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Lamotriginium crotonate and lamotriginium salicylate ethanol monosolvate: the role of solvent molecules in the packing organization

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Two lamotriginium salts, namely lamotriginium crotonate [systematic name: 3,5-diamino-6-(2,3-dichlorophenyl)-1,2,4-triazin-2-ium but-2-enoate, $C_9H_8Cl_2N_5^+ \cdot C_4H_5O_2^-$, (III)] and lamotriginium salicylate [systematic name: 3,5-diamino-6-(2,3-dichlorophenyl)-1,2,4-triazin-2-ium 2-hydroxybenzoate ethanol monosolvate, $C_9H_8Cl_2N_5^+ \cdot C_7H_5O_3^- \cdot C_2H_5OH$, (IV)] present extremely similar centrosymmetric hydrogen-bonded $A \cdots L \cdots L \cdots A$ packing building blocks (L is lamotriginium and A is the anion). The fact that salicylate salt (IV) is (ethanol) solvated, while crotonate salt (III) is not, has a profound effect on the way these elemental units aggregate to generate the final crystal structure. Possible reasons for this behaviour are analyzed and the hypothesis raised checked against similar structures in the literature.

1. Introduction

The study of different salts of lamotrigine [6-(2,3-dichlorophenyl)-1,2,4-triazine-3,5-diamine, hereinafter L] has been, and continues to be, an active field of research in pharmacological chemistry, striving to find an adequate answer to the problem posed by the poor water solubility and dissolution rates of the free base (Chadha *et al.*, 2013; Parmer *et al.*, 2009). This fact limits its bioavailability, thus jeopardizing the performance of this otherwise successful drug used in the treatment of epilepsy and related convulsive diseases. However, the molecule is an excellent hydrogen-bonding agent, with a large number of donor and acceptor sites which make it especially suitable for the formation of salts and cocrystals. These have potentially better solubility properties than the free base, and may thus allow for improved pharmacological formulations. Interest in new compounds of this sort has given rise to many synthetic and structural projects which resulted in an unusually large number of salts and cocrystals being reported. A search in the Cambridge Structural Database (CSD, Version 5.38 and upgrades; Groom *et al.*, 2016) disclosed 78 entries of the lamotrigine substructure, 55 of them in its cationic form (basically, salts) and 23 as a neutral molecule, a status shared by cocrystals, anhydrates, hydrates and solvates.

We have reported recently on two different solvatomorphs of L dithiobenzoate salts [(I) and (II); Freire *et al.*, 2016], where some characteristics of the preference of L in its hydrogen-bonding interactions were analyzed, either in reference to other L molecules or with the complementing

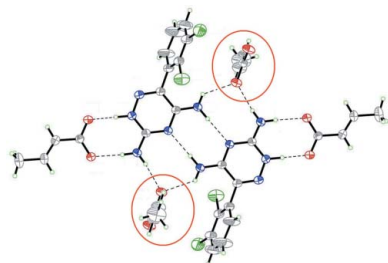


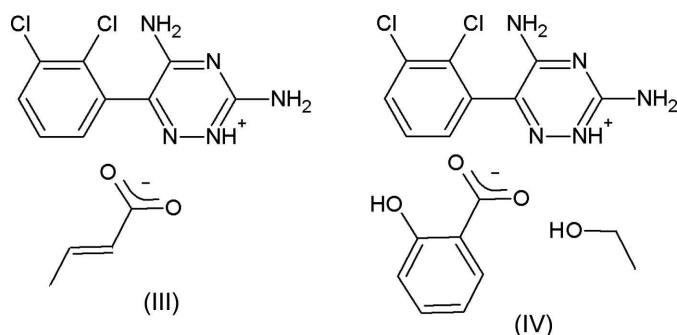
Table 1
Experimental details.

Experiments were carried out at 294 K with Mo $K\alpha$ radiation using a Rigaku OD Xcalibur Eos Gemini diffractometer. Absorption was corrected for by multi-scan methods (*CrysAlis PRO*; Rigaku OD, 2015). H atoms were treated by a mixture of independent and constrained refinement.

	(III)	(IV)
Crystal data		
Chemical formula	$C_9H_8Cl_2N_5^+ \cdot C_4H_5O_2^-$	$C_9H_8Cl_2N_5^+ \cdot C_7H_5O_3^- \cdot C_2H_6O$
M_r	342.18	440.28
Crystal system, space group	Tetragonal, $I4_1/a$	Triclinic, $P\bar{1}$
a, b, c (Å)	19.513 (3), 19.513 (3), 17.613 (4)	7.9389 (4), 12.2938 (9), 12.3282 (8)
α, β, γ (°)	90, 90, 90	61.781 (7), 79.379 (5), 72.313 (5)
V (Å ³)	6706 (2)	1008.92 (12)
Z	16	2
μ (mm ⁻¹)	0.40	0.36
Crystal size (mm)	0.35 × 0.22 × 0.16	0.42 × 0.28 × 0.18
Data collection		
T_{min}, T_{max}	0.88, 0.94	0.86, 0.96
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8373, 3726, 2148	8324, 4360, 2863
R_{int}	0.028	0.033
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.677	0.678
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.057, 0.185, 0.97	0.056, 0.168, 1.05
No. of reflections	3726	4360
No. of parameters	240	284
No. of restraints	7	0
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.25, -0.29	0.34, -0.37

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS97* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015), *XP* in *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

dithiobenzoate counter-anions. Following this line of research, we present herein two new lamotriginium carboxylate salts, *viz.* lamotriginium crotonate, (III), and lamotriginium salicylate ethanol monosolvate, (IV) (see Scheme 1), where the trends already discussed are confirmed; at the same time, further trends regarding carboxylate salts are suggested.



2. Experimental

2.1. Synthesis and crystallization

The title salts were obtained by similar methods. For the preparation of both salts, lamotrigine (50 mg, 0.2 mM) was dissolved completely in ethanol (10 ml) and kept under mechanical stirring while the acid was added and also dissolved, *i.e.* crotonic acid (18 mg, 0.2 mM) for salt (III) and salicylic acid (28 mg, 0.2 mM) for salt (IV), all at *ca* 328 K. Both solutions were kept in an oven at 328 K for a few days and, after slow evaporation, medium-sized prismatic crystals suitable for X-ray diffraction analysis were obtained.

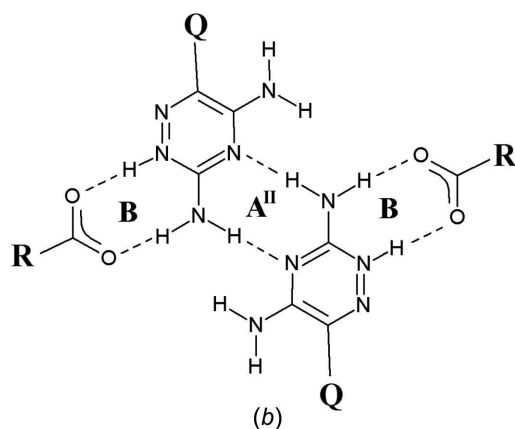
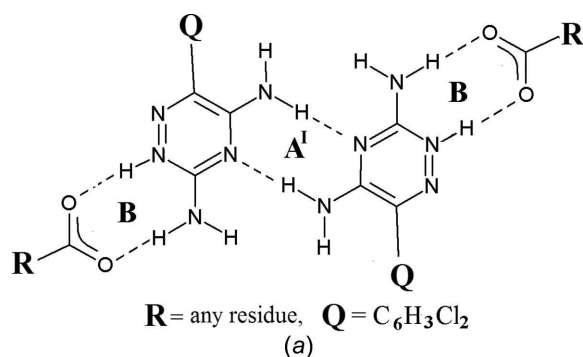
2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were confirmed in difference maps but were treated differently in the refinement. The positions of H atoms in $X-H$ groups ($X = O$ or N) were refined freely, while H atoms in $C-H$ groups were idealized and treated as riding ($C-H = 0.93$ Å). The $U_{iso}(H)$ value of atom H2 in compound (III) was refined and all other $U_{iso}(H)$ values were taken as $1.2U_{eq}(\text{carrier})$, except for methyl groups and ROH groups, where $U_{iso}(H)$ values were taken as $1.5U_{eq}(\text{carrier})$. In salt (III), the crotonate anion is slightly disordered through a rigid-body movement around one of the carboxylate O atoms (O1) [occupancies = 0.796 (4):0.204 (4); atom O1 was clamped with full occupancy]. Also, the 2,3-dichlorophenyl group is slightly disordered, through a small rotation around the C3–C4 axis [the angle between the dihedral planes is $\sim 17^\circ$; occupancies = 0.949 (2):0.051 (2)]. The extremely low occupancy of the minor fraction resulted in the impossibility of detecting the corresponding C atoms; only the disordered Cl atoms were visible in the difference map and were included in the model as two isolated fractions. [A similar model has been used for other *L* salts, *viz.* CSD refcode PEZKIQ (Chadha *et al.*, 2013).] In both disordered groups in (III), metric and displacement-parameter restraints were applied to the minor fractions.

