Three Crystal Structures of Terephthalic Acid Salts of Simple Amines

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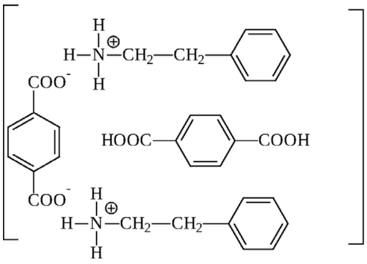
Diphenethylamine forms two adducts (1 : 1, **1a** and 2 : 1, **1b**) with terephthalic acid (H_2TPA). The former is bis(diphenethylammonium)$H_2TPA \cdot TPA^{2-}$ and the latter is bis(diphenethylammonium)$\cdot TPA^{2-}$. The amine *cis*-2,6-dimethylpiperidine forms a hydrated 2 : 1 adduct, bis(2,6-dimethylpiperidinium)$\cdot TPA^{2-} \cdot H_2O$ (**2**). The crystal structures of all three compounds were determined. All H_2TPA and TPA^{2-} residues display inversion symmetry, while the water oxygen atom of **2** lies on a twofold axis. Packing analyses have identified some supramolecular synthons known from related structures.

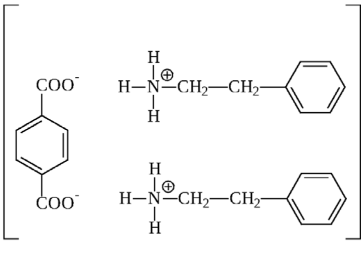
Key words: Terephthalic Acid Salts, Amines, Solid-state Structure, Hydrogen Bonds

Introduction

Terephthalic acid (H_2TPA) is a dibasic acid that is known to form a variety of adducts with simple amines. In principle various kinds of adducts are feasible, and the following cases are known: (i) there is no proton transfer, and the adduct consists of neutral molecules; (ii) alternatively and much more commonly, 2 : 1 salts may be formed with protonated amines and the dianion of the acid (TPA^{2-}); (iii) 1 : 1 salts may be formed with the monoanion of the acid ($HTPA^-$). Hydrates or other solvates are also known. The residues are linked by classical hydrogen bonds, typically N–H$\cdots$O or O–H$\cdots$N. A search of the Cambridge Database [1] provided the following examples of structurally characterized adducts (note that we have subjectively excluded some adducts of diamines, less simple amines and other multifunctional organic molecules): dimethylammonium $HTPA^-$ [2], in which the non-dissociated proton is disordered over both termini of the anion; ammonium $HTPA^-$ [3], which also suffers from disorder of the non-dissociated proton, and for which the space group assignment is ambiguous; bis(dimethylammonium) TPA^{2-} [4]; bis(imidazolium) TPA^{2-} [5]; bis(2-methylimidazolium) bis(2-methylimidazole) TPA^{2-} tetrahydrate [6]; piperazinium(2+) TPA^{2-} [7]; bis(dicyclohexylammonium) TPA^{2-} [8]; bis(*tert*-amylammonium) TPA^{2-} [9]; bis(2-aminopyridinium) TPA^{2-} [10] and its 1 : 1 neutral molecule counterpart [11]; bis(5-methyl-2-aminopyridinium) TPA^{2-} [10]. The analysis of hydrogen bonding patterns has been very variable in extent, ranging from bald statements of the kind ”the residues are connected to form a 3D network by hydrogen bonds” to detailed analyses [8 – 10] of supramolecular synthons.



