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Key indicators

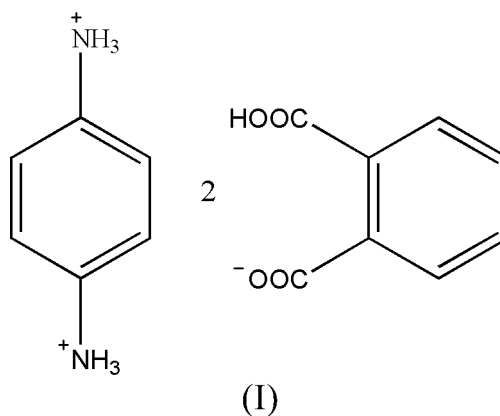
Single-crystal X-ray study
 $T = 153$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.032
 wR factor = 0.096
Data-to-parameter ratio = 14.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.1,4-Phenylenediammonium bis(hydrogen
phthalate)

The title compound, $\text{C}_6\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{C}_8\text{H}_5\text{O}_4^-$, is a proton-transfer compound obtained from 1,4-phenylenediamine and phthalic acid. The asymmetric unit contains half of a centrosymmetric cation and an anion. A strong intramolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond is found in the anion. The cations and anions are linked through a number of intermolecular $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, forming a three-dimensional network.

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Comment

Phthalic acid (PA) has frequently been selected for the preparation of crystalline adducts (Jin *et al.*, 2000, 2001, 2003; Janczak & Perpetuo, 2001; Pereira Silva *et al.*, 2006; Smith *et al.*, 1995, 1997). Hydrogen phthalates can crystallize with different hydrogen-bonding motifs, even in the presence of the same cation; this suggests that there is a small difference between the free energy of the two main hydrogen-bonding motifs (Langkilde *et al.*, 2004), *viz.* intra- or intermolecular carboxyl hydrogen bonds. Structures containing 1,4-phenylenediaminium (PDAM) have been reported recently, (Smith *et al.*, 2005; Wang, 2006). In these structures, both N atoms in PDAM were protonated, which is unusual considering that the second amine group is relatively acidic, $\text{p}K_{\text{a}1,2} = 2.67$ and 6.60 (Smith *et al.*, 2005). As a continuation of our research characterizing the hydrogen-bonding patterns of these compounds, the title compound, (I), was obtained from the reaction of PA with 1,4-phenyldiamine (PDA) in a 1:1 ethanol–water solution, and its crystal structure determined.



The structure of (I), Fig. 1, comprises a PDAM dication, disposed about a centre of inversion, and a PAH anion. As in other structures containing PDAM (Smith *et al.*, 2005; Wang 2006), both N atoms in (I) are protonated. An intramolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond is found in the anion (Table 2). The

C—O bond distances (Table 1) indicate that these groups have similar electronic structures, consistent with the almost equivalent sharing of the H₂O atom between atoms O2 and O3.

The crystal structure of (I) is characterized by extensive hydrogen bonding involving all available H-atom donors and acceptors (Table 2), which results in a three-dimensional structure.

Experimental

Compound (I) was prepared by heating PDA (1 mmol) and PA (2 mmol) in 50% ethanol–water (70 ml) for 10 min under reflux. After concentration to approximately 25 ml, partial room-temperature evaporation of the hot-filtered solution gave large red prisms of (I).

Crystal data

C ₆ H ₁₀ N ₂ ²⁺ ·2C ₈ H ₅ O ₄ ⁻	$V = 493.95(7) \text{ \AA}^3$
$M_r = 440.40$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.481 \text{ Mg m}^{-3}$
$a = 8.0828(6) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.2286(7) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 9.4515(8) \text{ \AA}$	$T = 153(2) \text{ K}$
$\alpha = 92.442(3)^\circ$	Prism, red
$\beta = 114.897(2)^\circ$	$0.51 \times 0.37 \times 0.30 \text{ mm}$
$\gamma = 115.694(2)^\circ$	

Data collection

Rigaku R-Axis RAPID diffractometer	2248 independent reflections
ω scans	2078 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.013$
4890 measured reflections	$\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.061P)^2 + 0.1408P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.096$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
2248 reflections	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$
151 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.035 (8)

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—C1	1.2304 (12)	N—C9	1.4608 (11)
O2—C1	1.2935 (12)	C1—C2	1.5153 (13)
O3—C8	1.2817 (13)	C7—C8	1.5189 (13)
O4—C8	1.2369 (13)		
O1—C1—O2	120.02 (9)	O3—C8—C7	119.60 (9)
O1—C1—C2	119.45 (9)	C11 ⁱ —C9—C10	121.61 (9)
O2—C1—C2	120.50 (9)	C11 ⁱ —C9—N	119.28 (8)
O4—C8—O3	122.49 (9)	C10—C9—N	119.11 (8)
O4—C8—C7	117.79 (9)		

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

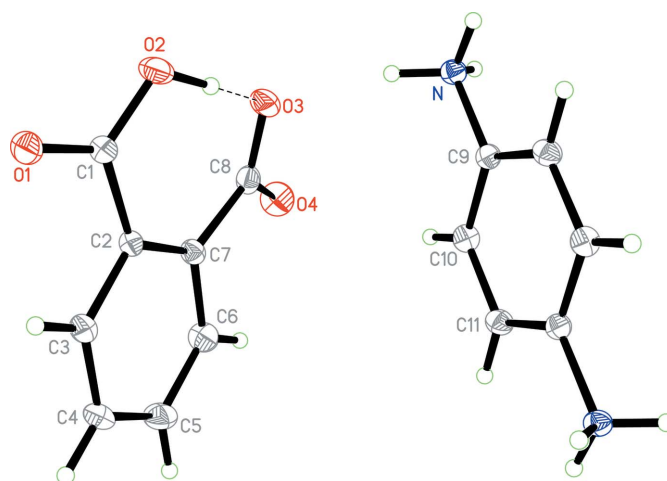


Figure 1

The molecular structure of (I), showing the atom-labelling scheme and displacement ellipsoids drawn at the 40% probability level. The PDAM cation is located about a centre of inversion with the second half of the molecule related by $(1 - x, 1 - y, 2 - z)$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2O \cdots O3	1.07 (2)	1.34 (2)	2.4081 (11)	174 (2)
N—H0A \cdots O1 ⁱⁱ	0.91	1.86	2.7654 (11)	170
N—H0B \cdots O3	0.91	1.92	2.8032 (11)	165
N—H0C \cdots O4 ⁱⁱⁱ	0.91	1.84	2.7278 (11)	163

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

The hydroxyl H atom was refined without constraints. The remaining H atoms were included in the riding-model approximation, with C—H = 0.95 \AA and N—H = 0.91 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$.

Data collection: *RAPID-AUTO* (Rigaku 2004); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sieens, 1994); software used to prepare material for publication: *SHELXTL*.

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