## organic compounds

Acta Crystallographica Section C Crystal Structure Communications ISSN 0108-2701

## N—H···O, O—H···O hydrogenbonded supramolecular sheet formation in the bis(2-aminoanilinium) fumarate, 3-methylanilinium hydrogen fumarate and 4-chloroanilinium hydrogen fumarate salts

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Received 28 April 2013 Accepted 26 June 2013

In bis(2-aminoanilinum) fumarate,  $2C_6H_9N_2^+ \cdot C_4H_2O_4^{-2-}$ , (I), the asymmetric unit consists of two aminoanilinium cations and one fumarate dianion, whereas in 3-methylanilinium hydrogen fumarate, C<sub>7</sub>H<sub>10</sub>N<sup>+</sup>·C<sub>4</sub>H<sub>3</sub>O<sub>4</sub><sup>-</sup>, (II), and 4-chloroanilinium hydrogen fumarate,  $C_6H_7ClN^+ \cdot C_4H_3O_4^-$ , (III), the asymmetric unit contains two symmetry-independent hydrogen fumate anions and anilinium cations with a slight difference in their geometric parameters; the two salts are isostructural. In (II) and (III), the carboxylic acid H atoms of the anions are disordered across both ends of the anion, with equal site occupancies of 0.50. Both the 4-chloroanilinium cations of (III) are disordered over two orientations with major occupancies fixed at 0.60 in each case. The hydrogen fumarate anions of (II) and (III) form one-dimensional anionic chains linked through O-H···O hydrogen bonds. Salts (II) and (III) form two-dimensional supramolecular sheets built from  $R_4^4(16)$ ,  $R_4^4(18)$ ,  $R_5^5(25)$  and  $C_2^2(14)$  motifs extending parallel to the (010) plane, whereas in (I), an (010) sheet is formed built from two  $R_4^3(13)$  motifs, two  $R_2^2(9)$  motifs and an  $R_4^4(18)$  motif.

Keywords: crystal structure; hydrogen bonding; fumarate salts.

#### 1. Introduction

Hydrogen bonding is considered to be one of the best noncovalent interactions in supramolecular networks because of its strength and highly directional nature (Desiraju, 2002; Aakeroy *et al.*, 2005). Various hydrogen-bonded motifs and frameworks revealed in the field of crystal engineering have become tools to explain various physicochemical properties,



such as nonlinear optical, magnetic, catalytic and storage properties (Gomes *et al.*, 2006; Fábry *et al.*, 2000; Ivasenko & Perepichka, 2011). Dicarboxylic acids possessing very good donors and acceptors are of special interest in forming strong intermolecular hydrogen bonds between cations, anions or molecular constituents when they form salts or cocrystals with amines, amides and other metal complexes (Jagan & Sivakumar, 2011; Lyakhov *et al.*, 2012; Jin *et al.*, 2011; Farrell *et al.*, 2002). Maleic and fumaric acids are the Z and E isomers, respectively, of butenedioic acid, and they form interesting one-, two- and three-dimensional supramolecular architectures as adducts with various amines (Franklin & Balasubramanian, 2009; Bowes *et al.*, 2003; Jin *et al.*, 2003; Batchelor *et al.*, 2000). *Cis-* and *trans-*dicarboxylic acids such as maleic and fumaric acids have the interesting property of forming



isomers on changes in their physical environment, such as heat, light etc., thereby enhancing their hydrogen-bonding capability (Kalita & Baruah, 2010). Consequently, numerous recent articles have focused on the construction of fumarate salts with different bases, showing innovative supramolecular assemblies (Haynes & Pietersen, 2008; Hemamalini & Fun, 2010). We report herein the crystal structures of the title salts, bis(2-aminoanilinum) fumarate, (I), 3-methylanilinium hydrogen fumarate, (II), and 4-chloroanilinium hydrogen fumarate, (III), in order to study their hydrogen-bonding patterns and the consequent network present in the solid state. Even though we have chosen maleic acid for (I) in the preparation of the salt, unexpectedly the isomerization of maleic to fumaric acid has taken place in the formation of the title salt. A similar kind of geometric isomerization has been observed in the previously reported structures of 4,4'-bipyridylamine and 4,4'-trimethylenedipyridine fumaric acids (Chatterjee et al., 1998; Bowes et al., 2003).

