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A Perforated Molecular Tape in the 1:1 Salt of 4,4'-Trimethylenedipyridine and 1,3,5-Benzenetricarboxylic Acid

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Abstract

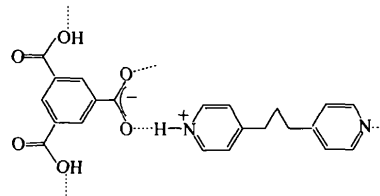
The 1:1 adduct formed between 4,4'-trimethylenedipyridine and 1,3,5-benzenetricarboxylic acid is a salt, $C_{13}H_{15}N_2^+ \cdot C_9H_5O_6^-$. The components are linked by a combination of O—H···O, O—H···N, N—H···O and C—H···O hydrogen bonds into molecular tapes perforated by $R_4^4(38)$ rings: these tapes are connected by further C—H···O hydrogen bonds into a three-dimensional network.

Comment

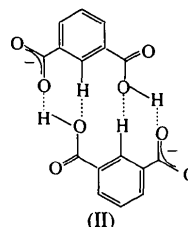
In its hydrogen-bonded adducts with phenols and weak acids, the aromatic base 4,4'-bipyridyl exhibits a very wide range of structural motifs. Thus, with 1,3,5-trihydroxybenzene, a 2:3 adduct is formed having a chain-of-rings structure (Coupar *et al.*, 1996), while with the larger aromatic triol 1,1,1-tris(4-hydroxyphenyl)ethane, the 2:3 adduct forms two-dimensional nets which exhibit tenfold interweaving (Bényei *et al.*, 1998). The adduct of 4,4'-bipyridyl with trimesic acid (1,3,5-benzenetricarboxylic acid) is also of 2:3 stoichiometry and again forms two-dimensional nets: there are eighteen independent nets within the structure and these are interwoven in sets of three (Sharma & Zaworotko, 1996). In all of these adducts, both N atoms of each bipyridyl molecule participate in the hydrogen-bonding scheme. On the other hand, phenylphosphonic acid forms a 1:1 adduct with 4,4'-bipyridyl in which only one of the two N atoms of the amine participates in the hydrogen bonding: the overall structural motif is of the stem-and-leaves type (Ferguson *et al.*, 1998).

In view of this great structural diversity in 4,4'-bipyridyl adducts, we have now initiated a study of the extended-chain analogue 4,4'-trimethylenedipyridine, and we report here the preparation and structure of the 1:1 adduct, (I), with trimesic acid, which proves to be the salt $[HNC_5H_4-(CH_2)_3-C_5H_4N]^+ [C_6H_3(COOH)_2(COO)]^-$ in which a single but complete proton transfer from acid to base has oc-

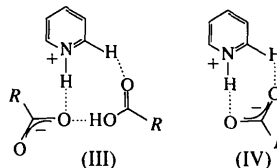
curred. The substantial excess of hard (Braga *et al.*, 1995) hydrogen-bond acceptors over hard donors in this system leads to the formation of a number of C—H···O hydrogen bonds, so generating a complex three-dimensional network: each cation is hydrogen bonded to five different anions, and each anion is hydrogen bonded to five different cations, as well as to one other anion.



(I)



(II)



(III)

(IV)

