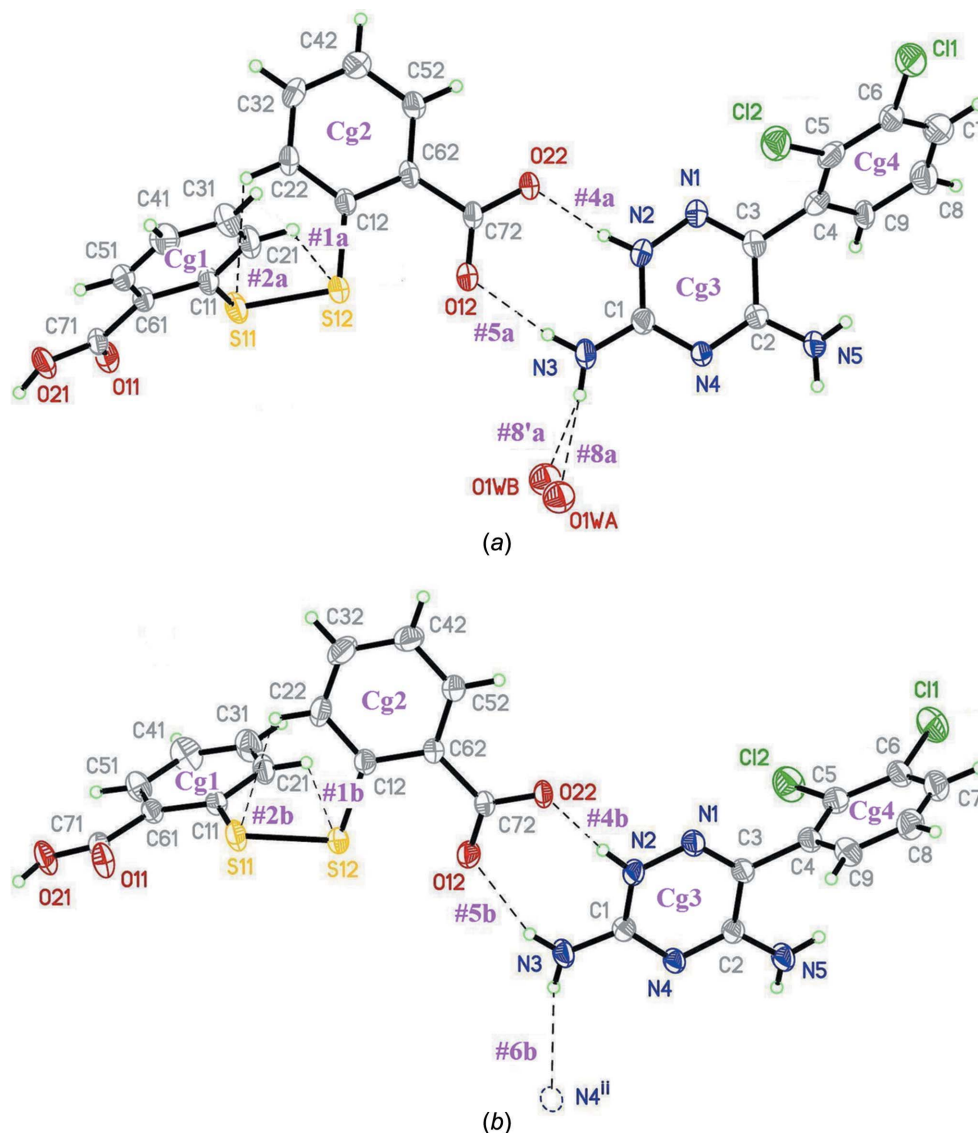
Figure 1
Views of the asymmetric units of (a) (I) and (b) (II), with displacement ellipsoids drawn at the 40% probability levels. Broken lines represent hydrogen bonds and the numbers with the hash (#) symbol refer to entry numbers in Tables 3 and 5. The two parts of the disordered water solvent molecule in (I) are shown. [Symmetry code: (ii) $-x$, $-y + 2$, $-z + 1$.]

The specified amounts of lamotrigine and thiosalicilic acid were added to the solvent and kept under mechanical stirring at the specified temperature until complete dissolution occurred. After slow evaporation, medium-sized pale-yellow prismatic crystals adequate for X-ray diffraction analysis were obtained.

In the case of (I), since no water was explicitly used in the synthesis, it is presumed that the hydration water molecule resulted from the (methanol) solvent, which was used as purchased without further purification.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All the H atoms in the lamotriginium and 2-[(2-carboxyphenyl)disulfanyl]benzoate ions were confirmed in a difference map, but were treated differently in the refinement. $X-H$ groups (X = O and N)

were refined with restrained $X-H$ distances of 0.85 (1) Å, as well as a restrained H⋯H distance within the $-NH_2$ groups of 1.35 (2) Å, while C−H groups were idealized and treated as riding (C−H = 0.93 Å). The $U_{iso}(H)$ values were taken as $1.2U_{eq}$(host). The water molecule in (I) is disordered over two positions, which were constrained to have identical anisotropic displacement ellipsoids. The occupancy of the more occupied site refined to 0.685 (4). The disordered water H atoms could not be found and were not included in the model. The short O1WA⋯O11($-x + 1$, $-y$, $-z + 1$) and O1WB⋯O11($-x + 1$, $-y$, $-z + 1$) contacts of 2.993 (5) and 2.772 (1) Å, respectively, probably represent hydrogen bonds involving omitted H atoms.

3. Results and discussion

Table 2 shows some selected parameters relevant for the foregoing discussion, while Tables 3 and 4, in turn, present the
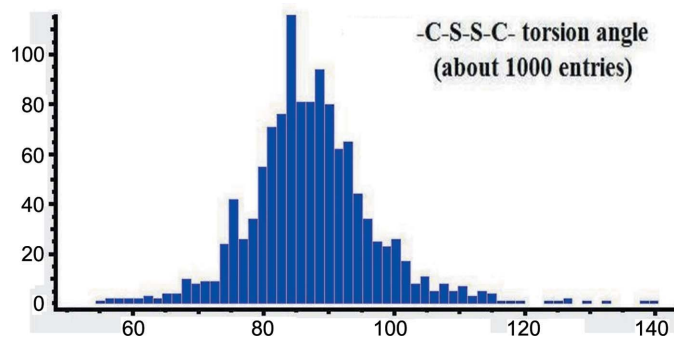
912 Freire et al. · $C_9H_8Cl_2N_5^+ \cdot C_{14}H_9O_4S_2^- \cdot H_2O$ and $C_9H_8Cl_2N_5^+ \cdot C_{14}H_9O_4S_2^-$

Acta Cryst. (2016). C72, 910–916

Figure 2
The distributuion of the C—S—S—C torsion angles in the CSD (Groom *et al.*, 2016) (1205 cases, 48 outliers left aside).

noncovalent interactions in (I), and Tables 5 and 6 present the noncovalent interactions in (II). For easy reference, these interactions have been labelled using the sequential codes shown in the first column.

Both compounds crystallize in the space group $P\bar{1}$, with an asymmetric unit composed of a lamotriginium cation (L) and a 2-[(2-carboxyphenyl)disulfanyl]benzoate anion (D). In the case of (I), a disordered solvent water molecule, split into two nearby positions, completes the structure (Fig. 1).

The lamotriginium cations are featureless, metrically similar to each other (see Table S1 in the *Supporting information* for a comparison of equivalent parameters) and to the many occurrences reported in the literature. The main difference between both moieties corresponds to the only degree of freedom in the molecule, the N1—C3—C4—C5 torsion angle, which measures the rotation between the planar rings
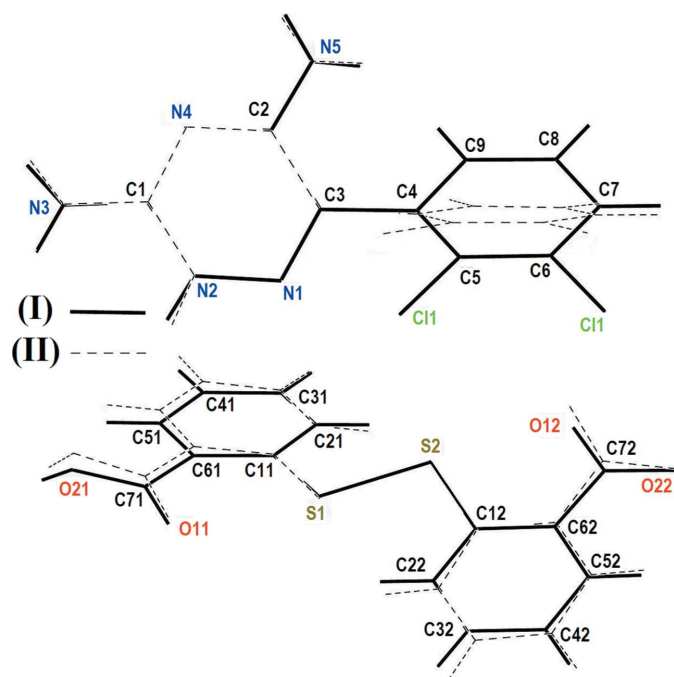

Figure 3
Overlapping representation of equivalent ions in (I) and (II), showing the main differences. Full lines represent structure (I) and broken lines represent structure (II).