Table 1

Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$2C_6H_9N_2^+ \cdot C_4H_2O_4^{2-}$	$C_7H_{10}N^+ \cdot C_4H_3O_4^-$	$C_6H_7ClN^+ \cdot C_4H_3O_4^-$
$M_{ m r}$	332.36	223.22	243.64
Crystal system, space group	Orthorhombic, Iba2	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	296	296	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.0424 (2), 42.9871 (11), 7.4930 (2)	9.4576 (3), 20.8915 (6), 10.8787 (3)	9.2335 (4), 23.8248 (11), 10.4424 (5)
$\alpha, \beta, \gamma$ (°)	90, 90, 90	90, 92.611 (2), 90	90, 94.338 (2), 90
$V(\text{\AA}^3)$	3234.68 (14)	2147.22 (11)	2290.60 (18)
Z	8	8	8
Radiation type	Μο Κα	Μο Κα	Μο <i>Κα</i>
$\mu \text{ (mm}^{-1})$	0.10	0.11	0.33
Crystal size (mm)	$0.35 \times 0.30 \times 0.20$	$0.35 \times 0.30 \times 0.25$	$0.35 \times 0.30 \times 0.25$
Data collection			
Diffractometer	Bruker Kappa APEXII CCD area-detector diffractometer	Bruker Kappa APEXII CCD area-detector diffractometer	Bruker Kappa APEXII CCD area-detector diffractometer
Absorption correction	Multi-scan (SADABS; Bruker, 2004)	Multi-scan (SADABS; Bruker, 2004)	Multi-scan (SADABS; Bruker, 2004)
$T_{\min}, T_{\max}$	0.916, 0.980	0.904, 0.974	0.903, 0.912
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	9034, 3406, 2751	37301, 6714, 5066	25081, 5334, 3844
R <sub>int</sub>	0.035	0.036	0.032
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.639	0.720	0.655
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.049, 0.140, 1.05	0.044, 0.130, 1.04	0.043, 0.122, 1.03
No. of reflections	3406	6714	5334
No. of parameters	247	322	428
No. of restraints	11	10	186
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	H atoms treated by a mixture of independent and constrained refinement
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min} (e A^{-})$	0.4/, -0.23	0.38, -0.21	0.40, -0.35

Computer programs: APEX2, SAINT and XPREP (Bruker, 2004), SHELXS97 (Sheldrick, 2008), SHELXL97 (Sheldrick, 2008), ORTEP-3 (Farrugia, 2012), Mercury (Macrae et al., 2008) and PLATON (Spek, 2009).

### 2. Experimental

#### 2.1. Synthesis and crystallization

A solution containing equimolar quantities of maleic acid and 2-aminoaniline in methanol was warmed for 10 min and set aside to crystallize. Brown crystals suitable for diffraction analysis were obtained by slow evaporation after a few days. Unexpectedly, the isomerization of maleic to fumaric acid had taken place during the salt formation. The resulting salt, (I), contained a 1:2 molar ratio of the fumarate dianion and the 2-aminoanilinium cation. Similarly, salts (II) and (III) were prepared from equimolar ratios of fumaric acid with 3-methylaniline and 4-chloroaniline, respectively, dissolved in ethanol. Both ethanol solutions were mixed together and stirred for 20 min and the resulting mixture was kept for crystallization. Good diffraction-quality colourless crystals were obtained by slow evaporation after a few days.