1a

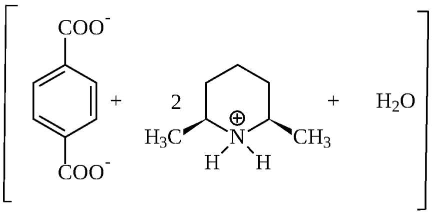


1b

Table 1. Hydrogen bonds (Å, deg) for compounds **1a**, **1b** and **2**.[a]

Compound	H bond no.	D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠ DHA)
1a[b]	*1a*	N–H(01)···O(4)	0.943(16)	1.973(16)	2.9007(11)	167.7(13)
	1b	N–H(01)···O(3)	0.943(16)	2.349(16)	3.0477(12)	130.6(12)
	2a	N–H(02)···O(3)$^{\#1}$	0.885(15)	2.435(14)	2.9950(12)	121.6(11)
	2b	N–H(02)···O(2)$^{\#1}$	0.885(15)	2.094(15)	2.9050(12)	151.8(13)
	3	N–H(03)···O(4)$^{\#2}$	0.928(14)	1.874(14)	2.7811(11)	165.2(12)
	4	O(1)–H(04)···O(3)	0.916(18)	1.639(19)	2.5443(11)	169.0(16)
	5	C(7)–H(7B)···O(2)$^{\#1}$	0.99	2.54	3.3042(14)	133.4
	6	C(8)–H(8A)···O(4)$^{\#3}$	0.99	2.60	3.5476(13)	160.2
1b[c]	*1*	N–H(01)···O(1)$^{\#1}$	0.930(19)	1.86(2)	2.7890(16)	176.2(16)
	2	N–H(02)···O(2)$^{\#2}$	0.94(2)	1.86(2)	2.7800(15)	163.6(16)
	3	N–H(03)···O(1)	0.926(19)	1.915(19)	2.8367(15)	172.9(16)
	4	C(8)–H(8B)···O(2)$^{\#4}$	0.99	2.39	3.3025(17)	152.8
	5	C(5)–H(5)···O(1)$^{\#3}$	0.95	2.56	3.3892(18)	145.6
	6	C(7)–H(7B)···O(2)$^{\#2}$	0.99	2.53	3.2338(17)	128.1
2[d]	*1*	N–H(01)···O(2)	0.925(12)	1.836(12)	2.7520(14)	170.2(12)
	2	N–H(02)···O(1)$^{\#2}$	0.965(11)	1.758(12)	2.7070(13)	167.0(12)
	3	O(1W)–H(03)···O(2)	0.878(15)	1.943(15)	2.8182(12)	174.4(16)
	4	C(11)–H(11C)···O(1)$^{\#2}$	0.98	2.65	3.3563(15)	129.2
	5	C(10)–H(10B)···O(1W)$^{\#2}$	0.98	2.61	3.5264(17)	154.9
	6	C(10)–H(10C)···O(1)	0.98	2.51	3.4037(17)	151.1

[a] C–H···O interactions are generally lower in the interaction hierarchy than classical hydrogen bonds. They are (with some exceptions) included only for completeness and are not discussed further. C–H distances are not normalized; [b] symmetry transformations used to generate equivalent atoms: $^{\#1}$ $x, y+1, z$; $^{\#2}$ $-x, y+1/2, -z+3/2$; $^{\#3}$ $-x, y-1/2, -z+3/2$; [c] symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+3/2, y, z+1/2$; $^{\#2}$ $-x+3/2, -y+3/2, z$; $^{\#3}$ $-x+1, -y+1, -z+1$; $^{\#4}$ $-x+3/2, y, z-1/2$; [d] symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+1, -y+1, -z+1$; $^{\#2}$ $x, y+1, z$.



2

In the course of experiments to investigate the solubility of terephthalic acid adducts with different amines we obtained from aqueous solutions several salts of this acid with a wide ranges of amines. Here we present three examples for which we have determined the crystal structures, which are discussed in detail below.

With phenethylamine, we obtained the typical 2 : 1 salt **1b** but also the 1 : 1 salt **1a**, which consists of two phenethylammonium cations, one H_2TPA molecule and one TPA^{2-} ion. The combustion analysis data of this salt was in agreement with expectation.

The amine 2,6-dimethylpiperazine (as the achiral *cis*-isomer) provided the typical 2 : 1 salt, albeit as a hydrate **2**.

Finally, we have redetermined the known structure of bis(dicyclohexylammonium) TPA^{2-} (see footnote to ref. [8]), which we mention briefly.