Table 2
Selected geometric parameters (Å, °).

HB denotes hydrogen bond.

	(I)	(II)	Comment
O11—C71	1.223 (4)	1.207 (3)	Double bond
O21—C71	1.330 (4)	1.323 (3)	HB donor
O12—C72	1.245 (4)	1.236 (3)	Double HB acceptor
O22—C72	1.269 (4)	1.283 (3)	Single HB acceptor
C12—S12—S11—C11	−83.70 (16)	−89.44 (12)	
N1—C3—C4—C5	71.0 (4)	100.9 (3)	

Table 3
Hydrogen-bond geometry (Å, °) in (I).

Code	D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
#1a	C21—H21$\cdots$S12	0.93	2.64	3.181 (4)	118
#2a	C22—H22$\cdots$S11	0.93	2.59	3.146 (4)	119
#3a	O21—H21O$\cdots$O22^{i}	0.850 (10)	1.778 (16)	2.599 (3)	162 (4)
#4a	N2—H2$\cdots$O22	0.847 (10)	1.844 (12)	2.686 (3)	172 (4)
#5a	N3—H3$B\cdots$O12	0.843 (10)	1.976 (11)	2.811 (4)	171 (3)
#6a	N5—H5$A\cdots$N4^{ii}	0.837 (10)	2.256 (13)	3.080 (4)	168 (4)
#7a	N5—H5$B\cdots$O11^{iii}	0.840 (10)	2.229 (15)	3.041 (4)	163 (3)
#8a	N3—H3$A\cdots$O1WA	0.841 (10)	2.217 (13)	3.052 (5)	172 (4)
#8a′	N3—H3$A\cdots$O1WB	0.841 (10)	1.81 (2)	2.607 (9)	157 (4)

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

Table 4
C—$X\cdots Cg$ (X = O or Cl) contacts (Å) in (I).

Ring codes are as shown in Fig. 1.

Label	C—$X\cdots Cg$	$X\cdots Cg$	$(X\cdots Cg)_{perp}$
#9a	C5—Cl2$\cdots Cg1^{iv}$	3.804 (2)	3.751
#10a	C6—Cl1$\cdots Cg2^{v}$	3.813 (2)	3.349
#11a	C71—O11$\cdots Cg4^{vi}$	3.474 (3)	3.337
#12a	C72—O21$\cdots Cg3^{vii}$	3.973 (3)	3.444

Symmetry codes: (iv) $x, y + 1, z$; (v) $−x + 1, −y + 1, −z$; (vi) $x + 1, y − 1, z$; (vii) $−x + 1, −y + 1, −z + 1$.

[71.0 (4)° in (I) and 100.9 (3)° in (II)] against a mean value of 73 (8)° (for 73 cases in the CSD; Groom *et al.*, 2016). As in all the occurrences of the molecule in its cationic form, proton transfer from the acid takes place at atom N2.

The singly deprotonated anion, in turn, is also severely twisted, with C11—S11—S21—C21 torsion angles of −83.70 (16) and −89.44 (12)°, and interplanar angles between the rings of 75.20 (17) and 83.18 (14)° for (I) and (II), respectively. These ~90° torsion angles correspond to the most stable form of disulfides, as disclosed by molecular orbital calculations (Boyd, 1972), which have shown that the S—S bond is stronger at a –C—S—S—C– dihedral angle of 90° and weakens at both sides of this maximum, due basically to the repulsion between 3p lone-pair orbitals on adjacent S atoms, which would go through a minimum at 90° and would increase below/above this value.

This behaviour is confirmed by an overwhelming majority of the molecules containing a noncyclic –C—S—S—C– group, with a mean value for the torsion angle of 87 (10)° (1205 cases in the CSD, 48 outliers left aside; Fig. 2). In the present case,
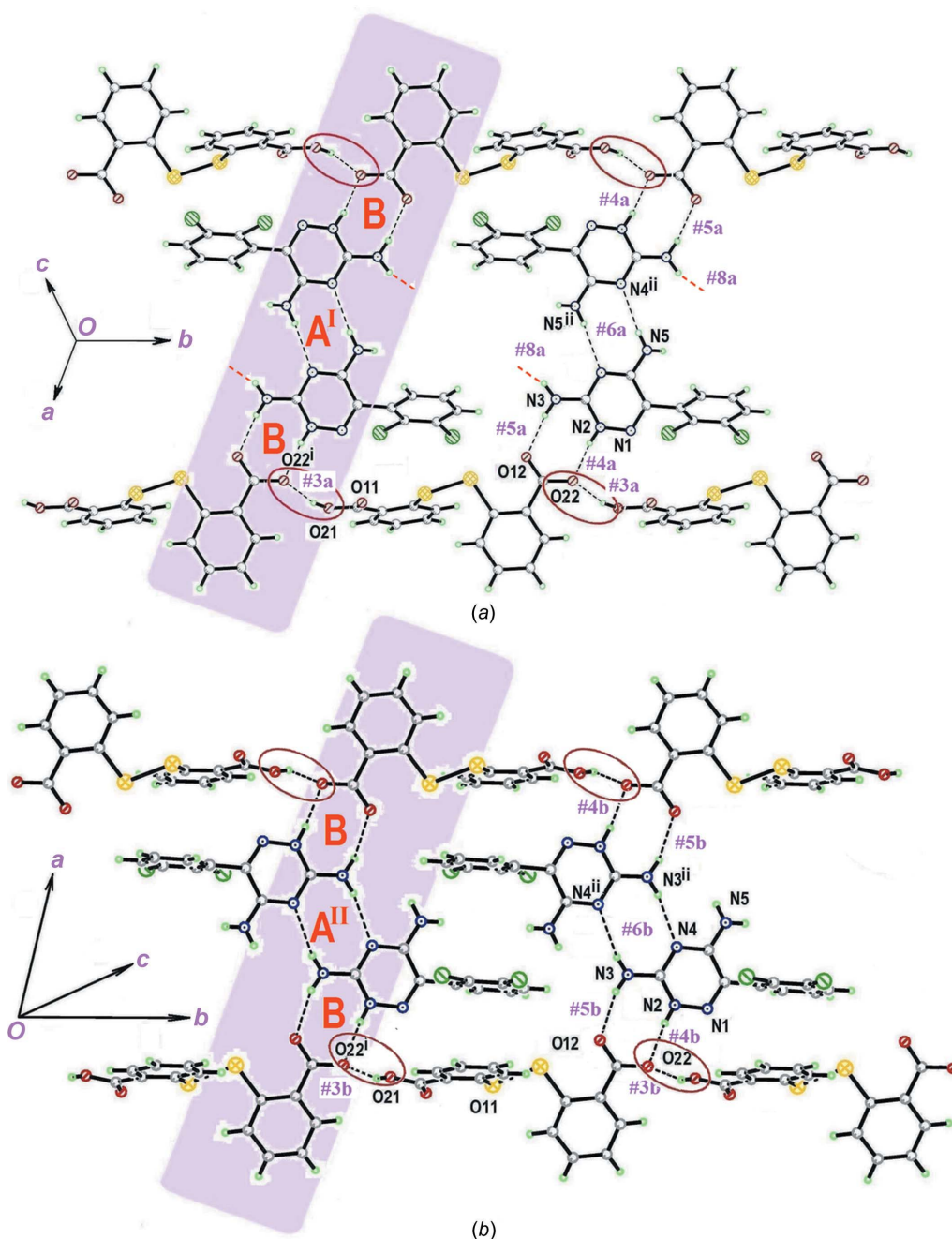
Figure 4
A view of the hydrogen-bonded tapes for (a) (I) and (b) (II), running along [010]. The tetrameric unit built up by the central homosynthon **A** and the two lateral heterosynthons **B** is highlighted. The hydrogen bonds responsible for the linkage between adjacent tetramers are highlighted with red ellipses. The symmetry codes for (I) are as in Table 3, while those for (II) are as in Table 5.

this geometry is facilitated by the presence of two intramolecular C—H···S hydrogen bonds (see interactions #1a and #1b in Table 3, and interactions #2a and 2#b in Table 5; see also Fig. 1).

Among the carboxylic acid and carboxylate groups, there is a clear correlation between the protonation state and the C—O distances (for numerical values, see Table 2). The COOH group shows well differentiated single and double bonds, while in the deprotonated COO⁻ group, both distances are rather similar, displaying much smaller differences. But in spite of their similarities, the C72—O12 and C72—O22 bond

lengths suggest, in turn, a trend between an enhanced involvement in hydrogen bonding and a lengthening of the C—$O_{acceptor}$ bonds (Table 2).