### 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. In salts (II) and (III), the carboxylic acid H atoms of the anions were disordered across both ends of the anion showing equal site occupancies of 0.50. The appearance of strong difference electron-density peaks, and their distances from the nearest atoms O1*A*, O1*B*, O4*A*  and O4B, revealed the presence of H atoms. The carboxyl C-O bond lengths and the improvement in the refinement confirmed the occupancy of the H atoms. Both the 4-chloroanilinium cations of (III) are disordered over two orientations. The site occupancies of the two orientations of each cation were initially refined and then fixed with the major occupancy being 0.60 in each case. For the disordered cations of (III), the disordered C-C bond lengths of the benzene rings were restrained to a distance of 1.39 (1) Å and the C-Cl bond lengths were restrained to 1.72 (1) Å. The atomic displacement parameters of the disordered components were made similar to those of neighbouring atoms using standard similarity restraints, with an s.u. of 0.02 Å<sup>2</sup> for ring atoms or  $0.04 \text{ Å}^2$  for terminal atoms, followed by rigid-bond restraints, with an s.u. of 0.01 Å. Finally, the disordered cations were also restrained to be planar. Salt (I) shows a meaningless Flack parameter (Flack, 1983) value of 0.1 (18). This is due to the molecular structure of (I) having light atoms (<Si) with no significant anomalous scattering effects. In this case, the Flack parameter is indeterminate with Mo radiation and hence the absolute structure cannot be determined. The positions of all the H atoms were initially identified from the difference electron-density map. The positions of the C-bound H atoms were then idealized and allowed to ride on their parent atom, with C-H = 0.96 Å and  $U_{iso}(H) = 1.5U_{eq}(C)$  for CH<sub>3</sub>, and



Figure 1

Displacement ellipsoid plot of salt (I), drawn at the 40% probability level and showing the atom-labelling scheme. The dashed lines between the ions represent hydrogen bonds.



#### Figure 2

Displacement ellipsoid plot of salt (II), drawn at the 40% probability level and showing the atom-labelling scheme. The dashed lines between the ions represent hydrogen bonds.



#### Figure 3

Displacement ellipsoid plot of salt (III), drawn at the 40% probability level and showing the atom-labelling scheme. The dashed lines between the ions represent hydrogen bonds. The bonds in the minor components of the disordered cations are represented as single dashed lines.

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

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - H \cdots A$	
$N4-H4C\cdots O4^{i}$	0.90(1)	1.85(1)	2.728 (3)	165 (3)	
$N2-H2A\cdots O2^{ii}$	0.90(1)	1.85 (1)	2.729 (3)	166 (3)	
N3-H3A···O3 <sup>iii</sup>	0.90(1)	2.29 (2)	3.106 (3)	150 (2)	
$N1-H1A\cdotsO1^{iv}$	0.90 (1)	2.23 (2)	3.101 (3)	161 (3)	
$N2-H2B\cdots O3^{v}$	0.92(1)	1.91 (1)	2.811 (3)	170 (2)	
N4-H4 $A$ ···O1 <sup>vi</sup>	0.91 (1)	1.93 (1)	2.820 (3)	167 (2)	
N3−H3 <i>B</i> ···O3	0.90 (1)	2.06(1)	2.956 (4)	175 (3)	
$N1 - H1B \cdots O1$	0.90(1)	2.05 (1)	2.926 (4)	166 (3)	
$N4 - H4B \cdot \cdot \cdot O4$	0.90 (1)	1.87 (1)	2.756 (3)	166 (3)	
$N2-H2C\cdots O2$	0.90 (1)	1.90 (2)	2.758 (4)	159 (3)	

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

C-H = 0.93 Å and  $U_{iso}(H) = 1.2U_{eq}(C)$  for aromatic H atoms. O-bound H atoms were positioned from the difference electron-density map and refined with O-H distance restraints of 0.85 (1) Å for salts (II) and (III), with  $U_{iso}(H) = 1.2U_{eq}(O)$ . The H atoms associated with both the NH<sub>2</sub> and NH<sub>3</sub><sup>+</sup> groups were refined with N-H distance restraints of 0.90 (1) Å for (I), (II) and (III), with  $U_{iso}(H) = 1.2U_{eq}(N)$ .

