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2,5-Dicarboxyanilinium chloride monohydrate

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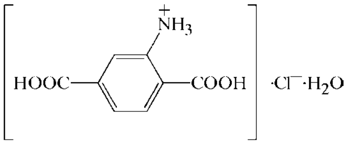
The title compound, $C_8H_8NO_4{}^+\cdot Cl^-\cdot H_2O$, is the chlorohydrated form of 2-aminobenzene-1,4-dicarboxylic acid, the basic crystal structure of which is still not known. Molecules are linked by classical N—H···O, O—H···O, N—H···Cl and O—H···Cl hydrogen bonds, mainly along the molecular plane, into sheets built by unusual $R_6^4(26)$, $R_6^4(22)$ and $R_4^3(22)$ rings. The stacking between layers is stabilized by another N—H···Cl hydrogen bond and by π–π interactions between aromatic rings facing each other.

Comment

It is known that several aromatic species with functional groups develop specific intermolecular interactions, providing tectons (specific building blocks; Hosseini, 2003) suitable for crystal engineering. In particular, aromatic carboxylic acid (Biradha *et al.*, 1998; Ferguson *et al.*, 1998; Félix *et al.*, 2000) and amino groups (Bensemann *et al.*, 2003; Karle *et al.*, 2003) can act as hydrogen-bond donors and acceptors, keeping the direction of the hydrogen bonds approximately along the molecular plane. Often, the flat extension of such hydrogen-bond interactions leads to one-dimensional supramolecular tapes or two-dimensional supramolecular layers (Russell & Ward, 1996), whereas π–π stacking interactions will link layers into a three-dimensional framework (Glidewell *et al.*, 2004). These substrates are widely harnessed in the design of functional organic solids, and also in the building of metal–organic scaffolds with specific properties (Shi *et al.*, 2005; Arora & Pedireddi, 2003). 2-Aminobenzene-1,4-dicarboxylic acid (2-aminoterephthalic acid, 2aTPT) is well known as a ligand for metal–organic frameworks (MOFs) for systematic structural design, with possible applications in methane storage (Eddaoudi *et al.*, 2002). Because of its interesting functional groups, in order to extend the π-conjugated system we have



(I)

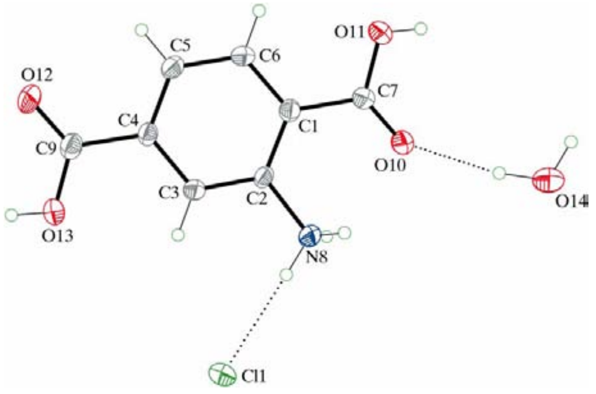


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dotted lines indicate hydrogen bonds.

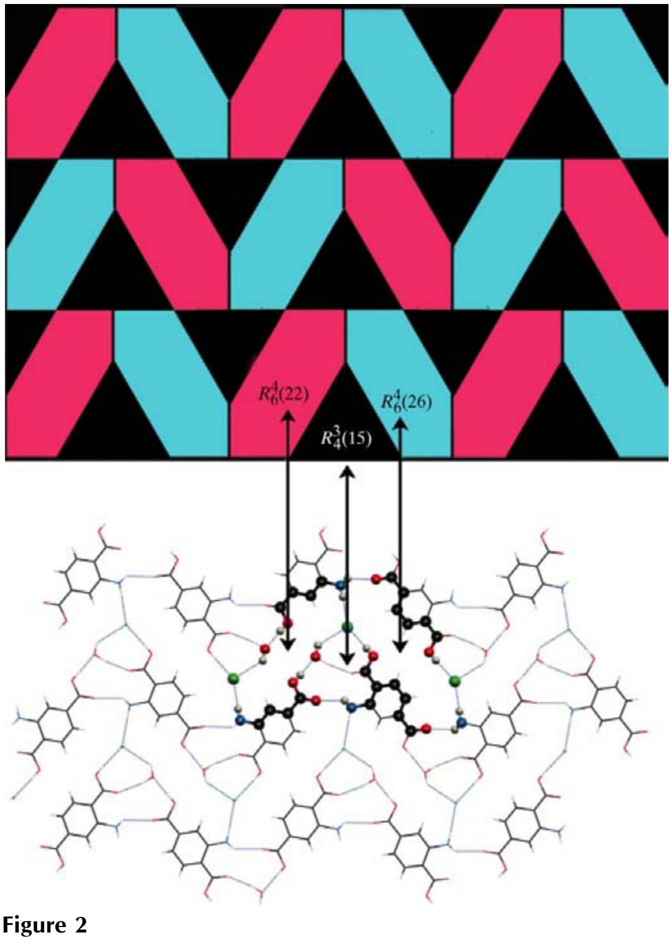


Figure 2
A perpendicular view of the (201) crystallographic plane covered by $R_6^4(26)$, $R_6^4(22)$ and $R_4^3(15)$ rings, whose disposition is shown also in the schematic representation. Dotted lines indicate hydrogen bonds.