3. Results and discussion

Tables 2 and 3 present the hydrogen-bonding interactions in (III) and (IV), respectively. For ease of reference, these

interactions have been labelled with a sequential code in the first column.



Scheme 2

Salt (III) crystallizes in the tetragonal space group $I4_1/a$, with a lamotriginium cation (L) and a crotonate anion (D) in the asymmetric unit (no solvent), while salt (IV) crystallizes in the triclinic space group $P\bar{1}$, with an independent lamotriginium cation, a salicylate anion (S) and an ethanol solvent molecule in the asymmetric unit. Fig. 1 presents the displacement ellipsoid plots of both asymmetric units.

The lamotriginium cations are basically unremarkable and are 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 only difference between the two cations corresponds to the sole degree of freedom in the molecule, *i.e.* the C2–C3–C4–C5 torsion angle, which measures the rotation between the planar rings. In our previous report on lamotriginium thiosalicylates, this difference was rather large, amounting to *ca* 30°. In the pair of structures reported herein, the difference (between major fractions) is much smaller, the

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

	$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
#1	N5–H5A \cdots N4 ⁱ	0.90 (3)	2.06 (3)	2.951 (3)	176 (3)
#2	N2–H2 \cdots O11	0.98 (3)	1.66 (3)	2.639 (3)	179 (3)
#3	N3–H3A \cdots O21	0.88 (3)	1.90 (3)	2.774 (4)	175 (3)
#4	N3–H3B \cdots O21 ⁱⁱ	0.81 (3)	2.12 (3)	2.899 (3)	162 (3)
#5	N5–H5B \cdots O21 ⁱⁱⁱ	0.85 (3)	2.23 (3)	2.870 (3)	132 (3)

Symmetry codes: (i) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $y + \frac{1}{4}, -x + \frac{3}{4}, -z + \frac{3}{4}$; (iii) $-y + \frac{5}{4}, x - \frac{1}{4}, z - \frac{1}{4}$.

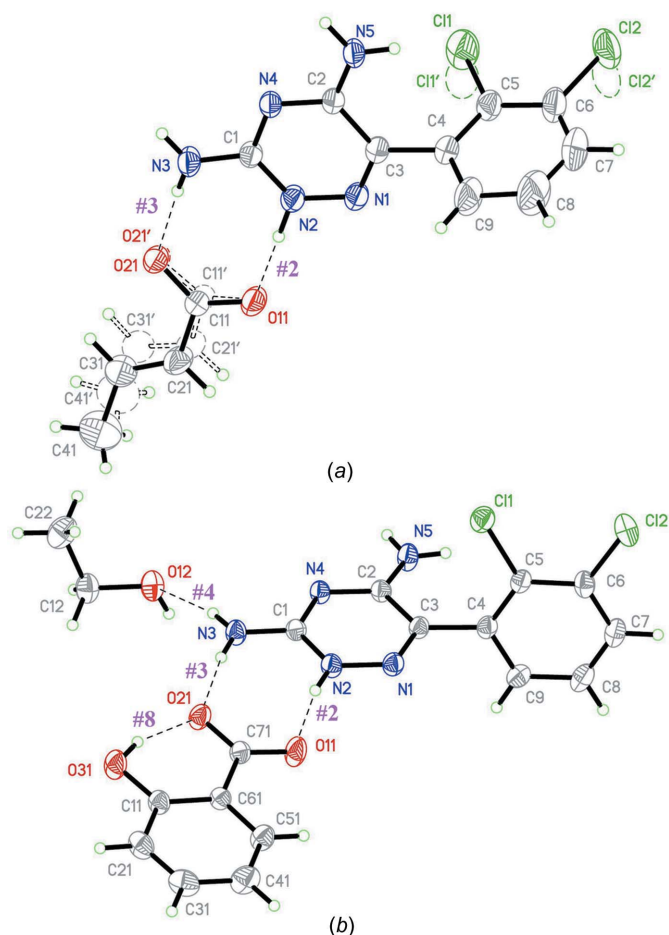


Figure 1

A view of the asymmetric units of (a) salt (III) and (b) salt (IV), showing anisotropic displacement ellipsoids (drawn at the 40% probability level) and the atom-labelling scheme used. Simple broken lines represent hydrogen bonds, while open ellipsoids connected by double broken lines represent the minor part of a disordered moiety. For interaction codes (# n), see Table 2 for (III) and Table 3 for (IV).

relevant C2–C3–C4–C5 torsion angles being 73.2 (4)° in (III) and 81.0 (4)° in (IV) [$\Delta = 7.8$ (8)°], both of which are very near the mean value obtained from 78 structures in the CSD (mean 73°, dispersion 7°), which shows the clear preference for the quasi-orthogonal disposition of both rings. As in all the occurrences of the molecule in its cationic form, lamotrigine is protonated at atom N2.

Table 3
Hydrogen-bond geometry (Å, °) for salt (IV).

	$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
#1	N5–H5A \cdots N4 ⁱ	0.82 (3)	2.16 (3)	2.972 (3)	174 (3)
#2	N2–H2 \cdots O11	0.84 (3)	1.77 (3)	2.599 (3)	168 (3)
#3	N3–H3A \cdots O21	0.85 (3)	2.03 (3)	2.872 (3)	171 (3)
#4	N3–H3B \cdots O12	0.84 (3)	2.24 (3)	3.057 (3)	164 (3)
#5	N5–H5B \cdots O12 ⁱ	0.82 (3)	2.24 (3)	2.870 (3)	134 (3)
#6	O12–H12 \cdots O31 ⁱⁱ	0.86 (4)	1.96 (4)	2.801 (3)	165 (4)
#7	C21–H21 \cdots Cl2 ⁱⁱⁱ	0.93	2.88	3.659 (3)	143
#8	O31–H31A \cdots O21	0.87 (4)	1.69 (4)	2.518 (3)	159 (4)