Fig. 3 presents a schematic summary of what has been discussed so far in the form of overlapping diagrams of equivalent moieties [i.e. $L_{(I)}/L_{(II)}$ and $D_{(I)}/D_{(II)}$], graphically showing the main differences between the molecular structures.

Of particular interest in these compounds is the way in which noncovalent interactions organize in order to build up the crystal structure. In particular, we will focus on the

Table 5
Hydrogen-bond geometry (Å, °) in (II).

Code	D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
#1b	C21—H21$\cdots$S12	0.93	2.64	3.150 (3)	115
#2b	C22—H22$\cdots$S11	0.93	2.60	3.152 (3)	118
#3b	O21—H21O$\cdots$O22^{i}	0.849 (10)	1.877 (16)	2.683 (2)	158 (3)
#4b	N2—H2$\cdots$O22	0.847 (10)	1.874 (11)	2.717 (2)	173 (3)
#5b	N3—H3$B\cdots$O12	0.839 (10)	2.111 (13)	2.906 (3)	158 (2)
#6b	N3—H3$A\cdots$N4^{ii}	0.838 (9)	2.364 (13)	3.168 (3)	161 (3)
#7b	N5—H5$B\cdots$O11^{iii}	0.833 (9)	2.252 (19)	2.941 (3)	140 (2)
#8b	N5—H5$A\cdots$O22^{iv}	0.841 (10)	2.176 (18)	2.932 (3)	149 (3)

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

Table 6
C—Cl$\cdots Cg$ contacts (Å) in (II).

Ring codes are as shown in Fig. 1.

Label	C—Cl$\cdots Cg$	Cl$\cdots Cg$	(Cl$\cdots Cg$)$_{perp}$
#9b	C6—Cl2$^{iv}\cdots Cg2$	3.581 (2)	3.299

Symmetry code: (iv) $-x + 1, -y + 1, -z + 2$.

substructure generated by the strong X—H$\cdots Y$ hydrogen bonds (X and Y = N and O).

There are two characteristic synthons in the supramolecular structures of (I) and (II), labelled in Fig. 4 as **A** and **B**. The synthon labelled **B** is a noncentrosymmetric heterosynthon, induced by interactions #4a and #5a for (I) (Table 3) and interactions #4b and #5b for (II) (Table 5), in the form of an $R_2^2(8)$ loop connecting a lamotriginium cation and a 2-[(2-carboxyphenyl)disulfanyl]benzoate anion. This synthon, identical in (I) and (II), is also characteristic of many lamotriginium carboxylate salts.

A more interesting situation arises with the centrosymmetric homosynthon **A**, where (I) and (II) differ in a rather subtle way. In both cases, the group gives rise to an $R_2^2(8)$ loop linking lamotriginium cations with each other, and this is achieved by way of the same acceptor in both synthons (N4), but different donors [N3 in (I) (interaction #6a in Table 3) and N5 in (II) (interaction #6b in Table 5)]. For future reference, we shall differentiate these synthons as $\mathbf{A^I}$ and $\mathbf{A^{II}}$, respectively. Inspection of Fig. 4 shows that the difference is due to a 'relative shift' between L cations in such a way that, in the case of the anhydrous form (II), atom N3 is fully involved in this 'tetrameric' construction, leaving atom N5 free to be involved in different connections, while in the case of the hydrate (I), one of the N3 hydrogens is 'blocked' by the hydrogen-bonding interaction with the solvent water molecule (#8a in Figs. 1 and Fig. 4), leaving just one H atom for the construction of the tetramer.

The resulting extremely similar tetrameric D–L–L–D substructures, highlighted in Fig. 4, are the result of the linkage of three $R_2^2(8)$ loops. The main difference is due to the diverse L–L interaction schemes. In (I), the link goes through the lamotriginium N-substituted ring, while in (II) it does not, neighbouring rings having the C1—N3 bond in common. This introduces a significant lengthening of the tetramer in the case of (I) (ca 17%), with a 23.06 (2) Å span between the outer-
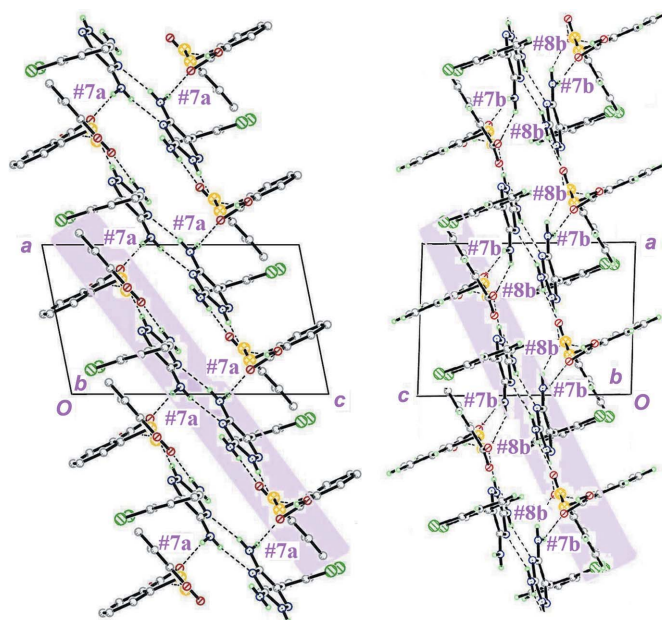
Figure 5
Packing diagrams of (a) (I) and (b) (II) viewed along [010] and depicting the way in which the tapes shown in Fig. 3 (in projection, highlighted) lean parallel to the (102) plane in (I) and to the ($\bar{1}$02) plane in (II), while running along [010]. Hydrogen bonds #7a [in (I); Table 3] and #7b and #8b [in (II); Table 5] finally join them into broad two-dimensional structures, which extend parallel to the (001) plane.

most C atoms, as compared with a span of 19.78 (2) Å in (II). In both cases, the tetramer (including the terminal arene rings) is basically planar [mean deviation from the least-squares plane for the C, N and O atoms in the highlighted zone in Fig. 4 is 0.16 Å for (I) and 0.24 Å for (II)].

The substructures described so far are the result of only three out of the six active X—H groups available (X = N or O), viz. H2, H3B and H5A [in (I)] or H3A [in (II)]; the remaining three X—H groups play important structural roles in the interconnection of tetramers, with the exception of atom H3A in (I), which is 'saturated' with some nonrelevant hydrogen bonds to the disordered solvent water molecule (#8a and #8a′ in Table 3, and Fig. 1)

To begin with, the acidic H21O atom [#3a in (I) (Table 3) and #3b in (II) (Table 5); circled in Fig. 4] serves to link the tetrameric substructures into broad planar tapes, which are inclined parallel to (102) in (I) and to ($\bar{1}$02) in (II), and (in both cases) run along [010]. These strips are further connected along [100], in the case of (I), through the single hydrogen-bond donor left to this structure (H5B; interaction #7a in Table 3), but in (II) with both H atoms attached to N5 (#7b and #8b in Table 5). These interactions define broad two-dimensional arrays, which run parallel to (001), as shown in Fig. 5.

There are additionally, in both structures, second-order Cl$\cdots\pi$ interactions (Tables 4 and 6), all of them connecting Cl atoms and rings within the planes and thus serving to strengthen the intraplanar linkage. It is interesting to note that in these broad two-dimensional structures, the hydrophilic part remains internal to the planes, and only a hydrophobic envelope is exposed to its surroundings (Fig. 5). In fact, the

915

outermost hydrophilic representatives are the Cl atoms, and even they are excluded from significant interplanar interactions. As a result, the interactions between planes are weak and mainly of a diffuse character (London forces, *etc.*)

An analysis in the CSD disclosed 74 structures of lamotrigine (53 as lamotriginium salts and 21 as cocrystals). When the characteristics of the *L–L* interactions were analyzed in detail, it was seen that the $R_2^2(8)$ loop connecting *L* moieties was rather frequent, with 41 appearances in total, 22 of which were found in salts and 19 in cocrystals. Thus, lamotrigine molecules in their neutral state (cocrystals) largely prefer (90% of the cases) to connect to each other *via* these $R_2^2(8)$ loops, with an even distribution of $\mathbf{A^I}$ and $\mathbf{A^{II}}$ homosynthon types (ten and nine cases, respectively).

The case of lamotriginium cations (salts) was distinctly different. In only 22 out of 53 cases (42%) do the molecules interact with each other through a type **A** synthon, with an overwhelming majority being of the $\mathbf{A^I}$ type (21 cases) and only one being of the $\mathbf{A^{II}}$ type. Thus, structure (II) in the present work appears to be rather singular in the general interaction scheme of lamotriginium anions.

The planar **B–A–B** centrosymmetric composite, in turn, is more restricted. There are 22 cases, most of which (*i.e.* 20) correspond to the $\mathbf{B}$–$\mathbf{A^I}$–$\mathbf{B}$ synthon, with 19 salts and only one cocrystal. Thus, and according to these figures, the tetrameric array appears as a preferred building brick for lamotriginium salts. The remaining two cases correspond to the $\mathbf{B}$–$\mathbf{A^{II}}$–$\mathbf{B}$ type and cover one salt and one cocrystal.

