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Two-dimensional hydrogen-bonded arrays in *p*-phenylazoanilinium oxalate

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Key indicators

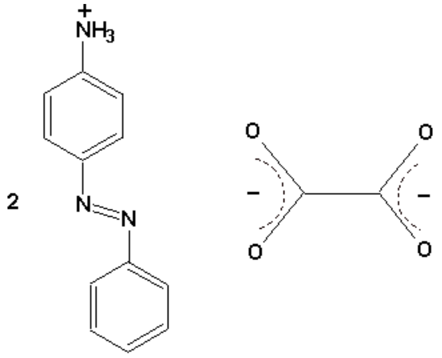
Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.002 Å
R factor = 0.041
wR factor = 0.129
Data-to-parameter ratio = 16.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $2C_6H_5N{=}NC_6H_4NH_3^+\cdot C_2O_4^{2-}$ or $2C_{12}H_{12}N_3^+\cdot C_2O_4^{2-}$, *p*-phenylazoaniline is protonated at the amine site to form an organic ammonium cation, and oxalic acid is deprotonated forming an oxalate dianion. The latter occupies a special position at the inversion centre. The structure exhibits a layered hydrogen-bonded framework built up by N—H···O hydrogen bonds.

Comment

Carboxylic acids have been widely used as pattern-controlling functional groups for rational design of organic solids (Desiraju, 1989; Melendez & Hamilton, 1998). Oxalic acid is a dicarboxylic acid which has been of interest in fundamental research and industrial applications. It can be deprotonated to form hydrogenoxalate or oxalate anions as two species in solution and the solid state. The oxalate ion is a bidentate ligand used in the preparation of metal complexes and inorganic salts, while hydrogenoxalate is the dominant form in the organic salts of oxalic acid. Data mining in the Cambridge Structural Database (Allen & Kennard, 1993; CSD Version 5.21, updated April 2001 with 233218 entries) for the structures of organic salts comprising hydrogenoxalate and oxalate ions shows that there are some reports which can be used to understand the packing patterns and utilize them in the context of crystal engineering. For instance, in the structure of methylammonium hydrogenoxalate (Thomas, 1975), hydrogen bonding is a complex three-dimensional network, while for anilinium hydrogenoxalate monohydrate (Paixão *et al.*, 2000), a two-dimensional hydrogen-bonded network is formed from a bilayer of alternating cations and anions, and water molecules are sandwiched between the bilayers. A series of diammonium salts of oxalic acid, with the general formula $H_3N(CH_2)_nNH_3^{2+}\cdot 2HC_2O_4^-.H_2O$, where n = 2, 3, 4 and 6, have been reported (Babu *et al.*, 1998; Barnes *et al.*, 1998; Vijayalakshmi & Srinivasan, 1983), in which hydrogenoxalate anions



(I)

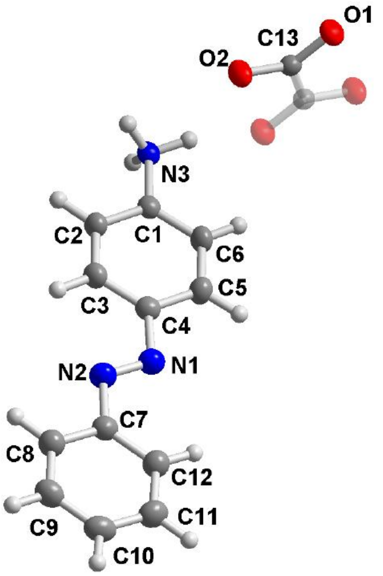


Figure 1
The molecular structure of (I) showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level. The symmetry-dependent part of the oxalate ion is shown by semi-transparent colors and is not labeled.