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

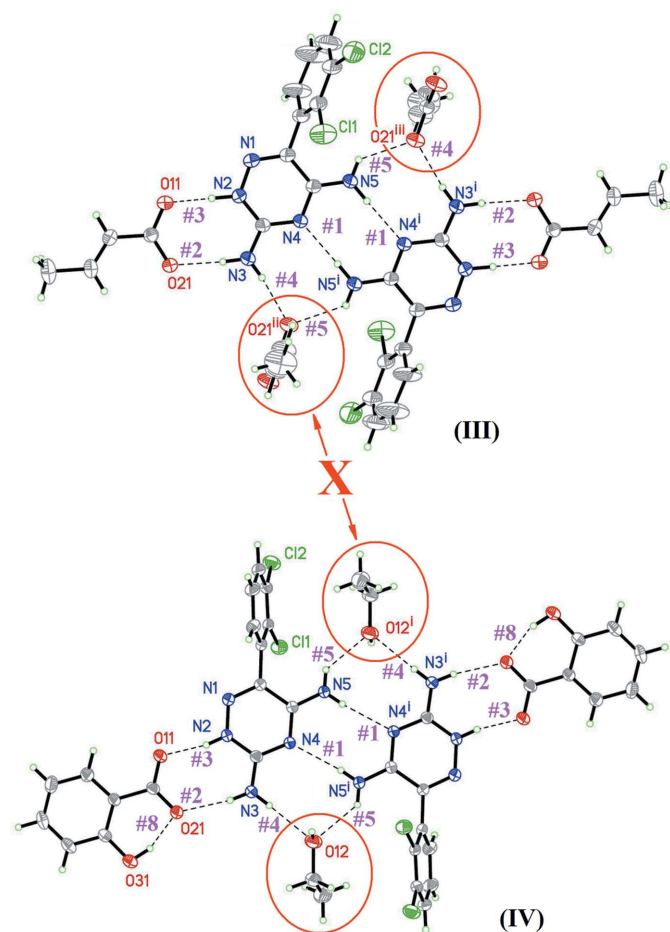


Figure 2
The tetrameric units in both salts, showing the labelling of the synthons. For interaction codes (#*n*), see Table 2 for (III) and Table 3 for (IV).

Also, the anions show predictable geometries: both show clear C—O delocalization at the carboxylate end, the crotonate group confirms a clear central double bond, the salicylate anion shows its characteristic intramolecular hydroxy-carboxylate O—H...O hydrogen bond (presented as #6 in Table 3) and no significant deviations from reported values were noted. Thus, the most interesting aspects remaining for discussion are to be found in the crystal structures, due to the conspicuous hydrogen-bonding capabilities of the *L* and COO groups, which provide a plethora of strong N—H...N and N—H...O interactions.

In many *L* carboxylates [*e.g.* our recently reported dithiobenzoate salts (I) and (II), among others], the supramolecular structures are built up by two characteristic synthons (labelled as **A** and **B** in Scheme 2), both of them giving rise to an $R_2^2(8)$ hydrogen-bond pattern.

Those of type **A** are homosynthons, linking lamotriginium cations with each other *via* N—H...N hydrogen bonds, and are found in the literature in two slightly different (usually centrosymmetric) versions, *viz.* one involving the N5—H5A groups as donors [the **A**^I type; see part (a) in Scheme 2] and a second where the N3—H3A group take part [the **A**^{II} type; see part (b) in Scheme 2]. We have discussed this point in depth in our previous contribution reporting the structures of dithio-

benzoate salts (I) and (II), and shall only mention here that in the restricted universe of *L* carboxylates, homosynthon **A**^I is much more frequent (18 cases) than **A**^{II} (only two cases). The present structures of salts (III) and (IV) confirm the trend, with the *L* cations in both structures being linked into dimeric units *via* the hydrogen bond involving the N5—H5A group as donor and atom N4 as acceptor (#1 in Tables 2 and 3).

On the other hand, there is a second type of synthon (labelled **B** in Scheme 2) characteristic of most lamotriginium carboxylate salts, which are noncentrosymmetric heterosynthons connecting a lamotriginium cation and a carboxylate anion, also present in salts (III) and (IV), induced by the contacts labelled #2 and #3 in Tables 2 and 3.

In the case of salt (III), hydrogen-bond #2 is distinctly stronger than the rest (see metrics of Table 2). This has an ‘anchoring’ effect in the disorder shown by the crotonate anion; the whole molecule appears to be rotated around a ‘clamped’ O11 atom, as shown in Fig. 1.

The two extremely similar (centrosymmetric) tetrameric substructures which result in salts (III) and (IV) from the linkage of the three $R_2^2(8)$ patterns in a **B**·**A**^I·**B** fashion are presented in Fig. 2.

But the similarities between the two structures come to an end when the inter-tetrameric interactions and the way tetramers organize are considered. In salt (III), the linkage between tetramers is achieved *via* hydrogen bonds having as donors those N—H groups not so far involved in hydrogen bonding, *viz.* the N5—H5B and N3—H3B groups. Since there are no further possible acceptors in the structure other than the carboxylate group itself, and due to steric reasons, the crotonate anion can only approach the planar tetramer in an almost perpendicular fashion, interacting by way of contacts #4 and #5 (Table 2). This kind of right-angle approach leads to a ‘crisscross’ crystal structure characterized by quasi-orthogonal tetramers, much in the way as sketched for (III) in Fig. 3(a).

Even if similar hydrogen bonds are found in salt (IV), they present subtle differences, with far-reaching effects. The same donors as in (III) are involved (*i.e.* the N5—H5B and N3—H3B groups), but since the structure includes a rather mobile ethanol solvent molecule able to act as an acceptor, it is in fact this molecule which binds to the tetrameric core through interactions #4 and #5 (Table 3), incorporating the ethanol solvent molecule into a larger ‘hexameric’ group (Fig. 2).

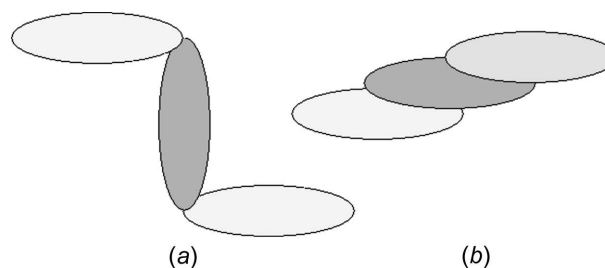


Figure 3
Schematic representation of the two different ways in which tetramers interact in (III) and (IV).