#### 3. Results and discussion

The asymmetric unit of (I) (Fig. 1) contains two 2-aminoanilinium cations and one fumarate dianion, whereas salts (II) and (III) (Figs. 2 and 3) consist of two sets of symmetryindependent cations and anions having a slight difference in their geometric parameters. The C–O bond lengths of (I) [C1-O1 = 1.242 (3) Å, C1-O2 = 1.259 (3) Å, C4-O3 =1.256 (3) Å and C4-O4 = 1.265 (3) Å] suggest the two carboxylate groups are deprotonated in the crystal structure. In salts (II) and (III), the carboxylic acid H atoms of the hydrogen fumarate anions are disordered over equally occupied alternate positions at opposite ends of the anion. Also in



#### Figure 4

Part of the crystal structure of (I), showing the formation of the supramolecular ladder linked through N-H···O hydrogen bonds. [Symmetry codes: (iii) -x + 1, y,  $z + \frac{1}{2}$ , (iv) -x, y,  $z - \frac{1}{2}$ .]



Figure 5

Part of the crystal strucure of (II), showing the formation of the one-dimensional anionic chain linked through  $O4A - H4A \cdots O1B^{iv}$  and  $O4B - H4B \cdots O1A$  hydrogen bonds. [Symmetry code: (iv) x - 1, y, z + 1.]

(III), both of the 4-chloroanilinium cations are disordered over two orientations with major occupancies of 0.60 in each case. In salt (I), the fumarate anion is almost planar compared with the hydrogen fumarate anions of (II) and (III), as shown by the dihedral angles between the carboxylic acid-carboxylate groups of 1.57 (6)° for (I), 40.03 (7) and 25.93 (2)° for (II), and 25.80 (3) and 42.43 (1)° for (III). Interestingly, the adjacent hydrogen fumarate anions of (II) and (III) form very strong hydrogen bonds, with donor–acceptor distances in the range 2.45–2.47 Å (Tables 3 and 4).

In (I), all the O atoms in the fumarate dianion form bifurcated hydrogen bonds with the anilinium cations. In the asymmetric unit, both carboxylate O atoms of the anion interact with adjacent 2-aminoanilinium cations through four  $N-H\cdots O$  hydrogen bonds  $(N1-H1B\cdots O1, N2-H2C\cdots O2,$  $N3-H3B\cdots O3$  and  $N4-H4B\cdots O4$ ; Table 2) forming two  $R_2^2(9)$  motifs (Bernstein *et al.*, 1995). These asymmetric unit pairs are further linked through four  $N-H\cdots O$  hydrogen bonds  $(N1-H1A\cdots O1^{iv}, N3-H3A\cdots O3^{iii}, N2^{iii}-H2A\cdots O2$ and  $N4^{iv}-H4C\cdots O4$ ; see Table 2 for symmetry codes), forming a molecular ladder in which the cations form the uprights and the anions form the rungs, built through  $R_4^2(18)$  and two  $R_2^2(9)$  motifs, as illustrated in Fig. 4. The molecular ladder runs along the line at  $(x, \frac{1}{4}, 0)$ . Protonated atoms N2 and N4 of the cations at (x, y, z) form hydrogen bonds with acceptors O2 at  $(-x + 1, y, z - \frac{1}{2})$  and O3 at (x, y, z - 1), and with O1 at (x, y, z + 1) and O4 at  $(-x, y, z + \frac{1}{2})$ , respectively, connecting adjacent molecular ladders and hence generating an infinite two-dimensional sheet parallel to the (010) plane. The (010) molecular sheet is constructed through two  $R_4^3(13)$  motifs, two  $R_2^2(9)$  motifs and an  $R_4^4(18)$  motif.

Adjacent A and B hydrogen fumarate anions of (II) are interlinked through two O-H···O hydrogen bonds (O4A-H4A···O1B<sup>iv</sup> and and O4B-H4B···O1A; see Table 3 for details), forming a  $C_2^2(14)$  chain motif which extends further along the [101] direction, generating an infinite cationic chain (Fig. 5). The disorder found in the positions of the carboxylic acid H atoms in the cations merely reflects a reversal in the direction of propagation of the hydrogen bonds in the chains represented by Fig. 5, as a consequence of a switch of which



#### Figure 6

Part of the crystal structure of (II), showing the formation of the  $O-H\cdots O$  and  $N-H\cdots O$  hydrogen-bonded supramolecular  $R_4^4(16)$  and  $R_6^6(32)$  motifs constructing a two-dimensional brick-wall structure propagating parallel to the (010) plane. The symmetry codes are as in Table 3.