The structure of (I) is most conveniently described and discussed first in terms of the hard intermolecular hydrogen bonds (O—H···O, O—H···N and N—H···O), and then in terms of the soft C—H···O hydrogen bonds. As usually observed in organic acid–base adducts of this type, N—H···N hydrogen bonds are absent. Pairs of the $[C_6H_3(COOH)_2(COO)]^-$ anions related by centres of inversion are linked by comparatively short O—H···O⁻ hydrogen bonds (Fig. 2 and Table 2) to give a motif with graph set $R_2^2(16)$ (Bernstein *et al.*, 1995); this pairwise connection of anions is not observed in any other of the salts of $[C_6H_3(COOH)_2(COO)]^-$ hitherto reported (Herbstein & Kapon, 1979; Melendez *et al.*, 1996; Meehan *et al.*, 1997). The robustness of this motif may be enhanced by the formation of two C—H···O cross-links within the $R_2^2(16)$ rings (Fig. 2 and Table 2), so generating the unique four-stranded supramolecular motif, (II), where the original $R_2^2(16)$ ring is divided into a central $R_2^2(10)$ sector and two peripheral $R_2^2(7)$ sectors. Neighbouring hydrogen-bonded anion dimers are linked by pairs of cations to generate molecular tapes running parallel to the [011] direction. Atom N21 in the cation at (x, y, z) acts as donor to O11, also at (x, y, z) , while atom N31 in the same unit acts

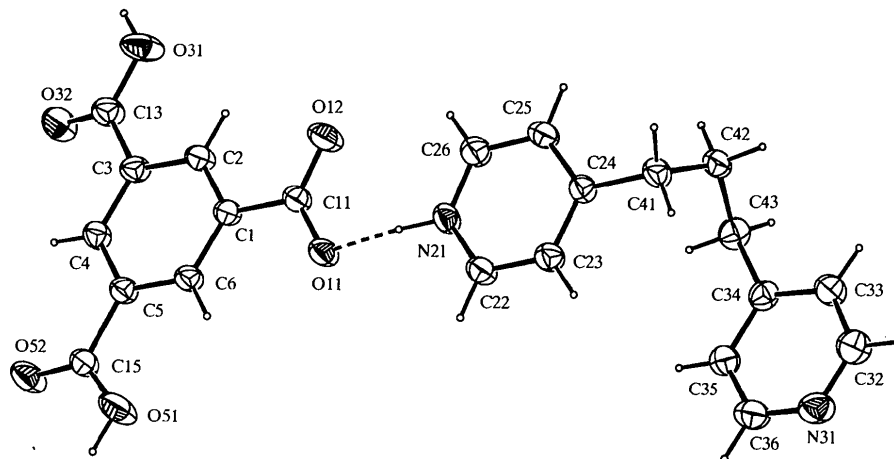


Fig. 1. A view of the asymmetric unit of (I) with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

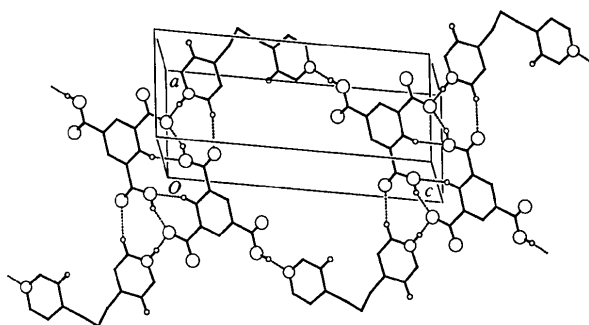


Fig. 2. A view of a section of the molecular tape, showing $R_2^2(16)$, $R_2^2(7)$, $R_3^2(9)$, $R_2^2(10)$, and $R_4^4(38)$ rings.

as acceptor from O31 in the anion at $(x, 1 + y, 1 + z)$, so generating the chain which forms one edge of the tape. Similar interactions involving the cation at $(-x, -y, -z)$ generate the other edge (Fig. 2). Each tape is perforated by a series of large $R_4^4(38)$ rings, centred at $(0, \frac{1}{2}n, \frac{1}{2}n)$ for odd n , while the linkage of the neighbouring anion pairs is further enhanced by the formation of an $R_3^2(9)$ motif, (III), involving one neutral and one ionized carboxylate, and one pyridinium group (Fig. 2). The common $R_2^2(7)$ pyridine–carboxylic acid motif, (IV) (Pedireddi *et al.*, 1996; Sharma & Zaworotko, 1996) is absent.