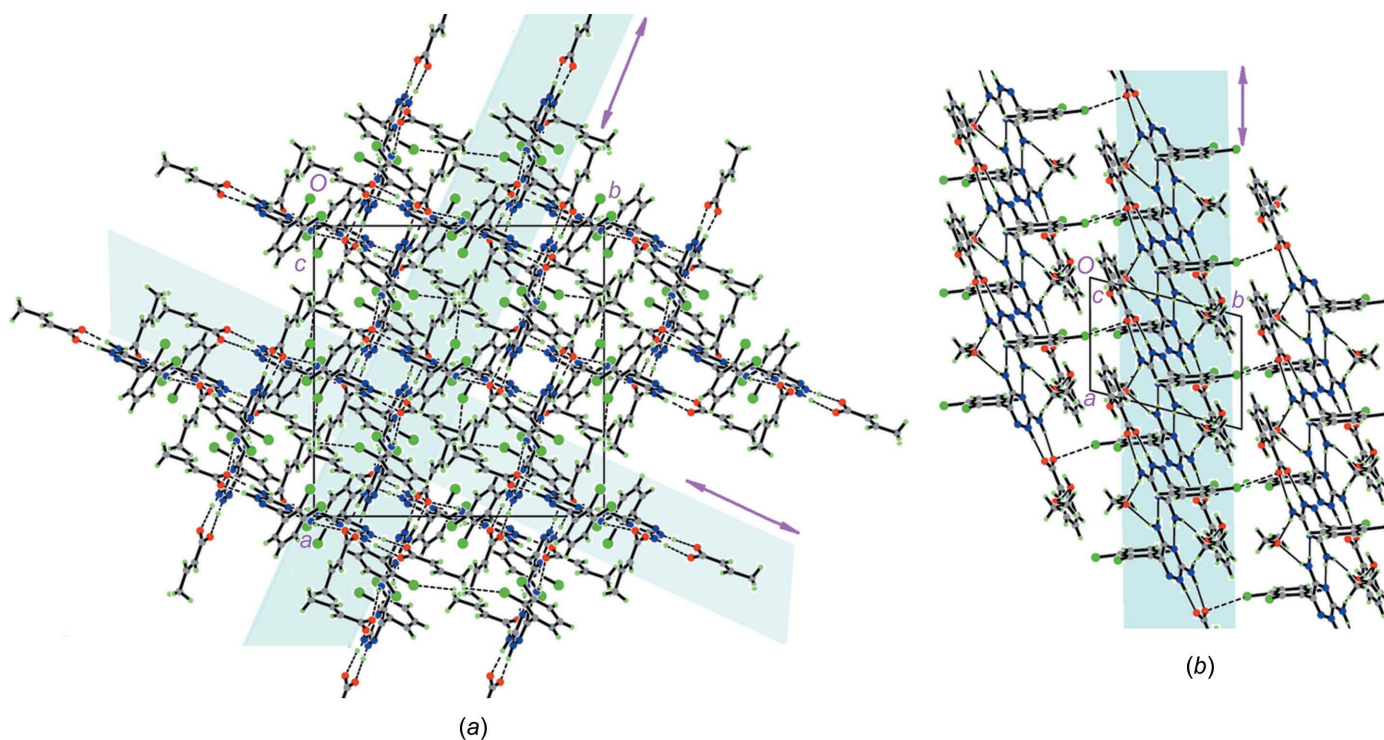


Figure 4

(a) Packing view of (III), projected along the tetragonal [001] axis, showing the 'crisscross' array. (b) Packing view for (IV), showing the [100] columns formed from stacked tetramers, and the (001) array resulting from the linkage of columns through interactions along [010] and involving atom Cl2. In both, single columns have been highlighted, for clarity.

These extended units, in turn, end up lying parallel to each other, as indicated for (IV) in Fig. 3(b), defining a basically planar supramolecular structure. Fig. 4 shows views of the packing arrays for both crystal structures, where differences are apparent. In salt (III), the set-up is absolutely three-dimensional. In salt (IV), instead, the hydrogen-bonded hexamers stack in a slanted way, defining columns along the [100] direction, which are in turn linked along the [010] direction by different forces involving atom Cl2, mainly the rather strong $C6-Cl2 \cdots O21(x, y + 1, z)$ halogen bond [$Cl \cdots O = 3.094(2) \text{ \AA}$ and $C-Cl \cdots O = 167.42(11)^\circ$] and hydrogen bond #7 in Table 3, resulting in planar arrays parallel to (001).

In trying to rationalize these dissimilar packing behaviours in structures with large identical constructive units, it should be noted that when these 'bricks' are put to work there are two competing requirements to comply with, *viz.* on one side, the unsatisfied hydrogen bonding of donors H5B and H3B towards site X (Fig. 2) and, on the other, the usual preference of extended groups for a planar arrangement, in order to facilitate delocalized $\pi-\pi$ interactions.

In this bid, the couple of strong $N-H \cdots O$ hydrogen bonds ranks higher in terms of stabilizing effects for the system, which tends to fill the acceptor site X whenever possible. In salt (III), and forced by steric reasons, the need to fill this acceptor site leads to the already discussed 'perpendicular' set-up, far from the otherwise expected parallel arrangement. On the other hand, when the X site can be occupied in a simpler way by a convenient acceptor, *viz.* by a mobile non-

interacting solvent molecule, the second point can then be readily addressed, and a planar packing becomes feasible.

It would seem then that without the need for orthogonality forced by steric reasons, the natural trend for these tetrameric moieties would be to adopt the much more relaxed plane parallel arrangement characteristic of extended delocalized groups.

In order to assess the degree of generality, this behaviour might have among similar structures, we analyzed the 17 *L*-

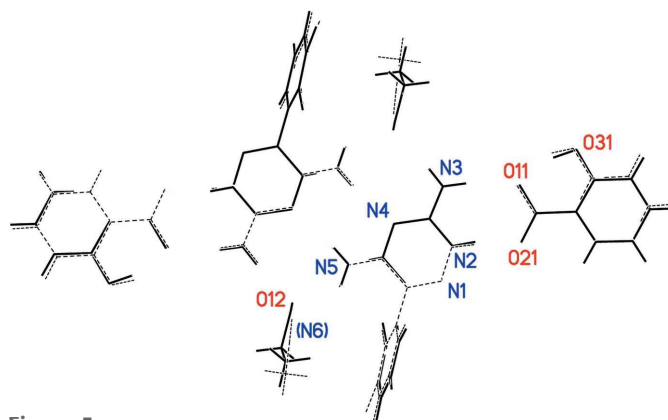


Figure 5

A least-squares fit of the 'hexameric groups' in (IV) (full lines) and YUYQEQ (dotted lines; Thipparaboina *et al.*, 2015). The analogy in orientation and relative disposition of the molecules in both hexamers is apparent. Note, however, the closer approach to the main structure of the ethanol molecule in (IV) compared to the acetonitrile molecule in YUYQEQ as a result of stronger hydrogen bonding.

carboxylate salts mentioned above, where the elemental packing unit is a comparable tetramer.

For this to be so, however, simple monocarboxylic acids had to be considered, since polycarboxylated ones, such as malate, adipate, pimelate, glutarate, fumarate and succinate, or even our recently reported dithiobenzoate (Freire *et al.*, 2016), usually give rise to more complex hydrogen-bonding patterns.

We found that unsolvated complexes of monocarboxylic acids (where the sole available hydrogen-bonding sites left are those provided by a single COO^- group) present a similar behaviour to (III), *viz.* ‘crisscross’ structures; examples are: LIBTUN (propionate) and PEZKIQ (acetate) in Chadha *et al.* (2013), and LIBYAY (4-hydroxybenzoate) in Chadha *et al.* (2011). An interesting case is that of OVUMEY (lamotriginium lamotrigine 4-fluorobenzoate 4-fluorobenzoic acid) in Sridhar & Ravikumar (2011), where the migration of the acidic H atom from the hydroxybenzoic acid group to atom N2 is not fully accomplished, meaning that the basic elemental building block is not a truly centrosymmetric tetramer anymore, but just a ‘pseudo’ one where the pseudocentrosymmetric halves are made up of a lamotriginium cation/fluorobenzoate anion pair on one side and a lamotrigine/fluorobenzoic acid pair on the other, but always fulfilling the ‘crisscross’ packing pattern.

On the other hand, solvated structures of similar simple acids were instead invariably packed as in salt (IV); examples are: GAVLEV (benzoate dimethylformamide solvate) in Sridhar & Ravikumar (2005), QIQHIJ (4-iodobenzoate *N,N*-dimethylformamide solvate) and QIQJAD (3,5-dinitro-2-hydroxybenzoate *N,N*-dimethylformamide solvate) in Sridhar *et al.* (2013), WOKXUR (4-bromobenzoate dimethylformamide solvate) in Sridhar *et al.* (2014) and YUYQEQ (salicylate acetonitrile solvate) in Thipparaboina *et al.* (2015). This last complex, which differs from salt (IV) only in the solvent present (acetonitrile replacing ethanol), provides an opportunity to analyze the subtle role which solvents play in the final crystal structure, even in cases where large elemental motifs are shared; this latter fact is fully assessed in Fig. 5, which shows the way in which both extended ‘hexameric’ building blocks in salt (IV) and YUYQEQ fit each other in a surprisingly similar way; the only detectable difference is to be found in the the $\text{N}-\text{H}\cdots\text{O}$ (ethanol) hydrogen bond in (IV) being stronger than the $\text{N}-\text{H}\cdots\text{N}$ (acetonitrile) hydrogen bond in YUYQEQ. Both structures display a stacked pattern, but when interplanar distances in the stacking sequence are analyzed, those in (IV) appear much shorter [$d_{(1\bar{2}1)} = 3.35 \text{ \AA}$] than those in YUYQEQ [$\frac{1}{2}d_{(1\bar{1}0)} = 3.55 \text{ \AA}$], and this has to do

with the strong ethanol–salicylate $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond (#8 in Table 3), which links adjacent planes in (IV) tightly, while the much less interactive acetonitrile, instead, acts as an acceptor of much weaker interplanar $\text{CH}_3\cdots\text{N}$ contacts.