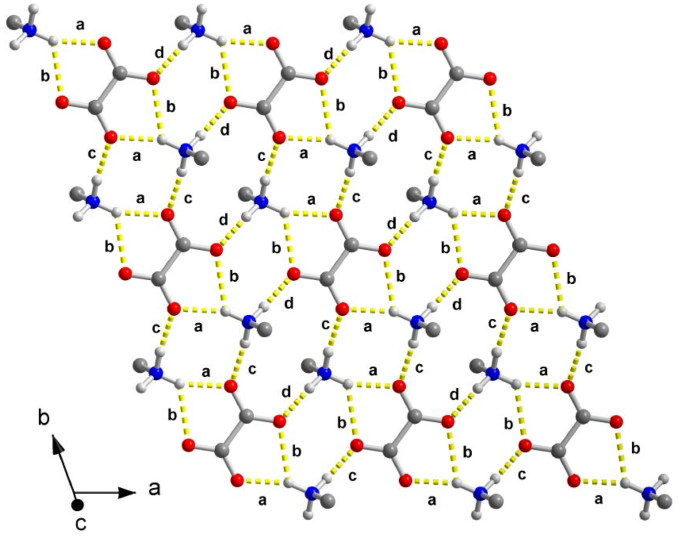


Figure 3
Representation of the hydrogen-bonding pattern in the structure of (I). Only α-C atoms are shown for clarity. A label is assigned to each hydrogen bond (see Table 2).

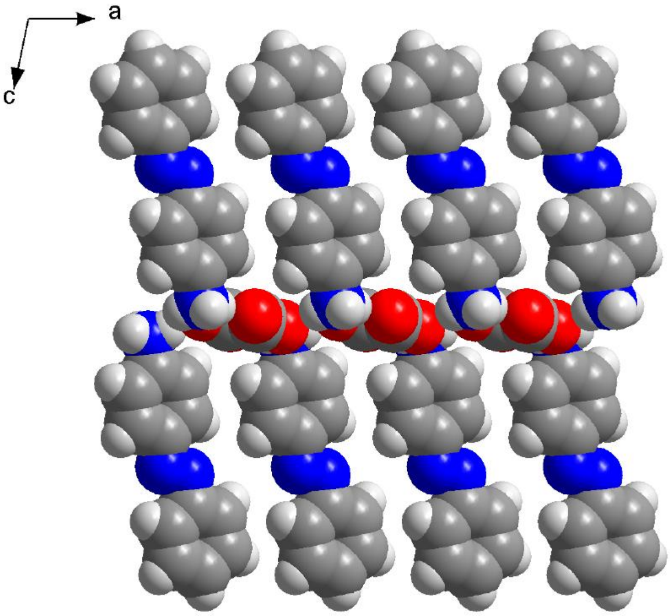


Figure 2
A space-filling representation of a hydrogen-bonded sheet in the crystal structure of (I). Aromatic tails are pointing out from the layer.

are involved in hydrogen bonds with organic ammonium cations. The packing of the homologue with n = 2, ethylenediammonium bis(monohydrogenoxalate) monohydrate (Barnes *et al.*, 1998), is unique in this series since it exhibits pillared–layered hydrogen-bonded arrays, in which water molecules are sandwiched between the bilayer sheets.

Here, we report the crystal structure of bis(p-phenylazoanilinium) oxalate, (I). This compound crystallizes in the triclinic system with space group $P\overline{1}$ (No. 2). The asymmetric unit consists of an independent organic ammonium cation and a half of an oxalate anion since it lies at a center of symmetry (see Fig. 1). They are linked together by N—H···O hydrogen bonds forming sheets parallel to the *ab* plane, as shown in Fig. 2. The p-phenylazoaniline molecules are protonated at the amine site forming ammonium cations which act as hydrogen-bond donors. There is no sign of protonation of azo groups or their participation in hydrogen bonding similar to that found in the crystal structure of p-phenylazoanilinium phenylphosphonate (Mahmoudkhani & Langer, 2001). This behavior of the organic cation is different from what is found in the crystal structure of p-phenylazoaniline hydrochloride, where protonation occurs at the azo group. Oxalic acid, on the other hand, is deprotonated to form an organic dianion which acts as the acceptor of hydrogen bonds.