The diversity of structures which may result from this common building block should be ascribed to the remaining nonsaturated hydrogen-bonding sites still available in the anion and/or solvates. As an example, the terminal H21 arom in (I) and (II) is responsible for the chain structures; compounds where this H atom is absent, instead, tend to form isolated tetramers as is the case for the structure with the CSD refcode GAVLEV (Sridhar & Ravikumar, 2005), where the anion is a plain benzoate. The abundance of solvates with poor (or none at all) bridging capabilities (methanol, dimethylformamide, *etc*) can, in turn, 'block' some of the possible N—H···*X* interactions, changing drastically the possible supramolecular landscape. Furthermore, in many carboxylate salts where the **B–A–B** synthon is not present, the reason lies in the interposition of some of these solvents, either through saturation of an existing hydrogen-bonding site or simply by opening of the ring into larger less symmetrical structures [*e.g.*

OVUMIC (Sridhar & Ravikumar, 2011) with dimethylformamide and water, and WOVLEFT (Cheney *et al.*, 2010) with methanol].

Finally, there are examples in the literature of subtleties where slight differences in the intervening species end up favouring (or disrupting) the formation of the **B–A–B** tetrameric synthon. An example can be found in the structures having 4-fluorobenzoic acid (OVUMEY; Sridhar & Ravikumar, 2011) and 4-bromobenzoic acid (WOKXUR; Sridhar *et al.*, 2014) as counter-anions. Even if in both structures the halogen atom appears as quite 'inert' (they are not involved in any significant nonbonding interactions), the brominated compound does generate the tetrameric **B–A–B** synthon, while the flourinated compound does not.

In any case, it is apparent that the supramolecular scenario for lamotrigine structures is vast and open to as many different possibilities as different hydrogen-bonding partners (or sets of them) can be thought of.

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Hydrogen-bonding synthons in lamotrigine salts: 3,5-diamino-6-(2,3-dichlorophenyl)-1,2,4-triazin-2-ium 2-[(2-carboxyphenyl)disulfanyl]benzoate in its monohydrate and anhydrous forms

Eleonora Freire, Griselda Polla and Ricardo Baggio

Computing details

For both compounds, data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008). Software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) andPLATON (Spek, 2009) for (I); *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009) for (II).

(I) 3,5-Diamino-6-(2,3-dichlorophenyl)-1,2,4-triazin-2-ium 2-[(2-carboxyphenyl)disulfanyl]benzoate monohydrate

Crystal data

$C_9H_8Cl_2N_5^+ \cdot C_{14}H_9O_4S_2^- \cdot H_2O$	$Z = 2$
$M_r = 580.45$	$F(000) = 596$
Triclinic, $P\bar{1}$	$D_x = 1.540$ Mg m^{-3}
$a = 8.0598$ (7) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 12.3474$ (13) Å	Cell parameters from 1591 reflections
$c = 13.4484$ (10) Å	$\theta = 4.0–24.6°$
$\alpha = 100.996$ (7)°	$\mu = 0.47$ mm^{-1}
$\beta = 98.101$ (7)°	$T = 294$ K
$\gamma = 103.659$ (8)°	Prism, pale_yellow
$V = 1252.1$ (2) Å^3	$0.50 \times 0.25 \times 0.15$ mm

Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer	5794 independent reflections
	3744 reflections with $I > 2\sigma(I)$
ω scans, thick slices	$R_{int} = 0.035$
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)	$\theta_{max} = 29.3°$, $\theta_{min} = 3.7°$
	$h = -10 \rightarrow 9$
$T_{min} = 0.84$, $T_{max} = 0.95$	$k = -16 \rightarrow 16$
11193 measured reflections	$l = -18 \rightarrow 17$

Refinement

Refinement on F^2	5794 reflections
Least-squares matrix: full	356 parameters
$R[F^2 > 2\sigma(F^2)] = 0.057$	8 restraints
$wR(F^2) = 0.166$	Hydrogen site location: mixed
$S = 1.00$	

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0716P)^2 + 0.7292P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.78$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ 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}	Occ. (<1)
S11	0.77327 (12)	−0.07472 (7)	0.28054 (7)	0.0412 (2)	
O11	0.8359 (3)	−0.2817 (2)	0.2858 (2)	0.0429 (6)	
O21	0.7123 (3)	−0.4436 (2)	0.1645 (2)	0.0466 (6)	
H21O	0.735 (5)	−0.483 (3)	0.207 (2)	0.056*	
C11	0.6798 (4)	−0.1567 (3)	0.1521 (3)	0.0352 (7)	
C21	0.6092 (4)	−0.1083 (3)	0.0785 (3)	0.0450 (9)	
H21	0.6096	−0.0317	0.0964	0.054*	
C31	0.5371 (5)	−0.1712 (3)	−0.0220 (3)	0.0487 (9)	
H31	0.4906	−0.1369	−0.0710	0.058*	
C41	0.5354 (5)	−0.2851 (3)	−0.0481 (3)	0.0467 (9)	
H41	0.4862	−0.3283	−0.1148	0.056*	
C51	0.6058 (4)	−0.3352 (3)	0.0239 (3)	0.0397 (8)	
H51	0.6041	−0.4120	0.0051	0.048*	
C61	0.6799 (4)	−0.2730 (3)	0.1249 (3)	0.0326 (7)	
C71	0.7506 (4)	−0.3306 (3)	0.1995 (3)	0.0367 (8)	
S12	0.69471 (11)	0.07312 (7)	0.29397 (7)	0.0398 (2)	
O12	0.6162 (3)	0.2656 (2)	0.3413 (2)	0.0481 (6)	
O22	0.7138 (3)	0.43096 (18)	0.29926 (17)	0.0362 (5)	
C12	0.8473 (4)	0.1655 (3)	0.2412 (2)	0.0315 (7)	
C22	0.9662 (4)	0.1253 (3)	0.1894 (3)	0.0391 (8)	
H22	0.9681	0.0493	0.1833	0.047*	
C32	1.0812 (4)	0.1955 (3)	0.1472 (3)	0.0433 (8)	
H32	1.1613	0.1672	0.1142	0.052*	
C42	1.0780 (5)	0.3079 (3)	0.1537 (3)	0.0465 (9)	
H42	1.1560	0.3557	0.1255	0.056*	
C52	0.9576 (4)	0.3485 (3)	0.2025 (3)	0.0370 (8)	
H52	0.9534	0.4236	0.2055	0.044*	
C62	0.8422 (4)	0.2791 (3)	0.2476 (2)	0.0309 (7)	
C72	0.7146 (4)	0.3283 (3)	0.2994 (2)	0.0333 (7)	
Cl1	0.16354 (15)	0.88548 (10)	0.09415 (8)	0.0631 (3)	
Cl2	0.18343 (14)	0.64446 (9)	0.12805 (8)	0.0564 (3)	
N1	0.4223 (4)	0.5934 (2)	0.3226 (2)	0.0399 (7)	
N2	0.4335 (3)	0.4952 (2)	0.3473 (2)	0.0375 (7)	
H2	0.519 (3)	0.469 (3)	0.334 (3)	0.045*	
N3	0.3547 (4)	0.3462 (3)	0.4241 (2)	0.0470 (8)	