Results and Discussion

The asymmetric units of compounds **1a**, **1b** and **2**, extended by symmetry to avoid showing half residues, are shown in Figs. 1 – 3, respectively. The special symmetries are as follows: **1a**, one cation with general

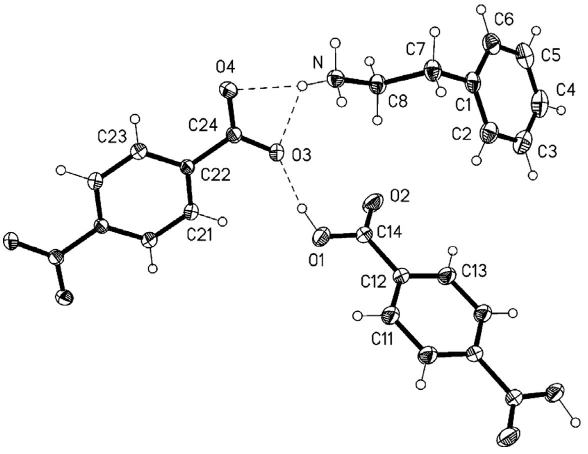


Fig. 1. Structure of compound **1a** in the crystal. Ellipsoids represent 50 % probability levels. The "half" residues of H_2TPA and TPA^{2-} have been extended by symmetry; this Figure does not correspond to the overall stoichiometry of **1a**. Hydrogen bonds are indicated by dashed lines.

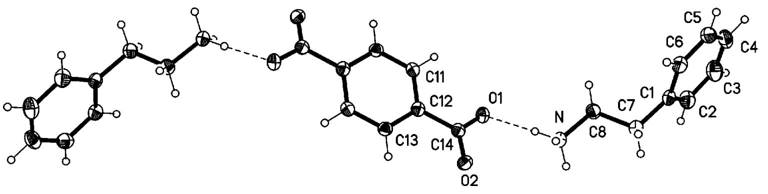


Fig. 2. Structure of compound **1b** in the crystal. Ellipsoids represent 50 % probability levels. The second half of the TPA^{2-} residue and the second cation have been generated by symmetry. Hydrogen bonds are indicated by dashed lines.

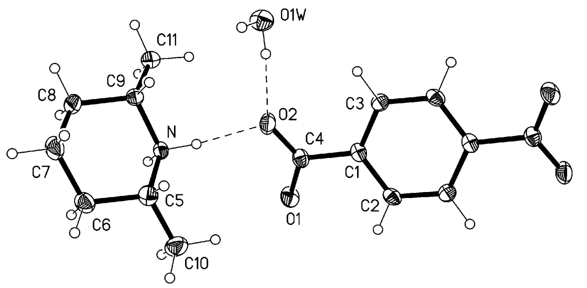


Fig. 3. Structure of compound **2** in the crystal. Ellipsoids represent 50 % probability levels. The "half" residues of TPA^{2-} and water have been extended by symmetry; this Figure does not correspond to the overall stoichiometry of **2**. Hydrogen bonds are indicated by dashed lines.

symmetry, one H_2TPA and one TPA^{2-} residue each with $\bar{1}$ symmetry; **1b**, one cation with general symmetry, one TPA^{2-} residue with $\bar{1}$ symmetry; **2**, one cation with general symmetry, one TPA^{2-} residue with $\bar{1}$ symmetry, one water molecule with twofold symmetry.

The acid H_2TPA and its anions are not necessarily planar; the interplanar angles between the ring planes and the carboxlic acid or carboxylate planes vary between *ca.* 0° and 35°, mean 13°, in 294 database [1] hits for the combination "TPA + N–H". Values for the structures presented here are: **1a**, anion 7°, acid 2°; **1b**, 15°; **2**, 20°.

The C–O bond lengths for the H_2TPA residue in **1a** are consistent with the formal bond orders. For all anionic carboxylate groups the C–O bond lengths are approximately equal, but are consistently slightly longer for those groups accepting more classical H bonds: **1b**, C–O1 1.271, C–O2 1.252 Å (2 and 1 H bonds, respectively); **2**, C–O1 1.251, C–O2 1.258 Å (both 1 H bond). For **1a**, the three-center H bonds make such a simple analysis impossible. For all compounds, e. s. d.'s are 0.001 – 0.002 Å.