4. Summary

We have analyzed the role played by the presence of a solvent molecule (able to act as a good hydrogen-bond acceptor) in the building up of the supramolecular structure of the title lamotrigine salts (III) (unsolvated) and (IV) (ethanol solvate). The analysis was extended to related structures in the literature to discover that similar packing patterns seemed to be present. The absence of solvent frequently results in what we have described as ‘crisscross’ structures, while its presence tends to give rise to parallel stacked structures. In any case, and as stated in our previous report (Freire *et al.*, 2016), the supramolecular scenario for lamotrigine salts is vast and open to many different possibilities, as many as there are different hydrogen-bonding partners.

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supporting information

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Lamotriginium crotonate and lamotriginium salicylate ethanol monosolvate: the role of solvent molecules in the packing organization

Eleonora Freire, Gustavo A. Echeverría and Ricardo Baggio

Computing details

For both compounds, data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008). Program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015) for (III); *SHELXL2014* (Sheldrick, 2015) for (IV). For both compounds, molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

(III) 3,5-Diamino-6-(2,3-dichlorophenyl)-1,2,4-triazin-2-ium but-2-enoate

Crystal data

$C_9H_8Cl_2N_5^+ \cdot C_4H_5O_2^-$

$M_r = 342.18$

Tetragonal, $I4_1/a$

$a = 19.513$ (3) Å

$c = 17.613$ (4) Å

$V = 6706$ (2) Å³

$Z = 16$

$F(000) = 2816$

$D_x = 1.356$ Mg m⁻³

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

Cell parameters from 2042 reflections

$\theta = 3.7$ – 26.8°

$\mu = 0.40$ mm⁻¹

$T = 294$ K

Fragment, pale_yellow

$0.35 \times 0.22 \times 0.16$ mm

Data collection

Rigaku OD Xcalibur Eos Gemini
diffractometer

Radiation source: fine-focus sealed X-ray tube,
Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.0604 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Rigaku OD, 2015)

$T_{\min} = 0.88$, $T_{\max} = 0.94$

8373 measured reflections

3726 independent reflections

2148 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 28.7^\circ$, $\theta_{\min} = 3.3^\circ$

$h = -25 \rightarrow 13$

$k = -14 \rightarrow 25$

$l = -17 \rightarrow 23$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.057$

$wR(F^2) = 0.185$

$S = 0.97$

3726 reflections

240 parameters

7 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0918P)^2 + 4.2506P]$

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

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.25$ e Å⁻³

$\Delta\rho_{\min} = -0.29$ 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>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C11	0.73692 (7)	0.34332 (6)	0.00171 (5)	0.0996 (5)	0.949 (3)
C12	0.77488 (6)	0.28325 (8)	-0.15600 (5)	0.1222 (6)	0.949 (3)
N1	0.57311 (12)	0.29306 (12)	0.10267 (12)	0.0557 (6)	
N2	0.55588 (12)	0.31338 (12)	0.17307 (12)	0.0538 (6)	
H2	0.5087 (16)	0.3303 (15)	0.1793 (16)	0.070 (9)*	
N3	0.57590 (14)	0.32645 (14)	0.29991 (14)	0.0607 (7)	
H3A	0.5373 (17)	0.3496 (16)	0.3028 (18)	0.073*	
H3B	0.6011 (17)	0.3250 (16)	0.3366 (19)	0.073*	
N4	0.66117 (10)	0.28023 (11)	0.22563 (11)	0.0484 (5)	
N5	0.74067 (12)	0.23232 (14)	0.14769 (15)	0.0596 (7)	
H5A	0.7687 (16)	0.2274 (16)	0.188 (2)	0.072*	
H5B	0.7544 (16)	0.2227 (16)	0.103 (2)	0.072*	
C1	0.59818 (13)	0.30640 (13)	0.23302 (14)	0.0476 (6)	
C2	0.67972 (13)	0.25935 (13)	0.15677 (14)	0.0479 (6)	
C3	0.63275 (14)	0.26608 (14)	0.09340 (14)	0.0518 (6)	
C4	0.65009 (15)	0.23897 (16)	0.01699 (16)	0.0616 (7)	
C5	0.69774 (16)	0.27052 (16)	-0.02847 (16)	0.0636 (8)	
C6	0.71503 (19)	0.2437 (2)	-0.09959 (18)	0.0848 (11)	
C7	0.6839 (3)	0.1856 (3)	-0.1233 (3)	0.1299 (18)	
H7	0.6943	0.1677	-0.1709	0.156*	
C8	0.6375 (3)	0.1529 (3)	-0.0785 (3)	0.156 (3)	
H8	0.6185	0.1119	-0.0953	0.188*	
C9	0.6176 (3)	0.1789 (2)	-0.0080 (2)	0.1163 (17)	
H9	0.5843	0.1573	0.0212	0.140*	
O11	0.42895 (10)	0.35815 (11)	0.18802 (11)	0.0673 (6)	
O21	0.45000 (12)	0.39226 (13)	0.30578 (10)	0.0552 (5)	0.794 (5)
C11	0.41111 (13)	0.38516 (16)	0.24903 (12)	0.0473 (7)	0.794 (5)
C21	0.34109 (18)	0.4106 (2)	0.25422 (17)	0.0696 (13)	0.794 (5)
H21	0.3136	0.4061	0.2114	0.083*	0.794 (5)
C31	0.31388 (13)	0.4390 (2)	0.31349 (18)	0.0833 (15)	0.794 (5)
H31	0.3420	0.4453	0.3555	0.100*	0.794 (5)
C41	0.24060 (16)	0.4627 (3)	0.3204 (4)	0.138 (3)	0.794 (5)
H41A	0.2397	0.5100	0.3353	0.208*	0.794 (5)
H41B	0.2174	0.4355	0.3578	0.208*	0.794 (5)
H41C	0.2180	0.4576	0.2723	0.208*	0.794 (5)
O21'	0.4500 (3)	0.4020 (3)	0.30177 (15)	0.0552 (5)	0.206 (5)
C11'	0.4156 (2)	0.3981 (2)	0.24123 (15)	0.0473 (7)	0.206 (5)
C21'	0.3521 (5)	0.4431 (3)	0.2369 (3)	0.0696 (13)	0.206 (5)
H21'	0.3258	0.4414	0.1929	0.083*	0.206 (5)