H3A	0.287 (4)	0.300 (2)	0.449 (3)	0.056*	
H3B	0.427 (4)	0.315 (3)	0.400 (3)	0.056*	
N4	0.1980 (3)	0.4814 (2)	0.43416 (19)	0.0319 (6)	
N5	0.0477 (4)	0.6160 (3)	0.4291 (3)	0.0423 (7)	
H5A	−0.026 (3)	0.581 (3)	0.458 (3)	0.051*	
H5B	0.008 (4)	0.657 (3)	0.395 (2)	0.051*	
C1	0.3283 (4)	0.4407 (3)	0.4026 (2)	0.0349 (7)	
C2	0.1771 (4)	0.5749 (3)	0.4059 (3)	0.0334 (7)	
C3	0.2964 (4)	0.6347 (3)	0.3510 (3)	0.0379 (8)	
C4	0.2864 (4)	0.7472 (3)	0.3306 (3)	0.0387 (8)	
C5	0.2374 (4)	0.7607 (3)	0.2317 (3)	0.0438 (9)	
C6	0.2278 (4)	0.8680 (3)	0.2161 (3)	0.0435 (9)	
C7	0.2656 (4)	0.9625 (4)	0.3006 (3)	0.0513 (10)	
H7	0.2608	1.0343	0.2906	0.062*	
C8	0.3099 (5)	0.9469 (3)	0.3983 (3)	0.0512 (9)	
H8	0.3308	1.0092	0.4540	0.061*	
C9	0.3249 (4)	0.8428 (3)	0.4180 (3)	0.0364 (8)	
H9	0.3583	0.8353	0.4849	0.044*	
O1WA	0.0946 (5)	0.1640 (4)	0.4904 (3)	0.0521 (10)	0.686 (4)
O1WB	0.2255 (12)	0.1963 (8)	0.5250 (7)	0.0521 (10)	0.314 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S11	0.0566 (5)	0.0269 (4)	0.0445 (5)	0.0196 (4)	0.0087 (4)	0.0093 (4)
O11	0.0468 (14)	0.0345 (13)	0.0537 (16)	0.0202 (11)	0.0079 (12)	0.0148 (12)
O21	0.0675 (16)	0.0252 (13)	0.0543 (16)	0.0198 (11)	0.0161 (13)	0.0142 (11)
C11	0.0354 (17)	0.0253 (16)	0.049 (2)	0.0136 (13)	0.0119 (15)	0.0095 (15)
C21	0.045 (2)	0.0317 (19)	0.062 (2)	0.0173 (15)	0.0090 (17)	0.0114 (18)
C31	0.054 (2)	0.042 (2)	0.054 (2)	0.0204 (17)	0.0032 (18)	0.0169 (19)
C41	0.050 (2)	0.041 (2)	0.045 (2)	0.0096 (16)	0.0078 (17)	0.0046 (17)
C51	0.0462 (19)	0.0267 (17)	0.052 (2)	0.0123 (14)	0.0203 (16)	0.0109 (16)
C61	0.0348 (16)	0.0235 (16)	0.0436 (19)	0.0103 (12)	0.0150 (14)	0.0097 (14)
C71	0.0359 (17)	0.0281 (17)	0.057 (2)	0.0174 (14)	0.0185 (16)	0.0169 (17)
S12	0.0536 (5)	0.0261 (4)	0.0491 (5)	0.0200 (4)	0.0215 (4)	0.0114 (4)
O12	0.0613 (16)	0.0322 (13)	0.0687 (18)	0.0268 (11)	0.0347 (14)	0.0203 (13)
O22	0.0475 (13)	0.0245 (11)	0.0441 (13)	0.0186 (10)	0.0174 (10)	0.0087 (10)
C12	0.0409 (17)	0.0258 (16)	0.0306 (16)	0.0149 (13)	0.0066 (13)	0.0059 (13)
C22	0.0474 (19)	0.0311 (18)	0.046 (2)	0.0230 (15)	0.0140 (16)	0.0078 (15)
C32	0.0443 (19)	0.043 (2)	0.050 (2)	0.0221 (16)	0.0208 (17)	0.0069 (17)
C42	0.054 (2)	0.042 (2)	0.049 (2)	0.0154 (17)	0.0221 (18)	0.0114 (17)
C52	0.0467 (19)	0.0267 (17)	0.0400 (19)	0.0135 (14)	0.0118 (15)	0.0064 (15)
C62	0.0393 (17)	0.0232 (15)	0.0319 (16)	0.0141 (13)	0.0047 (13)	0.0047 (13)
C72	0.0414 (18)	0.0271 (17)	0.0373 (18)	0.0181 (14)	0.0116 (14)	0.0074 (14)
Cl1	0.0787 (7)	0.0722 (7)	0.0600 (7)	0.0421 (6)	0.0246 (5)	0.0320 (6)
Cl2	0.0740 (7)	0.0533 (6)	0.0474 (6)	0.0274 (5)	0.0159 (5)	0.0090 (5)
N1	0.0438 (16)	0.0329 (15)	0.0527 (18)	0.0194 (12)	0.0203 (14)	0.0138 (14)
N2	0.0378 (15)	0.0361 (16)	0.0469 (17)	0.0196 (12)	0.0174 (13)	0.0111 (13)

N3	0.071 (2)	0.0416 (18)	0.0484 (19)	0.0381 (16)	0.0261 (16)	0.0192 (15)
N4	0.0430 (15)	0.0295 (14)	0.0315 (14)	0.0188 (12)	0.0136 (12)	0.0114 (12)
N5	0.0396 (16)	0.0386 (17)	0.065 (2)	0.0226 (13)	0.0246 (15)	0.0257 (15)
C1	0.0469 (19)	0.0323 (18)	0.0294 (16)	0.0172 (14)	0.0102 (14)	0.0061 (14)
C2	0.0338 (16)	0.0293 (17)	0.0401 (18)	0.0106 (13)	0.0103 (14)	0.0103 (14)
C3	0.0393 (18)	0.0360 (18)	0.046 (2)	0.0178 (14)	0.0124 (15)	0.0149 (16)
C4	0.0312 (17)	0.043 (2)	0.050 (2)	0.0160 (14)	0.0187 (15)	0.0159 (17)
C5	0.0370 (18)	0.049 (2)	0.051 (2)	0.0160 (16)	0.0222 (16)	0.0089 (18)
C6	0.0334 (18)	0.044 (2)	0.065 (2)	0.0185 (15)	0.0216 (17)	0.0238 (19)
C7	0.0342 (19)	0.055 (2)	0.070 (3)	0.0143 (16)	0.0125 (18)	0.024 (2)
C8	0.056 (2)	0.039 (2)	0.058 (2)	0.0161 (17)	0.0118 (19)	0.0065 (19)
C9	0.0331 (16)	0.0216 (15)	0.055 (2)	0.0095 (12)	0.0132 (15)	0.0048 (15)
O1WA	0.056 (2)	0.069 (3)	0.047 (2)	0.030 (2)	0.0202 (19)	0.0288 (19)
O1WB	0.056 (2)	0.069 (3)	0.047 (2)	0.030 (2)	0.0202 (19)	0.0288 (19)

Geometric parameters (Å, º)

S11—C11	1.783 (4)	C52—H52	0.9300
S11—S12	2.0538 (11)	C62—C72	1.499 (4)
O11—C71	1.223 (4)	Cl1—C6	1.718 (4)
O21—C71	1.330 (4)	Cl2—C5	1.721 (4)
O21—H21O	0.850 (10)	N1—C3	1.310 (4)
C11—C21	1.374 (5)	N1—N2	1.336 (4)
C11—C61	1.413 (4)	N2—C1	1.351 (4)
C21—C31	1.390 (5)	N2—H2	0.847 (10)
C21—H21	0.9300	N3—C1	1.311 (4)
C31—C41	1.380 (5)	N3—H3A	0.841 (10)
C31—H31	0.9300	N3—H3B	0.843 (10)
C41—C51	1.371 (5)	N4—C2	1.322 (4)
C41—H41	0.9300	N4—C1	1.353 (4)
C51—C61	1.395 (5)	N5—C2	1.313 (4)
C51—H51	0.9300	N5—H5A	0.837 (10)
C61—C71	1.463 (5)	N5—H5B	0.840 (10)
S12—C12	1.792 (3)	C2—C3	1.445 (4)
O12—C72	1.245 (4)	C3—C4	1.484 (5)
O22—C72	1.269 (4)	C4—C5	1.385 (5)
C12—C22	1.389 (4)	C4—C9	1.438 (5)
C12—C62	1.399 (4)	C5—C6	1.399 (5)
C22—C32	1.374 (5)	C6—C7	1.406 (5)
C22—H22	0.9300	C7—C8	1.373 (5)
C32—C42	1.380 (5)	C7—H7	0.9300
C32—H32	0.9300	C8—C9	1.390 (5)
C42—C52	1.382 (4)	C8—H8	0.9300
C42—H42	0.9300	C9—H9	0.9300
C52—C62	1.395 (4)		
C11—S11—S12	105.99 (11)	O12—C72—O22	123.7 (3)
C71—O21—H21O	118 (3)	O12—C72—C62	117.5 (3)