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The inversion-related (010) brick-wall structures fused together to form a two-dimensional supramolecular sheet of anions and cations extending parallel to the (010) plane, with the cations pendant from both faces, observed in (a) salt (II) and (b) salt (III). The two different colours represent the two inversion-related sheets.

side of the O···O contact each H atom is occupying. A similar type of motif is also observed in (III), as these two salts are isostructural. The molecular planes of the hydrogen fumarate anions are approximately perpendicular to one another, with angles between the planes of 87.70 (4) $^{\circ}$  for (II) and 87.64 (5) $^{\circ}$ for (III). Parallel anionic chains are crosslinked in (II) or (III) by anilinium cations through four N-H···O hydrogen bonds [for example, in (III),  $N1A - H1AC \cdots O4B^{iii}$ ,  $N1A - H1AC \cdots O4B^{$ H1AA···O3A, N1B-H1BB···O2A<sup>i</sup> and N1B-H1BC···  $O1B^{ii}$ ; see Table 3 for details], forming  $R_4^4(16)$  and  $R_6^6(32)$ motifs to construct a two-dimensional brick-wall structure propagating parallel to the (010) plane (Fig. 6). Inversionrelated two-dimensional (010) brick-wall structures are fused together through two N-H···O hydrogen bonds (N1B-H1BA···O3B and N1A-H1AB···O2B<sup>ii</sup>; Table 3) to form a molecular sheet built from a combination of  $R_4^4(16)$ ,  $R_4^4(18)$ ,  $R_5^5(25)$  and  $C_2^2(14)$  motifs and extending parallel to the ac plane. The A and B cations are pendant from both faces of the molecular network (Fig. 7a). Salt (III) (Table 4) also shows a similar two-dimensional supramolecular sheet along the (010) plane, with cations pendant from both faces of the (010) sheet (Fig. 7b).

Table 3
Hydrogen-bond geometry (Å, $^{\circ}$ ) for (II).

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - H \cdots A$
$N1B - H1BB \cdots O2A^{i}$	0.90(1)	2.01 (1)	2,8924 (14)	168 (1)
$N1A - H1AB \cdots O2B^{ii}$	0.93(1)	1.86(1)	2.7777 (15)	168(1)
$N1B - H1BC \cdots O1B^{ii}$	0.91 (1)	1.93 (1)	2.8111 (14)	165 (2)
$N1A - H1AC \cdots O4B^{iii}$	0.91 (1)	1.92 (1)	2.7993 (15)	162 (1)
$O4A - H4A \cdots O1B^{iv}$	0.85(1)	1.62 (1)	2.4703 (11)	175 (3)
$O1B - H1B \cdots O4A^{v}$	0.86(1)	1.62 (1)	2.4703 (11)	176 (3)
$N1A - H1AA \cdots O3A$	0.90(1)	1.97 (1)	2.8539 (15)	168 (1)
$N1B - H1BA \cdots O3B$	0.91 (1)	1.87 (1)	2.7757 (13)	173 (1)
$O4B - H4B \cdots O1A$	0.85(1)	1.62 (1)	2.4678 (11)	175 (3)
$O1A - H1A \cdots O4B$	0.85(1)	1.62 (1)	2.4678 (11)	176 (3)

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

# Table 4 Hydrogen-bond geometry (Å, $^\circ)$ for (III).

$D - H \cdot \cdot \cdot A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdot \cdot \cdot A$
$N1A - H1A2 \cdots O3B^{i}$	0.91 (1)	1.89(1)	2.7958 (19)	175 (3)
$N1A - H1A3 \cdots O4A^{ii}$	0.90 (1)	2.00(1)	2.8759 (19)	162 (2)
$N1B - H1B2 \cdot \cdot \cdot O3A^{ii}$	0.91 (1)	1.84 (1)	2.7354 (19)	170 (3)
$N1B - H1B3 \cdots O2A^{iii}$	0.91 (1)	2.03 (2)	2.860 (2)	153 (2)
$O2B - H2D \cdots O4A^{iv}$	0.85 (1)	1.62 (1)	2.4592 (15)	172 (6)
$N1A - H1A1 \cdots O1A$	0.91 (1)	1.83 (1)	2.7302 (18)	172 (3)
$N1B - H1B1 \cdots O1B$	0.91 (1)	1.89 (1)	2.787 (2)	173 (3)
$O2A - H2C \cdots O4B$	0.85 (1)	1.61 (1)	2.4590 (15)	175 (6)