The hydrogen-bonding pattern is presented in Fig. 3. For its analysis, we used the graph-set methodology of Bernstein *et al.* (1995) and Grell *et al.* (1999).

Although the first-level graph set contains only D descriptors, the second-level graph set comprises several motifs including $C^2_2(6)$, $C^2_2(7)$, $D^2_2(6)$, $R^2_1(5)$, $R^2_4(8)$, $R^4_2(8)$, $R^4_4(12)$ and $R^4_4(14)$. The assignment of graph-set descriptors were performed using the *PLUTO* program, as described by Motherwell *et al.* (1999). The N3 atom acts as a donor of N—H···O bifurcated hydrogen bonds to the O1 and O2 atoms, or *a* and *b* hydrogen bonds according to Table 2, forming a $R^2_1(5)$ ring motif. The O1 and O2 atoms act as bifurcated acceptors of hydrogen bonds. A pair of ammonium cations are linked together *via* N—H···O hydrogen bonds with the O1 or O2 atoms (*a* and *c* hydrogen bonds), forming $R^2_4(8)$ ring motifs. An $R^4_4(12)$ motif is also formed by hydrogen bonding of two cations and two anions (*c* and *d* hydrogen bonds). The arrangement of supramolecular motifs, including rings, provides a two-dimensional hydrogen-bonded network in the crystal structure of the title compound.

Experimental

Compound (I) was prepared by the reaction of oxalic acid and *p*-phenylazoaniline in ethanol and subsequent reflux for about 1 h. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the solution over a period of a few days.

Crystal data

$2C_{12}H_{12}N_3^+ \cdot C_2O_4^{2-}$
$M_r = 484.51$
Triclinic, $P\overline{1}$
$a = 6.4875$ (1) Å
$b = 7.0151$ (1) Å
$c = 14.2991$ (1) Å
$\alpha = 92.044$ (1)°
$\beta = 100.045$ (1)°
$\gamma = 112.955$ (1)°
$V = 586.169$ (13) Å^3

$Z = 1$
$D_x = 1.373$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5443 reflections
$\theta = 1$–30°
$\mu = 0.10$ mm^{-1}
$T = 297$ (2) K
Needle, yellow–orange
1.00 × 0.50 × 0.25 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.910$, $T_{\max} = 0.976$
7891 measured reflections

3499 independent reflections
2858 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.023$
$\theta_{\max} = 30.5°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.129$
$S = 1.04$
3499 reflections
211 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0677P)^2 + 0.0807P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C13	1.2571 (11)	O2—C13	1.2494 (11)
N1—N2	1.2487 (13)	N2—C7	1.4306 (14)
N1—C4	1.4359 (13)	C13—C13$^{\text{i}}$	1.5698 (17)
C1—N3	1.4645 (12)		
N2—N1—C4	113.51 (9)	O2—C13—C13$^{\text{i}}$	116.66 (10)
N1—N2—C7	114.92 (9)	O1—C13—C13$^{\text{i}}$	116.66 (9)
O2—C13—O1	126.67 (8)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
(*a*) N3—H31···O1	0.93 (1)	1.95 (1)	2.8325 (15)	158.0 (14)
(*b*) N3—H31···O2$^{\text{i}}$	0.93 (1)	2.33 (1)	2.9520 (12)	124.4 (12)
(*c*) N3—H32···O1$^{\text{ii}}$	0.91 (1)	1.89 (1)	2.7939 (11)	172.0 (12)
(*d*) N3—H33···O2$^{\text{iii}}$	0.90 (1)	1.88 (1)	2.7654 (11)	175.3 (15)
(*e*)C2—H2···O1$^{\text{iii}}$	1.02 (1)	2.52 (1)	3.4620 (13)	153.3 (12)

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

The (N—)H atoms were located from a difference Fourier map and refined isotropically with a restrained bond distance of 0.87 Å; other H atoms were placed in idealized positions and refined in the isotropic approximation (N—H = 0.90–0.93 Å and C—H = 0.96–1.02 Å).

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000).

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