C21—C11—C61	119.2 (3)	O22—C72—C62	118.8 (3)
C21—C11—S11	121.1 (3)	C3—N1—N2	116.7 (3)
C61—C11—S11	119.7 (3)	N1—N2—C1	123.8 (2)
C11—C21—C31	121.6 (3)	N1—N2—H2	119 (2)
C11—C21—H21	119.2	C1—N2—H2	117 (2)
C31—C21—H21	119.2	C1—N3—H3A	125 (2)
C41—C31—C21	119.0 (3)	C1—N3—H3B	123 (2)
C41—C31—H31	120.5	H3A—N3—H3B	110 (2)
C21—C31—H31	120.5	C2—N4—C1	116.5 (3)
C51—C41—C31	120.4 (4)	C2—N5—H5A	121 (2)
C51—C41—H41	119.8	C2—N5—H5B	121 (2)
C31—C41—H41	119.8	H5A—N5—H5B	112 (2)
C41—C51—C61	121.2 (3)	N3—C1—N2	118.1 (3)
C41—C51—H51	119.4	N3—C1—N4	120.7 (3)
C61—C51—H51	119.4	N2—C1—N4	121.2 (3)
C51—C61—C11	118.5 (3)	N5—C2—N4	119.9 (3)
C51—C61—C71	119.3 (3)	N5—C2—C3	118.9 (3)
C11—C61—C71	122.2 (3)	N4—C2—C3	121.2 (3)
O11—C71—O21	122.4 (3)	N1—C3—C2	120.5 (3)
O11—C71—C61	124.5 (3)	N1—C3—C4	118.2 (3)
O21—C71—C61	113.1 (3)	C2—C3—C4	121.3 (3)
C12—S12—S11	104.62 (10)	C5—C4—C9	120.3 (3)
C22—C12—C62	118.9 (3)	C5—C4—C3	122.0 (3)
C22—C12—S12	121.3 (2)	C9—C4—C3	117.6 (3)
C62—C12—S12	119.7 (2)	C4—C5—C6	120.2 (3)
C32—C22—C12	121.4 (3)	C4—C5—Cl2	120.0 (3)
C32—C22—H22	119.3	C6—C5—Cl2	119.8 (3)
C12—C22—H22	119.3	C5—C6—C7	120.3 (4)
C22—C32—C42	120.2 (3)	C5—C6—Cl1	120.7 (3)
C22—C32—H32	119.9	C7—C6—Cl1	119.0 (3)
C42—C32—H32	119.9	C8—C7—C6	118.7 (4)
C32—C42—C52	119.2 (3)	C8—C7—H7	120.6
C32—C42—H42	120.4	C6—C7—H7	120.6
C52—C42—H42	120.4	C7—C8—C9	123.3 (4)
C42—C52—C62	121.4 (3)	C7—C8—H8	118.3
C42—C52—H52	119.3	C9—C8—H8	118.3
C62—C52—H52	119.3	C8—C9—C4	117.1 (3)
C52—C62—C12	118.9 (3)	C8—C9—H9	121.4
C52—C62—C72	118.8 (3)	C4—C9—H9	121.4
C12—C62—C72	122.3 (3)		
S12—S11—C11—C21	13.6 (3)	C12—C62—C72—O22	−177.7 (3)
S12—S11—C11—C61	−167.2 (2)	C3—N1—N2—C1	−2.9 (5)
C61—C11—C21—C31	0.3 (5)	N1—N2—C1—N3	−178.4 (3)
S11—C11—C21—C31	179.5 (3)	N1—N2—C1—N4	2.4 (5)
C11—C21—C31—C41	0.5 (5)	C2—N4—C1—N3	−177.7 (3)
C21—C31—C41—C51	−0.8 (5)	C2—N4—C1—N2	1.5 (5)
C31—C41—C51—C61	0.3 (5)	C1—N4—C2—N5	176.5 (3)

C41—C51—C61—C11	0.5 (5)	C1—N4—C2—C3	−4.5 (5)
C41—C51—C61—C71	178.9 (3)	N2—N1—C3—C2	−0.2 (5)
C21—C11—C61—C51	−0.8 (4)	N2—N1—C3—C4	176.3 (3)
S11—C11—C61—C51	179.9 (2)	N5—C2—C3—N1	−177.0 (3)
C21—C11—C61—C71	−179.1 (3)	N4—C2—C3—N1	4.1 (5)
S11—C11—C61—C71	1.6 (4)	N5—C2—C3—C4	6.6 (5)
C51—C61—C71—O11	171.1 (3)	N4—C2—C3—C4	−172.3 (3)
C11—C61—C71—O11	−10.6 (5)	N1—C3—C4—C5	71.0 (4)
C51—C61—C71—O21	−9.3 (4)	C2—C3—C4—C5	−112.5 (4)
C11—C61—C71—O21	169.1 (3)	N1—C3—C4—C9	−110.8 (4)
S11—S12—C12—C22	9.4 (3)	C2—C3—C4—C9	65.7 (4)
S11—S12—C12—C62	−173.6 (2)	C9—C4—C5—C6	1.1 (5)
C62—C12—C22—C32	1.8 (5)	C3—C4—C5—C6	179.3 (3)
S12—C12—C22—C32	178.8 (3)	C9—C4—C5—Cl2	−177.5 (2)
C12—C22—C32—C42	−1.4 (6)	C3—C4—C5—Cl2	0.7 (4)
C22—C32—C42—C52	−0.3 (6)	C4—C5—C6—C7	−0.8 (5)
C32—C42—C52—C62	1.6 (5)	Cl2—C5—C6—C7	177.7 (2)
C42—C52—C62—C12	−1.1 (5)	C4—C5—C6—Cl1	−178.9 (2)
C42—C52—C62—C72	−180.0 (3)	Cl2—C5—C6—Cl1	−0.3 (4)
C22—C12—C62—C52	−0.5 (5)	C5—C6—C7—C8	−0.7 (5)
S12—C12—C62—C52	−177.6 (2)	Cl1—C6—C7—C8	177.3 (3)
C22—C12—C62—C72	178.3 (3)	C6—C7—C8—C9	2.2 (5)
S12—C12—C62—C72	1.2 (4)	C7—C8—C9—C4	−1.9 (5)
C52—C62—C72—O12	−178.1 (3)	C5—C4—C9—C8	0.2 (4)
C12—C62—C72—O12	3.1 (5)	C3—C4—C9—C8	−178.0 (3)
C52—C62—C72—O22	1.1 (5)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O21—H21O···O22[i]	0.85 (1)	1.78 (2)	2.599 (3)	162 (4)
C21—H21···S12	0.93	2.64	3.181 (4)	118
C22—H22···S11	0.93	2.59	3.146 (4)	119
N2—H2···O22	0.85 (1)	1.84 (1)	2.686 (3)	172 (4)
N3—H3A···O1WA	0.84 (1)	2.22 (1)	3.052 (5)	172 (4)
N3—H3A···O1WB	0.84 (1)	1.81 (2)	2.607 (9)	157 (4)
N3—H3B···O12	0.84 (1)	1.98 (1)	2.811 (4)	171 (3)
N5—H5A···N4[ii]	0.84 (1)	2.26 (1)	3.080 (4)	168 (4)
N5—H5B···O11[iii]	0.84 (1)	2.23 (2)	3.041 (4)	163 (3)

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

(II) 3,5-Diamino-6-(2,3-dichlorophenyl)-1,2,4-triazin-2-ium 2-[(2-carboxyphenyl)disulfanyl]benzoate

Crystal data

$C_9H_8Cl_2N_5{}^+ \cdot C_{14}H_9O_4S_2{}^-$	$b = 12.3100\,(8)$ Å
$M_r = 562.44$	$c = 12.9348\,(8)$ Å
Triclinic, $P\bar{1}$	$\alpha = 64.689\,(6)°$
$a = 8.5368\,(4)$ Å	$\beta = 86.474\,(5)°$

$\gamma = 77.230\ (5)°$
$V = 1197.56\ (14)$ Å^3
$Z = 2$
$F(000) = 576$
$D_x = 1.560$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2580 reflections
$\theta = 3.9–28.3°$
$\mu = 0.49$ mm^{-1}
$T = 294$ K
Prism, colourless
$0.44 \times 0.26 \times 0.16$ mm

Data collection

Oxford Diffraction Gemini CCD S Ultra
   diffractometer
ω scans, thick slices
Absorption correction: multi-scan
   (CrysAlis PRO; Oxford Diffraction, 2009)
$T_{min} = 0.82$, $T_{max} = 0.90$
10448 measured reflections

5165 independent reflections
3784 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 28.8°$, $\theta_{min} = 3.4°$
$h = -11 \rightarrow 10$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.118$
$S = 1.03$
5165 reflections
343 parameters
8 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent
   and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 0.5271P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.69$ 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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
S11	0.73570 (9)	1.26649 (6)	0.70633 (6)	0.04003 (18)
O11	0.7797 (2)	1.47988 (16)	0.70498 (17)	0.0447 (5)
O21	0.6634 (3)	1.56226 (16)	0.82134 (18)	0.0480 (5)
H21O	0.687 (4)	1.627 (2)	0.770 (2)	0.072*
C11	0.6616 (3)	1.2586 (2)	0.8408 (2)	0.0319 (5)
C21	0.6106 (3)	1.1548 (2)	0.9203 (2)	0.0410 (6)
H21	0.6180	1.0873	0.9039	0.049*
C31	0.5496 (3)	1.1506 (3)	1.0225 (3)	0.0478 (7)
H31	0.5163	1.0804	1.0743	0.057*
C41	0.5373 (4)	1.2488 (3)	1.0488 (3)	0.0504 (7)
H41	0.4942	1.2460	1.1175	0.061*
C51	0.5891 (3)	1.3514 (2)	0.9729 (2)	0.0421 (6)
H51	0.5824	1.4174	0.9915	0.050*
C61	0.6516 (3)	1.3585 (2)	0.8688 (2)	0.0317 (5)
C71	0.7057 (3)	1.4711 (2)	0.7898 (2)	0.0341 (6)
S12	0.65073 (8)	1.13349 (6)	0.68552 (6)	0.03733 (18)