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obtained the corresponding salicylideneimine by a condensation reaction (unpublished data). Starting from simple structural reports concerning directional intermolecular interactions (Bruno *et al.*, 2004), we decided to move on to the study of chlorohydrated 2aTPT, (I), since suitable crystals were obtained from water–methanol solutions.

Compound (I) crystallizes in the $P2_1/c$ space group. The asymmetric unit contains one 2,5-dicarboxyanilinium cation, a Cl^- counter-ion and a water molecule. The aromatic cation presents a planar conformation [maximum deviation from the mean molecular plane for atom O2 of 0.108 (5) Å; see also geometric parameters in Table 1].

The crystal packing of (I) is mainly stabilized by classical hydrogen bonds involving the water molecule and the Cl^- anion (Table 2). As the O—H and N—H groups are hydrogen-bond donors along the molecular plane, linked to coplanar acceptors, the development of a corrugated supramolecular layer is observed. In this bidimensional array lying roughly along the (201) crystallographic plane, several repeating ring units, determined by the above-mentioned hydrogen bonds, can be distinguished. The surface is covered by two centrosymmetric hexagon-shaped units, with graph-set motifs (Bernstein *et al.*, 1995) of $R_6^4(26)$ and $R_6^4(22)$, and by a triangular ring, with graph-set $R_4^3(15)$ (Fig. 2). Along the perpendicular direction, the undulating sheets are stacked by a vertical hydrogen bond [$N8\cdots Cl1^{i}$ = 3.229 (3) Å, $H8C\cdots Cl1^{i}$ = 2.35 Å and $N8—H8C\cdots Cl1^{i}$ = 167°; symmetry code: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$] and also by π–π interactions; the distance between close aromatic rings facing each other is 3.374 Å.

Experimental

2aTPT (4 mg) was dissolved in hot methanol (5 ml) and then 1 *M* aqueous hydrochloric acid (35 µl) was added. Brown crystals of (I) suitable for X-ray analysis were obtained after slow evaporation of the resulting mixture.

Crystal data

$C_8H_8NO_4^+\cdot Cl^-\cdot H_2O$
M_r = 235.62
Monoclinic, $P2_1/c$
a = 6.5170 (10) Å
b = 16.670 (3) Å
c = 9.560 (2) Å
β = 108.69 (2)°
V = 983.8 (3) Å^3
Z = 4
D_x = 1.591 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.39 mm^{-1}
T = 298 (2) K
Irregular, brown
0.40 × 0.19 × 0.11 mm

Data collection

Bruker *P*3 diffractometer
ω/2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.860, $T_{\max}$ = 0.962
2395 measured reflections
1741 independent reflections
1155 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.024
$\theta_{\max}$ = 25.1°
1 standard reflection every 50 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.117
S = 1.03
1743 reflections
140 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.3568P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.008
$\Delta\rho_{\max}$ = 0.25 e Å^{-3}
$\Delta\rho_{\min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C7—O10	1.214 (3)	C9—O12	1.211 (3)
C7—O11	1.318 (3)	C9—O13	1.315 (4)
C2—C1—C7—O10	7.5 (5)	C5—C4—C9—O12	−0.1 (4)
C6—C1—C7—O10	−169.0 (3)	C3—C4—C9—O12	−179.7 (3)
C2—C1—C7—O11	−174.1 (3)	C5—C4—C9—O13	179.9 (3)
C6—C1—C7—O11	9.4 (4)	C3—C4—C9—O13	0.3 (4)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N8—H8$A\cdots$Cl1	0.89	2.3	3.186 (3)	171
N8—H8$B\cdots$O12^{i}	0.89	2.16	2.720 (3)	120
N8—H8$C\cdots$Cl1^{ii}	0.89	2.35	3.229 (3)	168
O11—H11$\cdots$Cl1^{iii}	0.82	2.19	3.002 (2)	173
O13—H13$\cdots$O14^{iv}	0.82	1.78	2.600 (3)	173

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

H atoms were located in a difference Fourier map and placed in idealized positions using the riding-model technique, with C—H = 0.93 Å, N—H = 0.89 Å and O—H = 0.82 Å, and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C) or $1.5U_{\rm eq}$(N,O). The best refinement was obtained with the ψ-scan (North *et al.*, 1968) absorption correction performed by *XSCANS* (Siemens, 1989).

Data collection: *P3/V* (Bruker, 1989); cell refinement: *P3/V*; data reduction: *XDISK* (Bruker, 1989); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1997); software used to prepare material for publication: *PARST97* (Nardelli, 1995) and *WinGX-PC* (Version 1.6.4.05; Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3013). Services for accessing these data are described at the back of the journal.

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