C31'	0.33264 (19)	0.4836 (2)	0.2910 (3)	0.0833 (15)	0.206 (5)
H31'	0.3614	0.4880	0.3328	0.100*	0.206 (5)
C41'	0.2669 (2)	0.5242 (3)	0.2913 (17)	0.138 (3)	0.206 (5)
H41D	0.2410	0.5132	0.3360	0.208*	0.206 (5)
H41E	0.2405	0.5129	0.2470	0.208*	0.206 (5)
H41F	0.2773	0.5723	0.2910	0.208*	0.206 (5)
C11'	0.70186 (18)	0.3605 (3)	-0.00746 (18)	0.0996 (5)	0.051 (3)
C12'	0.74014 (19)	0.3010 (3)	-0.16535 (18)	0.1222 (6)	0.051 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.1377 (11)	0.0848 (7)	0.0763 (7)	-0.0353 (7)	0.0082 (6)	0.0146 (5)
C12	0.1006 (9)	0.2122 (15)	0.0539 (6)	0.0130 (9)	0.0176 (5)	0.0313 (7)
N1	0.0577 (14)	0.0688 (14)	0.0408 (13)	0.0039 (12)	-0.0053 (10)	-0.0046 (10)
N2	0.0496 (13)	0.0694 (15)	0.0424 (13)	0.0119 (11)	-0.0039 (10)	-0.0045 (11)
N3	0.0577 (14)	0.0851 (18)	0.0393 (13)	0.0208 (13)	0.0006 (11)	-0.0078 (12)
N4	0.0471 (11)	0.0621 (13)	0.0360 (11)	0.0073 (10)	0.0010 (9)	-0.0036 (9)
N5	0.0533 (13)	0.0900 (18)	0.0355 (12)	0.0171 (13)	0.0033 (10)	-0.0055 (12)
C1	0.0502 (14)	0.0522 (14)	0.0402 (14)	0.0042 (12)	-0.0012 (11)	-0.0009 (11)
C2	0.0494 (14)	0.0558 (15)	0.0384 (14)	0.0011 (12)	0.0002 (11)	-0.0012 (11)
C3	0.0532 (15)	0.0614 (16)	0.0408 (14)	0.0014 (13)	-0.0009 (11)	-0.0043 (12)
C4	0.0625 (17)	0.0777 (19)	0.0446 (16)	-0.0025 (16)	-0.0029 (13)	-0.0095 (14)
C5	0.0686 (18)	0.0792 (19)	0.0429 (16)	0.0057 (16)	-0.0042 (13)	0.0071 (14)
C6	0.087 (2)	0.125 (3)	0.0424 (18)	0.012 (2)	0.0002 (16)	-0.0035 (19)
C7	0.146 (4)	0.181 (5)	0.063 (3)	-0.016 (4)	0.013 (3)	-0.048 (3)
C8	0.191 (6)	0.177 (5)	0.101 (4)	-0.080 (5)	0.020 (4)	-0.074 (4)
C9	0.138 (4)	0.139 (4)	0.072 (3)	-0.059 (3)	0.014 (2)	-0.052 (2)
O11	0.0606 (12)	0.0911 (14)	0.0501 (12)	0.0128 (11)	-0.0086 (9)	-0.0218 (10)
O21	0.0535 (10)	0.0658 (13)	0.0462 (11)	0.0080 (10)	-0.0063 (8)	-0.0088 (9)
C11	0.0472 (14)	0.0504 (17)	0.0444 (15)	-0.0009 (13)	-0.0014 (12)	-0.0014 (13)
C21	0.057 (2)	0.087 (3)	0.064 (2)	0.020 (2)	-0.0159 (17)	-0.015 (2)
C31	0.058 (2)	0.111 (4)	0.081 (3)	0.035 (2)	-0.007 (2)	-0.014 (3)
C41	0.082 (4)	0.195 (7)	0.139 (6)	0.070 (4)	0.003 (3)	-0.016 (5)
O21'	0.0535 (10)	0.0658 (13)	0.0462 (11)	0.0080 (10)	-0.0063 (8)	-0.0088 (9)
C11'	0.0472 (14)	0.0504 (17)	0.0444 (15)	-0.0009 (13)	-0.0014 (12)	-0.0014 (13)
C21'	0.057 (2)	0.087 (3)	0.064 (2)	0.020 (2)	-0.0159 (17)	-0.015 (2)
C31'	0.058 (2)	0.111 (4)	0.081 (3)	0.035 (2)	-0.007 (2)	-0.014 (3)
C41'	0.082 (4)	0.195 (7)	0.139 (6)	0.070 (4)	0.003 (3)	-0.016 (5)
C11'	0.1377 (11)	0.0848 (7)	0.0763 (7)	-0.0353 (7)	0.0082 (6)	0.0146 (5)
C12'	0.1006 (9)	0.2122 (15)	0.0539 (6)	0.0130 (9)	0.0176 (5)	0.0313 (7)

Geometric parameters (Å, °)

C11—C5	1.698 (3)	C8—H8	0.9300
C12—C6	1.717 (4)	C9—H9	0.9300
N1—C3	1.288 (3)	O11—C11	1.247 (3)
N1—N2	1.345 (3)	O11—C11'	1.247 (3)

N2—C1	1.347 (3)	O21—C11	1.263 (2)
N2—H2	0.98 (3)	C11—C21	1.456 (4)
N3—C1	1.315 (3)	C21—C31	1.296 (4)
N3—H3A	0.88 (3)	C21—H21	0.9300
N3—H3B	0.81 (3)	C31—C41	1.508 (4)
N4—C2	1.330 (3)	C31—H31	0.9300
N4—C1	1.337 (3)	C41—H41A	0.9600
N5—C2	1.311 (3)	C41—H41B	0.9600
N5—H5A	0.90 (3)	C41—H41C	0.9600
N5—H5B	0.85 (3)	O21'—C11'	1.263 (2)
C2—C3	1.450 (4)	C11'—C21'	1.521 (9)
C3—C4	1.485 (4)	C21'—C31'	1.296 (4)
C4—C5	1.373 (4)	C21'—H21'	0.9300
C4—C9	1.403 (5)	C31'—C41'	1.508 (4)
C5—C6	1.399 (4)	C31'—H31'	0.9300
C6—C7	1.352 (6)	C41'—H41D	0.9600
C7—C8	1.359 (7)	C41'—H41E	0.9600
C7—H7	0.9300	C41'—H41F	0.9600
C8—C9	1.397 (6)		
C3—N1—N2	117.6 (2)	C9—C8—H8	119.0
N1—N2—C1	122.7 (2)	C8—C9—C4	117.2 (4)
N1—N2—H2	115.8 (17)	C8—C9—H9	121.4
C1—N2—H2	121.3 (17)	C4—C9—H9	121.4
C1—N3—H3A	119 (2)	O11—C11—O21	124.1 (2)
C1—N3—H3B	120 (2)	O11—C11—C21	117.4 (2)
H3A—N3—H3B	119 (3)	O21—C11—C21	118.5 (2)
C2—N4—C1	117.1 (2)	C31—C21—C11	125.5 (3)
C2—N5—H5A	120 (2)	C31—C21—H21	117.2
C2—N5—H5B	119 (2)	C11—C21—H21	117.2
H5A—N5—H5B	121 (3)	C21—C31—C41	125.8 (4)
N3—C1—N4	120.3 (2)	C21—C31—H31	117.1
N3—C1—N2	118.0 (2)	C41—C31—H31	117.1
N4—C1—N2	121.7 (2)	C31—C41—H41A	109.5
N5—C2—N4	118.8 (2)	C31—C41—H41B	109.5
N5—C2—C3	121.1 (2)	H41A—C41—H41B	109.5
N4—C2—C3	120.2 (2)	C31—C41—H41C	109.5
N1—C3—C2	120.7 (2)	H41A—C41—H41C	109.5
N1—C3—C4	117.8 (2)	H41B—C41—H41C	109.5
C2—C3—C4	121.4 (2)	O11—C11'—O21'	124.1 (2)
C5—C4—C9	119.8 (3)	O11—C11'—C21'	119.5 (3)
C5—C4—C3	121.5 (3)	O21'—C11'—C21'	116.2 (3)
C9—C4—C3	118.6 (3)	C31'—C21'—C11'	123.6 (6)
C4—C5—C6	121.2 (3)	C31'—C21'—H21'	118.2
C4—C5—C11	119.8 (2)	C11'—C21'—H21'	118.2
C6—C5—C11	119.0 (3)	C21'—C31'—C41'	124.9 (12)
C7—C6—C5	118.8 (4)	C21'—C31'—H31'	117.5
C7—C6—C12	120.3 (3)	C41'—C31'—H31'	117.5

C5—C6—C12	120.9 (3)	C31'—C41'—H41D	109.5
C6—C7—C8	120.9 (4)	C31'—C41'—H41E	109.5
C6—C7—H7	119.6	H41D—C41'—H41E	109.5
C8—C7—H7	119.6	C31'—C41'—H41F	109.5
C7—C8—C9	122.0 (5)	H41D—C41'—H41F	109.5
C7—C8—H8	119.0	H41E—C41'—H41F	109.5

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N5—H5 <i>A</i> ...N4 ⁱ	0.90 (3)	2.06 (3)	2.951 (3)	176 (3)
N2—H2...O11	0.98 (3)	1.66 (3)	2.639 (3)	179 (3)
N3—H3 <i>A</i> ...O21	0.88 (3)	1.90 (3)	2.774 (4)	175 (3)
N3—H3 <i>B</i> ...O21 ⁱⁱ	0.81 (3)	2.12 (3)	2.899 (3)	162 (3)
N5—H5 <i>B</i> ...O21 ⁱⁱⁱ	0.85 (3)	2.23 (3)	2.870 (3)	132 (3)

Symmetry codes: (i) $-x+3/2, -y+1/2, -z+1/2$; (ii) $y+1/4, -x+3/4, -z+3/4$; (iii) $-y+5/4, x-1/4, z-1/4$.