O12	0.5271 (2)	0.97209 (15)	0.65169 (16)	0.0404 (4)
O22	0.65550 (19)	0.79103 (14)	0.65987 (15)	0.0341 (4)
C12	0.8020 (3)	0.9961 (2)	0.7504 (2)	0.0305 (5)
C22	0.9368 (3)	0.9932 (3)	0.8073 (3)	0.0438 (7)
H22	0.9500	1.0646	0.8107	0.053*
C32	1.0506 (3)	0.8864 (3)	0.8584 (3)	0.0525 (8)
H32	1.1406	0.8865	0.8953	0.063*
C42	1.0333 (3)	0.7795 (3)	0.8559 (3)	0.0497 (7)
H42	1.1099	0.7070	0.8919	0.060*
C52	0.9007 (3)	0.7810 (2)	0.7991 (2)	0.0388 (6)
H52	0.8890	0.7085	0.7972	0.047*
C62	0.7838 (3)	0.8881 (2)	0.7445 (2)	0.0277 (5)
C72	0.6447 (3)	0.8848 (2)	0.6814 (2)	0.0281 (5)
Cl1	0.13956 (11)	0.45741 (7)	0.85919 (7)	0.0587 (2)
Cl2	0.14555 (11)	0.18571 (7)	0.90091 (8)	0.0671 (3)
N1	0.3716 (2)	0.65097 (18)	0.63653 (19)	0.0358 (5)
N2	0.3601 (2)	0.76963 (19)	0.61448 (19)	0.0345 (5)
H2	0.4487 (19)	0.782 (2)	0.628 (2)	0.041*
N3	0.2263 (3)	0.96928 (19)	0.5602 (2)	0.0396 (5)
H3A	0.1440 (19)	1.0264 (18)	0.541 (2)	0.048*
H3B	0.3078 (19)	0.990 (2)	0.573 (2)	0.048*
N4	0.0856 (2)	0.82868 (17)	0.56417 (18)	0.0309 (5)
N5	−0.0450 (2)	0.6778 (2)	0.5876 (2)	0.0414 (6)
H5A	−0.1348 (19)	0.7259 (18)	0.581 (2)	0.050*
H5B	−0.050 (3)	0.6039 (10)	0.614 (2)	0.050*
C1	0.2237 (3)	0.8559 (2)	0.5791 (2)	0.0293 (5)
C2	0.0902 (3)	0.7111 (2)	0.5919 (2)	0.0308 (5)
C3	0.2401 (3)	0.6199 (2)	0.6266 (2)	0.0320 (5)
C4	0.2482 (3)	0.4890 (2)	0.6501 (2)	0.0354 (6)
C5	0.2010 (3)	0.4083 (2)	0.7538 (2)	0.0383 (6)
C6	0.2043 (3)	0.2872 (2)	0.7723 (3)	0.0427 (7)
C7	0.2552 (3)	0.2480 (3)	0.6893 (3)	0.0488 (7)
H7	0.2567	0.1675	0.7021	0.059*
C8	0.3044 (3)	0.3279 (3)	0.5863 (3)	0.0478 (7)
H8	0.3410	0.3003	0.5307	0.057*
C9	0.2996 (3)	0.4478 (2)	0.5655 (2)	0.0411 (6)
H9	0.3305	0.5016	0.4954	0.049*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S11	0.0611 (4)	0.0278 (3)	0.0380 (4)	−0.0185 (3)	0.0065 (3)	−0.0166 (3)
O11	0.0587 (12)	0.0332 (10)	0.0514 (12)	−0.0235 (9)	0.0149 (10)	−0.0216 (9)
O21	0.0724 (14)	0.0251 (9)	0.0529 (13)	−0.0144 (9)	0.0075 (10)	−0.0213 (9)
C11	0.0319 (13)	0.0269 (12)	0.0376 (14)	−0.0085 (10)	−0.0014 (10)	−0.0131 (11)
C21	0.0517 (16)	0.0305 (13)	0.0452 (17)	−0.0177 (12)	0.0016 (13)	−0.0161 (12)
C31	0.0542 (17)	0.0415 (16)	0.0474 (18)	−0.0243 (14)	0.0107 (14)	−0.0131 (14)
C41	0.0549 (18)	0.0504 (17)	0.0465 (18)	−0.0147 (14)	0.0197 (14)	−0.0219 (14)

C51	0.0468 (16)	0.0316 (13)	0.0503 (18)	−0.0046 (12)	0.0056 (13)	−0.0221 (13)
C61	0.0310 (13)	0.0231 (12)	0.0411 (15)	−0.0039 (10)	−0.0018 (11)	−0.0142 (11)
C71	0.0355 (13)	0.0277 (12)	0.0428 (16)	−0.0060 (11)	−0.0040 (11)	−0.0182 (11)
S12	0.0473 (4)	0.0266 (3)	0.0427 (4)	−0.0061 (3)	−0.0077 (3)	−0.0187 (3)
O12	0.0336 (10)	0.0332 (9)	0.0603 (13)	−0.0015 (8)	−0.0101 (8)	−0.0266 (9)
O22	0.0345 (9)	0.0251 (8)	0.0494 (11)	−0.0093 (7)	−0.0026 (8)	−0.0201 (8)
C12	0.0364 (13)	0.0277 (12)	0.0309 (13)	−0.0095 (10)	0.0022 (10)	−0.0147 (10)
C22	0.0452 (16)	0.0408 (15)	0.0570 (18)	−0.0130 (13)	−0.0063 (13)	−0.0290 (14)
C32	0.0419 (16)	0.0614 (19)	0.063 (2)	−0.0055 (15)	−0.0169 (14)	−0.0345 (17)
C42	0.0446 (16)	0.0472 (16)	0.0564 (19)	0.0050 (13)	−0.0179 (14)	−0.0256 (15)
C52	0.0450 (15)	0.0320 (13)	0.0434 (16)	−0.0056 (12)	−0.0068 (12)	−0.0200 (12)
C62	0.0290 (12)	0.0268 (12)	0.0302 (13)	−0.0092 (10)	0.0030 (10)	−0.0135 (10)
C72	0.0297 (12)	0.0257 (12)	0.0319 (13)	−0.0116 (10)	0.0043 (10)	−0.0126 (10)
Cl1	0.0803 (6)	0.0491 (4)	0.0488 (5)	−0.0151 (4)	0.0096 (4)	−0.0232 (4)
Cl2	0.0863 (6)	0.0453 (4)	0.0607 (5)	−0.0300 (4)	0.0017 (4)	−0.0066 (4)
N1	0.0291 (11)	0.0292 (11)	0.0498 (14)	−0.0056 (9)	−0.0029 (9)	−0.0172 (10)
N2	0.0249 (11)	0.0309 (11)	0.0507 (14)	−0.0093 (9)	−0.0037 (9)	−0.0178 (10)
N3	0.0329 (12)	0.0264 (11)	0.0597 (15)	−0.0123 (9)	−0.0014 (11)	−0.0152 (11)
N4	0.0248 (10)	0.0252 (10)	0.0409 (12)	−0.0085 (8)	0.0008 (8)	−0.0108 (9)
N5	0.0275 (11)	0.0285 (11)	0.0656 (16)	−0.0095 (9)	−0.0035 (11)	−0.0153 (12)
C1	0.0258 (12)	0.0307 (12)	0.0313 (13)	−0.0088 (10)	0.0039 (10)	−0.0124 (10)
C2	0.0273 (12)	0.0298 (12)	0.0354 (14)	−0.0090 (10)	0.0010 (10)	−0.0126 (11)
C3	0.0287 (12)	0.0261 (12)	0.0399 (15)	−0.0060 (10)	−0.0012 (10)	−0.0124 (11)
C4	0.0278 (13)	0.0278 (12)	0.0487 (16)	−0.0040 (10)	−0.0046 (11)	−0.0146 (12)
C5	0.0331 (13)	0.0354 (14)	0.0450 (16)	−0.0057 (11)	−0.0017 (11)	−0.0163 (12)
C6	0.0377 (14)	0.0283 (13)	0.0555 (18)	−0.0089 (11)	−0.0067 (13)	−0.0096 (13)
C7	0.0481 (17)	0.0341 (15)	0.067 (2)	−0.0054 (13)	−0.0061 (15)	−0.0248 (15)
C8	0.0462 (16)	0.0458 (16)	0.059 (2)	−0.0044 (13)	−0.0020 (14)	−0.0312 (15)
C9	0.0389 (15)	0.0336 (14)	0.0475 (17)	−0.0066 (11)	0.0056 (12)	−0.0152 (12)

Geometric parameters (Å, º)