Table 1 shows the hydrogen bonds for all compounds; they are numbered for ease of identification. The packing of **1a** involves a three-dimensional network of hydrogen bonds, but these are easily analyzed into two separate patterns. All NH donors are involved in N–H···O interactions; two of these (*1a*, *1b*, *2a*, *2b* in Table 1) are three-center systems. These systems and the O–H···O interaction *4* combine to link all three independent residues to form broad ribbons parallel to

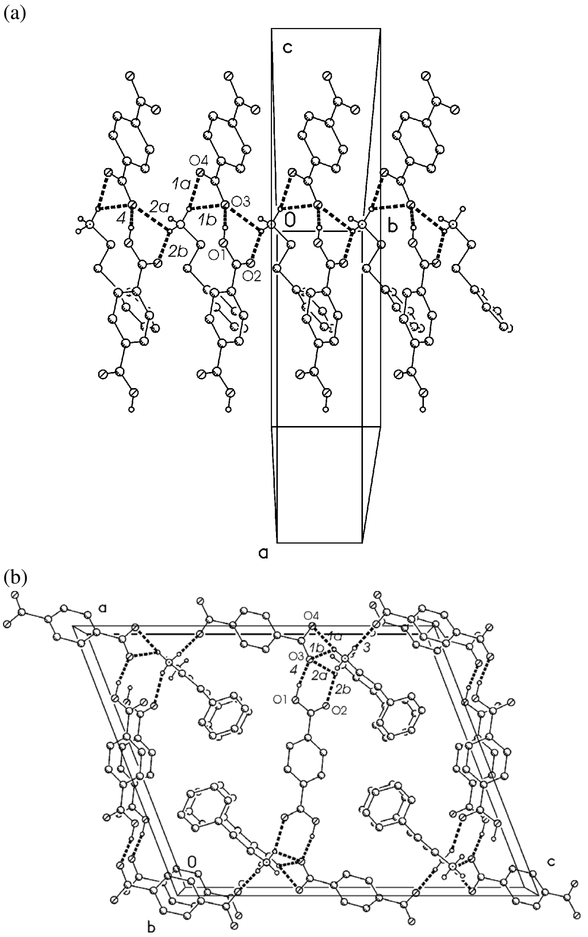


Fig. 4. (a) Packing diagram of compound **1a** viewed perpendicular to the crystallographic *xy* plane in the region $z \approx 1/4$. The upper horizontal layer of TPA residues consists of the dianions TPA^{2-} and the lower layer of undissociated H_2TPA. *General features of all packing diagrams*: Hydrogen bonds are indicated by thick dashed lines and numbered in italics. Labelled atoms do not necessarily correspond to the asymmetric unit. (b) Packing diagram of compound **1a** viewed parallel to the crystallographic *y* axis.

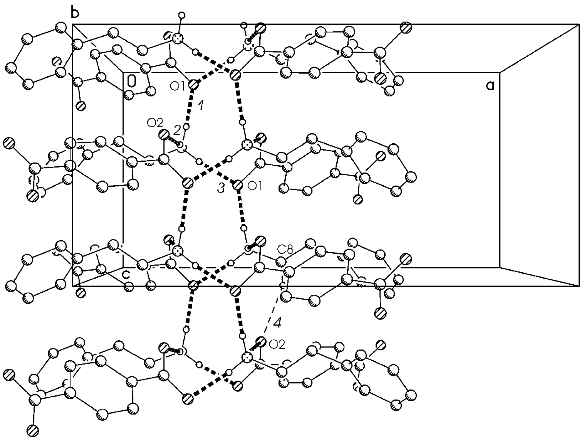


Fig. 5. Packing diagram of compound **1b** viewed parallel to the crystallographic y axis in the region x, $y \approx 1/4$. One representative C–H···O interaction (see text) is indicated by a thin dashed line.