(IV) 3,5-Diamino-6-(2,3-dichlorophenyl)-1,2,4-triazin-2-ium 2-hydroxybenzoate ethanol monosolvate

Crystal data

$C_9H_8Cl_2N_5^+ \cdot C_7H_5O_3^- \cdot C_2H_6O$

$M_r = 440.28$

Triclinic, $P\bar{1}$

$a = 7.9389$ (4) Å

$b = 12.2938$ (9) Å

$c = 12.3282$ (8) Å

$\alpha = 61.781$ (7)°

$\beta = 79.379$ (5)°

$\gamma = 72.313$ (5)°

$V = 1008.92$ (12) Å³

$Z = 2$

$F(000) = 456$

$D_x = 1.449$ Mg m⁻³

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

Cell parameters from 1967 reflections

$\theta = 3.2$ – 25.9 °

$\mu = 0.36$ mm⁻¹

$T = 294$ K

Fragment, pale yellow

$0.42 \times 0.28 \times 0.18$ mm

Data collection

Rigaku OD Xcalibur Eos Gemini
diffractometer

Radiation source: fine-focus sealed X-ray tube,
Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.0604 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2015)

$T_{\min} = 0.86, T_{\max} = 0.96$

8324 measured reflections

4360 independent reflections

2863 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 28.8$ °, $\theta_{\min} = 2.9$ °

$h = -10 \rightarrow 9$

$k = -16 \rightarrow 15$

$l = -15 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.168$

$S = 1.05$

4360 reflections

284 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2 + 0.1003P]$

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

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

$\Delta\rho_{\max} = 0.34$ e Å⁻³

$\Delta\rho_{\min} = -0.37$ 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.55710 (10)	0.81807 (7)	0.59053 (7)	0.0550 (2)
C12	0.53000 (11)	0.96585 (8)	0.74551 (9)	0.0641 (3)
N1	0.5333 (3)	0.4790 (2)	0.7616 (2)	0.0425 (5)
N2	0.5259 (3)	0.4109 (2)	0.7047 (2)	0.0428 (6)
H2	0.442 (4)	0.375 (3)	0.727 (3)	0.051*
N3	0.6164 (3)	0.3362 (2)	0.5606 (2)	0.0433 (6)
H3A	0.528 (4)	0.303 (3)	0.584 (3)	0.052*
H3B	0.694 (4)	0.321 (3)	0.510 (3)	0.052*
N4	0.7847 (3)	0.4482 (2)	0.58172 (19)	0.0368 (5)
N5	0.9385 (3)	0.5594 (3)	0.6148 (3)	0.0481 (6)
H5A	1.012 (4)	0.553 (3)	0.561 (3)	0.058*
H5B	0.941 (4)	0.607 (3)	0.644 (3)	0.058*
C1	0.6440 (3)	0.3985 (2)	0.6155 (2)	0.0358 (6)
C2	0.7992 (3)	0.5132 (3)	0.6391 (2)	0.0372 (6)
C3	0.6650 (3)	0.5315 (3)	0.7307 (2)	0.0375 (6)
C4	0.6723 (3)	0.6047 (3)	0.7962 (2)	0.0391 (6)
C5	0.6182 (3)	0.7363 (3)	0.7423 (2)	0.0383 (6)
C6	0.6126 (3)	0.8027 (3)	0.8083 (3)	0.0444 (7)
C7	0.6668 (4)	0.7374 (3)	0.9282 (3)	0.0513 (7)
H7	0.6637	0.7818	0.9724	0.062*
C8	0.7248 (4)	0.6073 (4)	0.9816 (3)	0.0573 (8)
H8	0.7635	0.5638	1.0615	0.069*
C9	0.7267 (4)	0.5395 (3)	0.9176 (3)	0.0497 (7)
H9	0.7640	0.4510	0.9552	0.060*
O21	0.3024 (2)	0.2441 (2)	0.65319 (18)	0.0503 (5)
O11	0.2676 (3)	0.3002 (2)	0.8044 (2)	0.0639 (6)
O31	0.0951 (3)	0.1304 (2)	0.6420 (2)	0.0583 (6)
H31A	0.177 (5)	0.169 (4)	0.629 (4)	0.087*
C11	0.0087 (4)	0.1393 (3)	0.7446 (3)	0.0430 (6)
C21	-0.1392 (4)	0.0895 (3)	0.7930 (3)	0.0555 (8)
H21	-0.1753	0.0500	0.7562	0.067*
C31	-0.2308 (4)	0.0989 (3)	0.8947 (3)	0.0615 (9)
H31	-0.3299	0.0661	0.9262	0.074*
C41	-0.1794 (4)	0.1563 (4)	0.9516 (3)	0.0640 (9)
H41	-0.2430	0.1625	1.0206	0.077*
C51	-0.0317 (4)	0.2041 (3)	0.9041 (3)	0.0501 (7)
H51	0.0045	0.2422	0.9424	0.060*
C61	0.0640 (3)	0.1968 (2)	0.8008 (2)	0.0377 (6)
C71	0.2219 (3)	0.2512 (3)	0.7493 (2)	0.0408 (6)