S11—C11	1.784 (3)	C52—H52	0.9300
S11—S12	2.0506 (9)	C62—C72	1.498 (3)
O11—C71	1.207 (3)	Cl1—C5	1.725 (3)
O21—C71	1.323 (3)	Cl2—C6	1.726 (3)
O21—H21O	0.849 (10)	N1—C3	1.294 (3)
C11—C21	1.396 (3)	N1—N2	1.345 (3)
C11—C61	1.407 (3)	N2—C1	1.341 (3)
C21—C31	1.375 (4)	N2—H2	0.847 (10)
C21—H21	0.9300	N3—C1	1.315 (3)
C31—C41	1.371 (4)	N3—H3A	0.838 (9)
C31—H31	0.9300	N3—H3B	0.839 (10)
C41—C51	1.374 (4)	N4—C2	1.326 (3)
C41—H41	0.9300	N4—C1	1.341 (3)
C51—C61	1.392 (4)	N5—C2	1.319 (3)
C51—H51	0.9300	N5—H5A	0.841 (10)
C61—C71	1.481 (3)	N5—H5B	0.833 (9)

S12—C12	1.785 (2)	C2—C3	1.450 (3)
O12—C72	1.236 (3)	C3—C4	1.492 (3)
O22—C72	1.283 (3)	C4—C5	1.387 (4)
C12—C22	1.389 (3)	C4—C9	1.401 (4)
C12—C62	1.407 (3)	C5—C6	1.399 (4)
C22—C32	1.371 (4)	C6—C7	1.366 (4)
C22—H22	0.9300	C7—C8	1.383 (4)
C32—C42	1.369 (4)	C7—H7	0.9300
C32—H32	0.9300	C8—C9	1.374 (4)
C42—C52	1.380 (4)	C8—H8	0.9300
C42—H42	0.9300	C9—H9	0.9300
C52—C62	1.393 (3)		
C11—S11—S12	103.92 (8)	O12—C72—O22	123.3 (2)
C71—O21—H21O	109 (2)	O12—C72—C62	119.1 (2)
C21—C11—C61	118.2 (2)	O22—C72—C62	117.6 (2)
C21—C11—S11	121.4 (2)	C3—N1—N2	116.6 (2)
C61—C11—S11	120.40 (18)	C1—N2—N1	123.87 (19)
C31—C21—C11	121.1 (3)	C1—N2—H2	124.3 (19)
C31—C21—H21	119.5	N1—N2—H2	111.8 (19)
C11—C21—H21	119.5	C1—N3—H3A	123.2 (17)
C41—C31—C21	120.6 (3)	C1—N3—H3B	123.4 (17)
C41—C31—H31	119.7	H3A—N3—H3B	113 (2)
C21—C31—H31	119.7	C2—N4—C1	116.2 (2)
C31—C41—C51	119.5 (3)	C2—N5—H5A	121.3 (18)
C31—C41—H41	120.3	C2—N5—H5B	121.4 (18)
C51—C41—H41	120.3	H5A—N5—H5B	114 (2)
C41—C51—C61	121.3 (3)	N3—C1—N4	119.7 (2)
C41—C51—H51	119.4	N3—C1—N2	118.7 (2)
C61—C51—H51	119.4	N4—C1—N2	121.5 (2)
C51—C61—C11	119.3 (2)	N5—C2—N4	118.6 (2)
C51—C61—C71	119.2 (2)	N5—C2—C3	120.1 (2)
C11—C61—C71	121.5 (2)	N4—C2—C3	121.2 (2)
O11—C71—O21	123.2 (2)	N1—C3—C2	120.3 (2)
O11—C71—C61	123.9 (2)	N1—C3—C4	118.2 (2)
O21—C71—C61	112.9 (2)	C2—C3—C4	121.5 (2)
C12—S12—S11	105.17 (8)	C5—C4—C9	119.4 (2)
C22—C12—C62	119.2 (2)	C5—C4—C3	120.6 (2)
C22—C12—S12	121.56 (19)	C9—C4—C3	119.9 (2)
C62—C12—S12	119.25 (18)	C4—C5—C6	119.6 (3)
C32—C22—C12	120.9 (2)	C4—C5—Cl1	119.9 (2)
C32—C22—H22	119.6	C6—C5—Cl1	120.6 (2)
C12—C22—H22	119.6	C7—C6—C5	120.4 (3)
C42—C32—C22	120.9 (3)	C7—C6—Cl2	119.5 (2)
C42—C32—H32	119.6	C5—C6—Cl2	120.1 (2)
C22—C32—H32	119.6	C6—C7—C8	120.1 (3)
C32—C42—C52	119.0 (3)	C6—C7—H7	119.9
C32—C42—H42	120.5	C8—C7—H7	119.9

C52—C42—H42	120.5	C9—C8—C7	120.4 (3)
C42—C52—C62	121.8 (2)	C9—C8—H8	119.8
C42—C52—H52	119.1	C7—C8—H8	119.8
C62—C52—H52	119.1	C8—C9—C4	120.0 (3)
C52—C62—C12	118.2 (2)	C8—C9—H9	120.0
C52—C62—C72	119.4 (2)	C4—C9—H9	120.0
C12—C62—C72	122.4 (2)		
S12—S11—C11—C21	19.1 (2)	C12—C62—C72—O22	165.4 (2)
S12—S11—C11—C61	−160.19 (18)	C3—N1—N2—C1	−2.8 (4)
C61—C11—C21—C31	1.1 (4)	C2—N4—C1—N3	−175.8 (2)
S11—C11—C21—C31	−178.2 (2)	C2—N4—C1—N2	3.3 (4)
C11—C21—C31—C41	0.0 (4)	N1—N2—C1—N3	179.9 (2)
C21—C31—C41—C51	−1.1 (5)	N1—N2—C1—N4	0.8 (4)
C31—C41—C51—C61	1.1 (4)	C1—N4—C2—N5	174.6 (2)
C41—C51—C61—C11	0.1 (4)	C1—N4—C2—C3	−5.2 (4)
C41—C51—C61—C71	179.9 (2)	N2—N1—C3—C2	0.8 (4)
C21—C11—C61—C51	−1.1 (4)	N2—N1—C3—C4	179.8 (2)
S11—C11—C61—C51	178.21 (19)	N5—C2—C3—N1	−176.5 (3)
C21—C11—C61—C71	179.0 (2)	N4—C2—C3—N1	3.4 (4)
S11—C11—C61—C71	−1.7 (3)	N5—C2—C3—C4	4.5 (4)
C51—C61—C71—O11	170.2 (3)	N4—C2—C3—C4	−175.7 (2)
C11—C61—C71—O11	−9.9 (4)	N1—C3—C4—C5	100.9 (3)
C51—C61—C71—O21	−10.3 (3)	C2—C3—C4—C5	−80.1 (3)
C11—C61—C71—O21	169.6 (2)	N1—C3—C4—C9	−81.0 (3)
S11—S12—C12—C22	4.2 (2)	C2—C3—C4—C9	98.1 (3)
S11—S12—C12—C62	−176.30 (17)	C9—C4—C5—C6	−0.4 (4)
C62—C12—C22—C32	−0.7 (4)	C3—C4—C5—C6	177.8 (2)
S12—C12—C22—C32	178.8 (2)	C9—C4—C5—Cl1	179.27 (19)
C12—C22—C32—C42	−0.8 (5)	C3—C4—C5—Cl1	−2.6 (3)
C22—C32—C42—C52	1.2 (5)	C4—C5—C6—C7	0.6 (4)
C32—C42—C52—C62	−0.1 (5)	Cl1—C5—C6—C7	−179.1 (2)
C42—C52—C62—C12	−1.3 (4)	C4—C5—C6—Cl2	−179.89 (19)
C42—C52—C62—C72	178.4 (3)	Cl1—C5—C6—Cl2	0.4 (3)
C22—C12—C62—C52	1.7 (4)	C5—C6—C7—C8	0.2 (4)
S12—C12—C62—C52	−177.84 (19)	Cl2—C6—C7—C8	−179.3 (2)
C22—C12—C62—C72	−178.0 (2)	C6—C7—C8—C9	−1.3 (4)
S12—C12—C62—C72	2.5 (3)	C7—C8—C9—C4	1.5 (4)
C52—C62—C72—O12	166.6 (2)	C5—C4—C9—C8	−0.6 (4)
C12—C62—C72—O12	−13.8 (3)	C3—C4—C9—C8	−178.8 (2)
C52—C62—C72—O22	−14.3 (3)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O21—H21O···O22[i]	0.85 (1)	1.88 (2)	2.683 (2)	158 (3)
C21—H21···S12	0.93	2.64	3.150 (3)	115
C22—H22···S11	0.93	2.60	3.152 (3)	118

N2—H2⋯O22	0.85 (1)	1.87 (1)	2.717 (2)	173 (3)
N3—H3A⋯N4[ii]	0.84 (1)	2.36 (1)	3.168 (3)	161 (3)
N3—H3B⋯O12	0.84 (1)	2.11 (1)	2.906 (3)	158 (2)
N5—H5A⋯O22[iii]	0.84 (1)	2.18 (2)	2.932 (3)	149 (3)
N5—H5B⋯O11[iv]	0.83 (1)	2.25 (2)	2.941 (3)	140 (2)

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