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

The cations of salts (I), (II) and (III) are closely similar, as all three have cations which are substituted anilines with a protonated  $NH_3^+$  group. The substitution differs in each, being 2-amino in (I), 3-methyl in (II) and 4-chloro in (III). Interestingly, salts (II) and (III) show similar hydrogen-bonded supramolecular architectures, as described above. It is observed that, for (I), the anion is doubly dissociated, although the difference in the supramolecular networks can be explained by the presence of the amino group in the *ortho* position which forms additional hydrogen-bond donors with neighbouring acceptor O atoms. The methyl and chloro substitutents in (II) and (III) are nonfunctional groups and do not form hydrogen bonds with adjacent anions.

A search for fumarate salts in the Cambridge Structural Database (CSD, Version 5.31; Allen, 2002) shows some specific features. The supramolecular frameworks observed in bis(2-phenylethylammonium) fumarate fumaric acid (CSD refcode COCPEQ; Haynes & Pietersen, 2008), bis(anilinium) fumarate fumaric acid (COCPOA; Haynes & Pietersen, 2008) and benzylammonium hydrogen fumarate (XINSAO; Ballabh et al., 2002), the cations of which are closely similar to the NH<sub>3</sub><sup>+</sup> substitution, form one-dimensional anionic supramolecular chains similar to those observed in (II) and (III). The presence of the NH<sub>3</sub><sup>+</sup> group in (II) and (III) results in strong N-H···O hydrogen bonds interconnecting the anionic chains through  $R_4^4(16)$  and  $R_5^5(25)$  motifs, constructing a twodimensional sheet along with the  $C_2^2(14)$  chain. In all these structures, cations pendant from both faces of the twodimensional supramolecular network are observed, as in (II) and (III). Also, bis(2-cyanoethylammonium) fumarate (CSD refcode JIZJUX; Fawcett et al., 1991) and bis(isopropylammonium) fumarate (NARDIT: Hosomi et al., 1998), though they exhibit  $NH_3^+$  substitution, do not follow the supramolecular pattern observed in the above structures. Obviously, JIZJUX and NARDIT have a fumarate dianion and the cations are different from those in the structures discussed above. A search for previously reported structures of dianionic fumarate salts shows that most of the fumarate dianions are situated over a crystallographic centre of inversion. However, the anion of (I) is not constrained to a crystallographic inversion centre as the structure was resolved in a noncentrosymmetric space group. Only one structure, namely bis[cis-(4S,5R)-4,5-diethyl-2-iminio-1,3-selenazolidine] fumarate (YAHQOO; Ueda et al., 2005), was found to crystallize in a noncentrosymmetric space group with a fumarate dianion. The CSD search does not show any close similarities between the supramolecular structures of that compound and (I).

It is of interest to note that, in fumarate salts with a dianion, a heterocyclic amine with a substituted NH<sub>2</sub> group in the *ortho* position is the most common category of cation. It is observed that the NH<sub>2</sub> group and the ring NH<sup>+</sup> group form strong hydrogen bonds with both  $-COO^-$  groups of the anion, constructing a ring motif of the type  $R_2^2(8)$ , whereas in (I) the anions and cations form an  $R_2^2(9)$  motif. From the above discussions it is to be concluded that, in salts, the formation of a hydrogen-bonded supramolecular network relies strongly on the choice of cation in fumarate and hydrogen fumarate salts.

The authors thank Dr Babu Varghese, Senior Scientific Officer I, and the SAIF, IIT Madras, for helping with the data collection.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: UK3068). Services for accessing these data are described at the back of the journal.