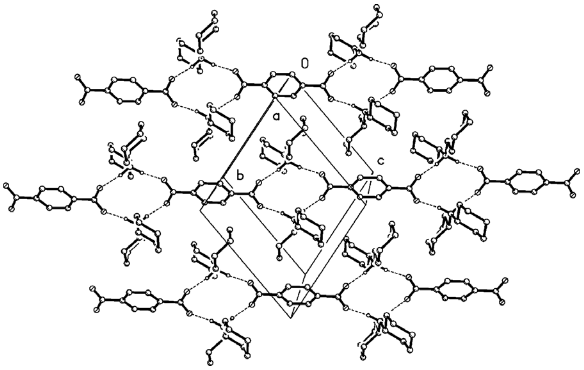


Fig. 6. Packing diagram of bis(dicyclohexylammonium) TPA^{2-} [8] showing the H-bonded rings ("synthon B"). The Figure was generated from our own structure because the published coordinates were not available.

the short y axis (Fig. 4a). These ribbons are connected in the c direction at the other end of the TPA^{2-} residue by the N–H···O contact *3* and in the a direction at the other end of the H_2TPA residue by *2b* and *4* (Fig. 4b). If one considers only the H_2TPA and TPA^{2-} residues the result is an infinite zigzag chain generated by H bond *4*, with overall direction parallel to the x axis. The same synthon was observed for the 2 : 1 : 1 adduct of trimethoprim cation × H_2TPA × TPA^{2-} [12].

In compound **2** all classical H bonds *1*–*3* are of the standard two-center form and combine to form "tubes" (Fig. 5) parallel to the z axis at x, y = $1/4$,$1/4$ and $3/4$,$3/4$. Such tubes have been identified as a standard supramolecular synthon for primary ammonium salts with carboxylates [9]. The very short C–H···O interaction *4* lies within one such "tube" arrangement.

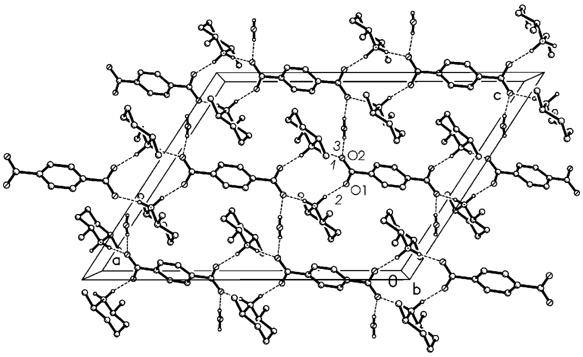


Fig. 7. Packing diagram of compound **2** viewed parallel to the crystallographic y axis. The initial impression of a layer structure is not correct, because the horizontal chains of residues are not parallel; the upper and lower chains are parallel to $[1\bar{1}0]$, whereas the central chain is parallel to $[\bar{1}10]$.

In bis(cyclohexylammonium) salts of dicarboxylic acids a further standard synthon, called "synthon B", was identified [8]. It is a ring of graph set $R_4^4(12)$ involving two carboxylate and two NH_2 groups (Fig. 6); for the TPA^{2-} salt, the rings are linked *via* the anions to form chains. The packing diagram of compound **2** (Fig. 7) also involves synthon B, again linked *via* the anions (H bonds *1* and *2*) to form chains parallel to $[1\bar{1}0]$ and $[\bar{1}10]$. The chains are crosslinked *via* the water molecules (H bond *3*).

Experimental Section

Salt **1** was prepared by refluxing a mixture of terephthalic acid and phenethylamine in the molar ratio 1 : 2 until complete dissolution of the acid was achieved. After cooling, a white precipitate had formed. For the synthesis, a molar ratio of 1 : 2 was sufficient. Typical batches were in a molar ratio of 0.05 : 0.1 (8.3 g of terephthalic acid and 16.4 g of phenethylamine). No solvent was used.