The tapes running parallel to $[011]$ are linked into a three-dimensional continuum by inter-tape C—H...O hydrogen bonds. Atom C35 in the cation at (x, y, z) acts as donor to O32 in the anion at $(1 - x, -y, -z)$, while C35 at $(1 - x, -y, -z)$ acts as donor to O32 at (x, y, z) ; these hydrogen bonds generate an $R_4^4(36)$ ring (Fig. 3) around the inversion centre at $(\frac{1}{2}, 0, 0)$ and serve to link a series of tapes stacked along the $[100]$ direction into a sheet lying parallel to $(01\bar{1})$. Finally, atom C25 in the cation at (x, y, z) acts as donor to O12 in the anion at $(2 - x, 1 - y, -z)$, while C25 at $(2 - x, 1 - y, -z)$ acts

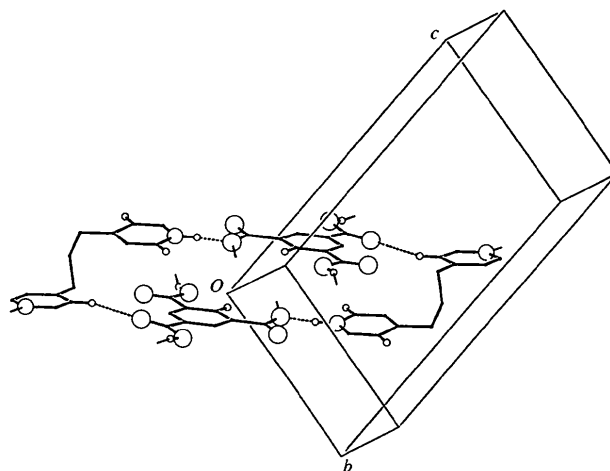


Fig. 3. A view of the centrosymmetric $R_4^4(36)$ rings joining neighbouring tapes in the $[100]$ direction.

as donor to O12 at (x, y, z) : the resulting $R_4^4(16)$ ring lying across the inversion centre at $(1, \frac{1}{2}, 0)$ provides links between adjacent sheets, so completing the construction of the three-dimensional network.

In the anion, the carboxylate groups are approximately coplanar with the aromatic ring, and the whole anion has approximate C_{2v} ($mm2$) symmetry (Fig. and Table 1), although it lies in a general position: similarly, the non-H atoms in the cation adopt a conformation which is close to C_2 symmetry (Table 1), although again this ion lies in a general position. The C—O bond lengths clearly reflect the deprotonation of just one of the COOH groups.

Examination of the structure with *PLATON* (Spek, 1997a) showed that there were small voids, volume *ca* 38 \AA^3 , centred at $(\frac{1}{2}, 0, \frac{1}{2})$ but devoid of electron density: there are no solvent-accessible voids in the crystal lattice.

Experimental

Methanolic solutions of 1,3,5-benzenetricarboxylic acid and 4,4'-trimethylenedipyridine were mixed in the molar ratio 1:2 and the mixture was set aside to crystallize, providing analytically pure (I). Analysis: found C 65.3, H 5.1, N 6.8%; C₂₂H₂₀N₂O₆ requires C 64.7, H 4.9, N 6.9%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample. When molar ratios of 1:1 or 2:1 were employed, phase separation occurred on crystallization to give materials from which pure (I) could be manually isolated: regardless of the input stoichiometry within the range of molar ratios 1:2 to 2:1, the 1:1 compound (I) was the only adduct isolated.