O12	0.9291 (3)	0.2327 (2)	0.4205 (2)	0.0604 (6)
H12	0.980 (5)	0.188 (4)	0.490 (4)	0.091*
C12	0.9330 (4)	0.1557 (3)	0.3627 (3)	0.0583 (8)
H12A	0.8547	0.0997	0.4082	0.070*
H12B	1.0520	0.1035	0.3613	0.070*
C22	0.8745 (5)	0.2409 (4)	0.2342 (3)	0.0775 (11)
H22A	0.9516	0.2968	0.1901	0.116*
H22B	0.7555	0.2906	0.2364	0.116*
H22C	0.8787	0.1901	0.1934	0.116*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0618 (5)	0.0581 (5)	0.0480 (5)	-0.0133 (4)	-0.0083 (3)	-0.0249 (4)
C12	0.0603 (5)	0.0586 (5)	0.0901 (7)	-0.0127 (4)	-0.0084 (4)	-0.0462 (5)
N1	0.0420 (13)	0.0527 (14)	0.0425 (13)	-0.0199 (11)	0.0068 (10)	-0.0271 (11)
N2	0.0391 (13)	0.0544 (15)	0.0491 (14)	-0.0246 (11)	0.0106 (10)	-0.0311 (12)
N3	0.0384 (13)	0.0546 (15)	0.0509 (15)	-0.0192 (11)	0.0063 (10)	-0.0331 (13)
N4	0.0319 (11)	0.0431 (13)	0.0436 (13)	-0.0131 (9)	0.0038 (9)	-0.0255 (11)
N5	0.0393 (13)	0.0700 (18)	0.0581 (17)	-0.0273 (12)	0.0139 (11)	-0.0445 (15)
C1	0.0348 (13)	0.0373 (14)	0.0374 (14)	-0.0094 (11)	-0.0033 (10)	-0.0174 (11)
C2	0.0346 (13)	0.0409 (15)	0.0412 (15)	-0.0125 (11)	0.0024 (11)	-0.0221 (12)
C3	0.0363 (14)	0.0439 (15)	0.0385 (15)	-0.0134 (12)	0.0029 (11)	-0.0229 (12)
C4	0.0353 (13)	0.0508 (17)	0.0406 (15)	-0.0178 (12)	0.0088 (11)	-0.0274 (13)
C5	0.0305 (13)	0.0543 (17)	0.0392 (15)	-0.0158 (12)	0.0045 (10)	-0.0271 (13)
C6	0.0331 (14)	0.0574 (18)	0.0586 (18)	-0.0161 (12)	0.0044 (12)	-0.0380 (15)
C7	0.0442 (16)	0.074 (2)	0.0556 (19)	-0.0199 (15)	0.0052 (13)	-0.0444 (17)
C8	0.0582 (19)	0.081 (2)	0.0447 (18)	-0.0200 (17)	0.0010 (14)	-0.0370 (17)
C9	0.0562 (18)	0.0559 (19)	0.0383 (16)	-0.0172 (15)	0.0038 (13)	-0.0223 (14)
O21	0.0509 (12)	0.0732 (14)	0.0454 (12)	-0.0327 (10)	0.0094 (9)	-0.0350 (11)
O11	0.0658 (14)	0.1030 (18)	0.0624 (14)	-0.0541 (13)	0.0188 (10)	-0.0563 (14)
O31	0.0568 (13)	0.0817 (16)	0.0625 (14)	-0.0342 (12)	0.0009 (10)	-0.0442 (13)
C11	0.0410 (15)	0.0474 (16)	0.0470 (17)	-0.0148 (13)	-0.0062 (12)	-0.0227 (13)
C21	0.0468 (17)	0.061 (2)	0.070 (2)	-0.0233 (15)	-0.0104 (15)	-0.0294 (17)
C31	0.0394 (16)	0.071 (2)	0.074 (2)	-0.0293 (15)	0.0032 (15)	-0.0255 (18)
C41	0.0451 (17)	0.090 (3)	0.062 (2)	-0.0265 (17)	0.0131 (14)	-0.0377 (19)
C51	0.0438 (16)	0.066 (2)	0.0485 (18)	-0.0190 (14)	-0.0002 (13)	-0.0293 (16)
C61	0.0336 (13)	0.0422 (15)	0.0405 (15)	-0.0113 (11)	-0.0044 (11)	-0.0189 (12)
C71	0.0427 (15)	0.0464 (16)	0.0401 (16)	-0.0177 (12)	-0.0044 (11)	-0.0201 (13)
O12	0.0626 (14)	0.0663 (15)	0.0688 (16)	-0.0174 (12)	-0.0092 (11)	-0.0401 (13)
C12	0.0554 (19)	0.068 (2)	0.068 (2)	-0.0180 (16)	-0.0043 (15)	-0.0407 (18)
C22	0.072 (2)	0.101 (3)	0.066 (2)	-0.020 (2)	-0.0096 (19)	-0.042 (2)

Geometric parameters (\AA , $^\circ$)

C11—C5	1.734 (3)	C9—H9	0.9300
C12—C6	1.724 (3)	O21—C71	1.267 (3)
N1—C3	1.298 (3)	O11—C71	1.251 (3)

N1—N2	1.342 (3)	O31—C11	1.360 (3)
N2—C1	1.343 (3)	O31—H31A	0.87 (4)
N2—H2	0.84 (3)	C11—C61	1.391 (3)
N3—C1	1.319 (3)	C11—C21	1.394 (4)
N3—H3A	0.85 (3)	C21—C31	1.365 (5)
N3—H3B	0.84 (3)	C21—H21	0.9300
N4—C2	1.331 (3)	C31—C41	1.380 (4)
N4—C1	1.341 (3)	C31—H31	0.9300
N5—C2	1.317 (3)	C41—C51	1.380 (4)
N5—H5A	0.82 (3)	C41—H41	0.9300
N5—H5B	0.82 (3)	C51—C61	1.385 (4)
C2—C3	1.453 (3)	C51—H51	0.9300
C3—C4	1.483 (3)	C61—C71	1.495 (4)
C4—C5	1.382 (4)	O12—C12	1.420 (3)
C4—C9	1.400 (4)	O12—H12	0.86 (4)
C5—C6	1.386 (3)	C12—C22	1.492 (5)
C6—C7	1.385 (4)	C12—H12A	0.9700
C7—C8	1.368 (5)	C12—H12B	0.9700
C7—H7	0.9300	C22—H22A	0.9600
C8—C9	1.388 (4)	C22—H22B	0.9600
C8—H8	0.9300	C22—H22C	0.9600
C3—N1—N2	117.6 (2)	C4—C9—H9	120.1
N1—N2—C1	123.1 (2)	C11—O31—H31A	101 (3)
N1—N2—H2	117 (2)	O31—C11—C61	121.6 (2)
C1—N2—H2	120 (2)	O31—C11—C21	118.3 (2)
C1—N3—H3A	120 (2)	C61—C11—C21	120.1 (3)
C1—N3—H3B	119 (2)	C31—C21—C11	119.7 (3)
H3A—N3—H3B	121 (3)	C31—C21—H21	120.1
C2—N4—C1	116.6 (2)	C11—C21—H21	120.1
C2—N5—H5A	120 (2)	C21—C31—C41	121.4 (3)
C2—N5—H5B	120 (2)	C21—C31—H31	119.3
H5A—N5—H5B	119 (3)	C41—C31—H31	119.3
N3—C1—N4	120.5 (2)	C51—C41—C31	118.7 (3)
N3—C1—N2	117.7 (2)	C51—C41—H41	120.7
N4—C1—N2	121.8 (2)	C31—C41—H41	120.7
N5—C2—N4	119.8 (2)	C41—C51—C61	121.6 (3)
N5—C2—C3	119.3 (2)	C41—C51—H51	119.2
N4—C2—C3	120.9 (2)	C61—C51—H51	119.2
N1—C3—C2	119.9 (2)	C51—C61—C11	118.6 (2)
N1—C3—C4	116.7 (2)	C51—C61—C71	120.8 (2)
C2—C3—C4	123.4 (2)	C11—C61—C71	120.6 (2)
C5—C4—C9	118.8 (2)	O11—C71—O21	123.8 (2)
C5—C4—C3	121.4 (2)	O11—C71—C61	118.0 (2)
C9—C4—C3	119.6 (2)	O21—C71—C61	118.2 (2)
C4—C5—C6	120.7 (2)	C12—O12—H12	111 (3)
C4—C5—C11	119.16 (19)	O12—C12—C22	108.6 (3)
C6—C5—C11	120.1 (2)	O12—C12—H12A	110.0

C7—C6—C5	120.0 (3)	C22—C12—H12A	110.0
C7—C6—C12	119.0 (2)	O12—C12—H12B	110.0
C5—C6—C12	120.9 (2)	C22—C12—H12B	110.0
C8—C7—C6	119.9 (3)	H12A—C12—H12B	108.4
C8—C7—H7	120.1	C12—C22—H22A	109.5
C6—C7—H7	120.1	C12—C22—H22B	109.5
C7—C8—C9	120.7 (3)	H22A—C22—H22B	109.5
C7—C8—H8	119.7	C12—C22—H22C	109.5
C9—C8—H8	119.7	H22A—C22—H22C	109.5
C8—C9—C4	119.9 (3)	H22B—C22—H22C	109.5
C8—C9—H9	120.1		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N5—H5 <i>A</i> \cdots N4 ⁱ	0.82 (3)	2.16 (3)	2.972 (3)	174 (3)
N2—H2 \cdots O11	0.84 (3)	1.77 (3)	2.599 (3)	168 (3)
N3—H3 <i>A</i> \cdots O21	0.85 (3)	2.03 (3)	2.872 (3)	171 (3)
N3—H3 <i>B</i> \cdots O12	0.84 (3)	2.24 (3)	3.057 (3)	164 (3)
N5—H5 <i>B</i> \cdots O12 ⁱ	0.82 (3)	2.24 (3)	2.870 (3)	134 (3)
O12—H12 \cdots O31 ⁱⁱ	0.86 (4)	1.96 (4)	2.801 (3)	165 (4)
O31—H31 <i>A</i> \cdots O21	0.87 (4)	1.69 (4)	2.518 (3)	159 (4)

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