The precipitate thus obtained was crystallized in part from water (crystals **1b** were obtained) and in part from methanol (crystals **1a** were obtained). The elemental analysis of **1b** was correct; the elemental analysis for the precipitate from methanol was correct for mixed salts **1a** and **1b** in the ratio 1 : 2. Very slow recrystallization of this salt from water gave single crystals of **1b**. Very slow recrystallization of this salt from methanol gave single crystals of **1a**. The elemental analysis data from both crystallizations were similar: $C_{24}H_{28}N_2O_4$ (408.48): calcd. C 70.57, H 6.91, N 6.86; found (recryst. from H_2O) C 70.18, H 7.08, N 6.93.

1 × **1a** + 2 × **1b** ($C_{80}H_{90}N_6O_{16}$): calcd: C 69.05, H 6.52, N 6.04; found (recryst. from methanol) C 69.21, H 6.90,

	1a	**1b**	**2**
Formula	$C_{32}H_{34}N_2O_8$	$C_{24}H_{28}N_2O_4$	$C_{22}H_{38}N_2O_5$
M_r	574.62	408.48	410.54
Temperature, K	133	100	100
Crystal size, mm^3	$0.4 \times 0.3 \times 0.2$	$0.29 \times 0.07 \times 0.04$	$0.35 \times 0.15 \times 0.1$
Crystal habit	colorless tablet	colorless prism	colorless plate
Radiation; λ, Å	MoK_α; 0.71073	CuK_α; 1.54184	MoK_α; 0.71073
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$Pccn$	$C2/c$
a, Å	16.5735(15)	15.7354(6)	21.892(2)
b, Å	4.5304(5)	16.8225(6)	7.8951(5)
c, Å	20.632(2)	8.1446(3)	16.524(2)
β, deg	111.177(3)	90	123.051(12)
Volume, Å^3	1444.6(2)	2155.95(14)	2393.8(4)
Z	2	4	4
Calcd. density, g cm^3	1.321	1.258	1.139
$F(000)$, e	608	872	896
$2\theta_{\max}$, deg	61	66.85	56.6
Reflections collect./indep.	16151/4411	1893/1893	20953/2981
R_{int}	0.032	–	0.055
Completeness to 2θ	99.9 % to 60°	98.9 % to $2\theta_{\max}$	99.9 % to $2\theta_{\max}$
Number of parameters	206	148	146
$wR2$ (all refls.)	0.117	0.106	0.102
$R1$ $[I \geq 2\theta\sigma(I)]$	0.041	0.039	0.042
Goodness-of-fit on F^2	1.04	1.11	0.92
Largest diff. peak/hole, e Å^{-3}	0.44/−0.17	0.26/−0.28	0.40/−0.18

Table 2. Crystallographic data for compounds **1a**, **1b** and **2**.

N 6.81.

Salts **2** and bis(cyclohexylammonium)TPA^{2-} were prepared in a way similar to **1**. Very slow recrystallization of these salts from a mixture of methanol/acetone and methanol, respectively, gave single crystals suitable for X-ray diffraction. – IR: The bands assigned to COO$^-$ stretching are observed near 1573 (antisymmetric) and 1366 cm^{-1} (symmetric) for compounds **1a** and **1b**, and at 1618 and 1404 cm^{-1} for compound **2**.

Crystal structure determinations

Data were recorded on a Bruker SMART 1000 diffractometer (MoK_α) for **1a**, a Bruker SMART 6000 diffractometer (CuK_α, rotating anode) for **1b** and an Oxford Diffraction Xcalibur S diffractometer (MoK_α) for **2**. An absorption correction was performed for **1b** using the multi-scan method. Structures were refined using the program SHELXL-97 [13]. Hydrogen atoms were included as follows: NH and OH refined freely, rigid methyl groups, others riding. Numerical details are given in Table 2. Note that the Z values and related parameters depend on how the formula unit is defined.

Special features and exceptions: Crystals of compound **1b** were twinned by 180° rotation about the diagonal [011]. The untwinning routines merge equivalent reflections from both components; the number of measured reflections is not clearly definable.

Complete crystallographic data have been deposited at The Cambridge Crystallographic Data Centre under the numbers CCDC 718666 (**1a**), CCDC 718667 (**1b**), CCDC 718668 (**2**). Copies can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

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structure ourselves and deposited the data as CCDC 653485 (refcode VAWRIV01).

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