Crystal data

C₁₃H₁₅N₂⁺·C₉H₅O₆⁻M_r = 408.40

Triclinic

P $\bar{1}$

a = 6.7233 (8) Å

b = 8.8573 (8) Å

c = 17.0033 (12) Å

α = 99.151 (8)°

β = 94.253 (10)°

γ = 92.019 (7)°

V = 995.77 (16) Å³

Z = 2

D_x = 1.362 Mg m⁻³D_m not measured

Mo Kα radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 8.11–19.10°

μ = 0.100 mm⁻¹

T = 294 (1) K

Plate

0.40 × 0.36 × 0.18 mm

Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

θ/2θ scans

Absorption correction: none

4548 measured reflections

4548 independent reflections

2593 reflections with

I > 2σ(I)

θ_{max} = 27.38°

h = -8 → 8

k = 0 → 11

l = -22 → 21

3 standard reflections

frequency: 240 min

intensity decay: 10.7%

Refinement

Refinement on F²R[F² > 2σ(F²)] = 0.051wR(F²) = 0.123

S = 1.028

4548 reflections

278 parameters

H atoms constrained

w = 1/[σ²(F_o²) + (0.0547P)² + 0.0047P]where P = (F_o² + 2F_c²)/3(Δ/σ)_{max} < 0.001Δρ_{max} = 0.158 e Å⁻³Δρ_{min} = -0.168 e Å⁻³

Extinction correction:

SHELXL97

Extinction coefficient:

0.0069 (18)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O11—C11	1.286 (2)	O32—C13	1.211 (2)
O12—C11	1.224 (2)	O51—C15	1.307 (2)
O31—C13	1.309 (2)	O52—C15	1.198 (2)
C2—C1—C11—O12	6.0 (3)	C23—C24—C41—C42	108.9 (2)
C6—C1—C11—O11	5.2 (3)	C25—C24—C41—C42	-69.8 (2)
C4—C3—C13—O32	-9.1 (3)	C24—C41—C42—C43	-65.7 (2)
C2—C3—C13—O31	-10.8 (3)	C35—C34—C43—C42	114.3 (2)
C4—C5—C15—O52	-1.8 (3)	C33—C34—C43—C42	-64.8 (2)
C6—C5—C15—O51	0.1 (3)	C41—C42—C43—C34	-61.6 (2)

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

D—H...A	D—H	H...A	D...A	D—H...A
N21—H21...O11	0.99 (2)	1.60 (2)	2.585 (2)	175.1 (13)
O31—H31...N31 ⁱ	1.00 (2)	1.64 (2)	2.625 (2)	170.3 (17)
O51—H51...O11 ⁱⁱ	0.89 (3)	1.76 (3)	2.588 (2)	154.8 (16)
C6—H6...O51 ⁱⁱ	0.93	2.30	3.193 (2)	162
C22—H22...O52 ⁱⁱ	0.93	2.42	3.316 (2)	163
C25—H25...O12 ⁱⁱⁱ	0.93	2.33	3.256 (2)	175
C35—H35...O32 ^{iv}	0.93	2.49	3.353 (2)	153

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

Compound (I) crystallized in the triclinic system, space group P $\bar{1}$ or P1; P $\bar{1}$ was assumed and confirmed by the analysis. Significant decay of the data crystal (10.7%) was allowed for by scaling. Difference maps showed clearly that one carboxyl group (C11, O11, O12) was ionized and the H atom had been transferred to N21 of an adjacent pyridine ring. The H atoms bonded to C were treated as riding atoms (C—H 0.93 and 0.97 Å); the O—H and N—H H atoms were initially positioned at sites determined from difference maps and allowed to refine using respectively the AFIX-148 and AFIX-48 controls in SHELXL97 (Sheldrick, 1997a).

Data collection: CAD-4-PC (Enraf–Nonius, 1992). Cell refinement: SET4 and CELDIM in CAD-4-PC. Data reduction: DATRD2 in NRCVAX96 (Gabe *et al.*, 1989). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997b). Program(s) used to refine structure: NRCVAX96 and SHELXL97. Molecular graphics: NRCVAX96, ORTEPII (Johnson, 1976), PLATON (Spek, 1997a) and PLUTON (Spek, 1997b). Software used to prepare material for publication: NRCVAX96, SHELXL97 and WordPerfect macro PRPCIF97 (Ferguson, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1242). Services for accessing these data are described at the back of the journal.

