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 (H₂TPA). The former is bis(diphenethylammonium)H₂TPA²⁻ and the latter is bis(diphenethylammonium)-TPA²⁻. The amine cis-2,6-dimethylpiperidine forms a hydrated 2:1 adduct, bis(2,6-dimethylpiperidinium)-TPA²⁻·H₂O (2). The crystal structures of all three compounds were determined. All H₂TPA and TPA²⁻ 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 (H₂TPA) 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 (TPA²⁻); (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···O or O–H···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) TPA²⁻ [4]; bis(imidazolium) TPA²⁻ [5]; bis(methylimidazolium) bis(methylimidazole) TPA²⁻ tetrahydrate [6]; piperazinium(2+) TPA²⁻ [7]; bis(dicyclohexylammonium) TPA²⁻ [8]; bis(tert-amylammonium) TPA²⁻ [9]; bis(2-aminopyridinium) TPA²⁻ [10] and its 1:1 neutral molecule counterpart [11]; bis(5-methyl-2-aminopyridinium) TPA²⁻ [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.
Table 1. Hydrogen bonds (Å, deg) for compounds 1a, 1b and 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>H bond no.</th>
<th>D–H</th>
<th>A</th>
<th>d(D–H)</th>
<th>d(H···A)</th>
<th>d(D···A)</th>
<th>∠ DHA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1a</td>
<td>N–H(01)···O(4)</td>
<td>0.943(16)</td>
<td>1.973(16)</td>
<td>2.9007(11)</td>
<td>167.7(13)</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>1b</td>
<td>N–H(01)···O(3)</td>
<td>0.943(16)</td>
<td>2.349(16)</td>
<td>3.0477(12)</td>
<td>130.6(12)</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>2a</td>
<td>N–H(02)···O(3)</td>
<td>0.885(15)</td>
<td>2.094(15)</td>
<td>2.9505(12)</td>
<td>151.8(13)</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>2b</td>
<td>N–H(02)···O(2)#1</td>
<td>0.885(15)</td>
<td>2.094(15)</td>
<td>2.9505(12)</td>
<td>151.8(13)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>N–H(03)···O(4)#2</td>
<td>0.928(14)</td>
<td>1.874(14)</td>
<td>2.7811(11)</td>
<td>165.2(12)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>O(1)–H(04)···O(3)</td>
<td>0.916(18)</td>
<td>1.639(19)</td>
<td>2.5443(11)</td>
<td>169.0(11)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>C(7)–H(7B)···O(2)#1</td>
<td>0.99</td>
<td>2.54</td>
<td>3.5476(13)</td>
<td>160.2</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>C(8)–H(8A)···O(4)#3</td>
<td>0.99</td>
<td>2.60</td>
<td>3.5476(13)</td>
<td>160.2</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>1b</td>
<td>N–H(01)···O(1)#1</td>
<td>0.930(19)</td>
<td>1.86(2)</td>
<td>2.7890(16)</td>
<td>176.2(16)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>N–H(02)···O(2)#2</td>
<td>0.94(2)</td>
<td>1.86(2)</td>
<td>2.7800(15)</td>
<td>163.6(16)</td>
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</tr>
<tr>
<td>3</td>
<td>3</td>
<td>N–H(03)···O(1)</td>
<td>0.926(19)</td>
<td>1.915(19)</td>
<td>2.7890(16)</td>
<td>176.2(16)</td>
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<tr>
<td>4</td>
<td>4</td>
<td>C(8)–H(8B)···O(2)#2</td>
<td>0.99</td>
<td>2.53</td>
<td>3.3238(17)</td>
<td>128.1</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>C(10)–H(10B)···O(1)#1</td>
<td>0.98</td>
<td>2.61</td>
<td>3.3238(17)</td>
<td>128.1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>C(10)–H(10C)···O(1)</td>
<td>0.98</td>
<td>2.61</td>
<td>3.3238(17)</td>
<td>128.1</td>
<td></td>
</tr>
</tbody>
</table>

* 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.

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...
symmetry, one H₂TPA and one TPA²⁻ residue each with 1 symmetry; 1b, one cation with general symmetry, one TPA²⁻ residue with 1 symmetry; 2, one cation with general symmetry, one TPA²⁻ residue with 1 symmetry, one water molecule with twofold symmetry.

The acid H₂TPA and its anions are not necessarily planar; the interplanar angles between the ring planes and the carboxylic 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 H₂TPA 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 # combine to link all three independent residues to form broad ribbons parallel to
Three Crystal Structures of Terephthalic Acid Salts of Simple Amines

Fig. 5. Packing diagram of compound 1b viewed parallel to the crystallographic y axis in the region x, y ≈ 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$_2$TPA residue by 2b and 4 (Fig. 4b).

If one considers only the H$_2$TPA 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$_2$TPA × 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.

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 [110] and [110]. 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$_{31}$N$_2$O$_4$ (408.48); calcd: C 70.57, H 6.91, N 6.86; found (recryst. from H$_2$O) C 70.18, H 7.08, N 6.93.

1 × 1a + 2 × 1b (C$_{40}$H$_{50}$N$_6$O$_{16}$): calcd: C 69.05, H 6.52, N 6.04; found (recryst. from methanol) C 69.21, H 6.90.
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.

Crystal size, mm$^3$ 0.4 × 0.3 × 0.2 0.29 × 0.07 × 0.04 0.35 × 0.15 × 0.1

Crystal habit colorless tablet colorless prism colorless plate

Radiation; $\lambda$, Å MoK$\alpha$, 0.71073 CuK$\alpha$: 1.54184 MoK$\alpha$: 0.71073

Crystal system monoclinic orthorhombic monoclinic

Space group $P2_1/c$ $Pccn$ $C2/c$

$\alpha$, Å 16.5735(15) 15.7354(6) 21.892(2)

$\beta$, Å 20.632(2) 8.1446(3) 16.524(2)

$\gamma$, Å 111.177(3) 90 123.051(12)

Volume, Å$^3$ 1444.6(2) 2155.95(14) 2393.8(4)

Goodness-of-fit on $F^2$ 0.032 – 0.055

Special features and exceptions: Crystals of compound 1b were twinned by 180° rotation about the diagonal [011]. The untwining 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.
structure ourselves and deposited the data as CCDC 653485 (refcode VAWRIV01).