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(+)-3-Oxo-23,24-dinor-5 α -cholan-22-oic Acid: Hydrogen-Bonding Patterns in a Steroidal Keto Acid and its Monohydrate

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Abstract

The X-ray crystal structures of the title steroidal keto acid in both its anhydrous, C₂₂H₃₄O₃, (I), and monohydrate, C₂₂H₃₄O₃·H₂O, (II), forms have been determined. Neither hydrogen-bonding pattern involves the ketone. Compound (I) forms infinite carboxyl-to-carboxyl hydrogen-bonding chains. This is the first observed case of a keto carboxylic acid forming such an acid-to-acid catemer. In (II), each carboxyl is hydrogen bonded to three water molecules and each water forms hydrogen bonds with carboxyl groups from three steroid molecules, creating a network of connected ten-membered hydrogen-bonding rings.

Comment

For keto carboxylic acids, the most common of the four previously known solid-state hydrogen-bonding patterns is acid dimerization (both centrosymmetric and non-centrosymmetric), with no ketone involvement. The others, in order of diminishing prevalence, are carboxyl-to-ketone catemers, intramolecular hydrogen bonds and carboxyl-to-ketone dimers, of which only two instances are known. Several additional patterns are known for

hydrates. Numerous examples of these patterns have been referenced and discussed previously (Thompson *et al.*, 1992; Coté *et al.*, 1996).

The crystalline states of acetic (Jones & Templeton, 1958) and formic acids (Nahringbauer, 1978; Jong & Chen, 1994) involve catemers created by repeating intermolecular O—H···O=C hydrogen bonds (acid-to-acid catemer), a pattern uncommon among functionally unelaborated carboxylic acids, which typically form hydrogen-bonding dimers (Leiserowitz, 1976). Having recently published the case of a 3-oxo-17-carboxysteroid which forms carboxyl-to-ketone catemers (Brunskill *et al.*, 1997), we now report the hydrogen-bonding behavior of the title compound, a steroidal keto acid present as a single enantiomer and existing in both anhydrous, (I), and monohydrate, (II), forms. The anhydrous form, (I), presents an instance of catemeric hydrogen bonding which involves only the carboxyl function, a hydrogen-bonding mode known in unelaborated acids (see above), but not previously observed in keto acids. The hydrogen-bonding pattern of the monohydrate, (II), involves insertion of water into the acid-to-acid catemer structure observed for (I), with minimal changes to overall packing. Catemer formation is uncommon in carboxylic acids, but is expected to occur more frequently in mono-enantiomeric species (von Sydow, 1958; Abrahamsson, 1959; Lin *et al.*, 1974), where centrosymmetry is excluded and absence of an antipode lessens the number of possible packing arrangements (Leiserowitz, 1976).

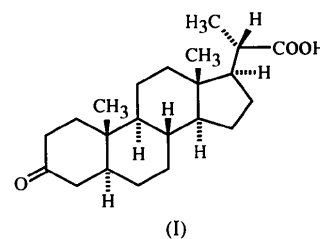


Fig. 1 shows the title compound with its steroid numbering and with the water of hydration which is present in (II). Because each water is also hydrogen bonded to the carboxyl C=O group of two other molecules, the choice of which of those relationships to show for (II) is arbitrary. Among the few conformational options present, the substituents at C20, which have the *S* configuration, are staggered with respect to those at C17, and the carboxyl group is turned, with its carbonyl toward the top (β) face of the molecule, so that the carboxyl plane coincides approximately with the C20—H20 bond [torsion angle H20A—C20—C22—O2 4.4(7) $^\circ$]. The asymmetric units of (I) and (II) differ very slightly in the torsion angles around these sites. In (I), the C16—C17—C20—C21 torsion angle is 178.4(6) $^\circ$ and the C17—C20—C22—O2 torsion