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Molecular Tiling in the 1:1 Adduct of 1,4-Diazabicyclo[2.2.2]octane and 1,3,5-Benzenetricarboxylic Acid

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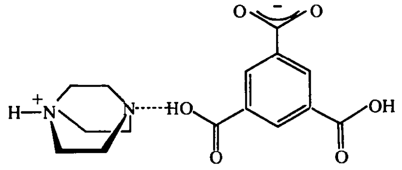
Abstract

The 1:1 adduct formed between 1,4-diazabicyclo[2.2.2]octane and 1,3,5-benzenetricarboxylic acid is a salt, $C_6H_{13}N_2^+.C_9H_5O_6^-$. The components both lie on a mirror plane and are linked by O—H···O, O—H···N and N—H···O hydrogen bonds into planar two-dimensional sheets; these sheets are formed by repetition of a single $R_6^6(38)$ ring which thus generates a tiling pattern with plane group *pg*.

Comment

In the structure of 1,1,1-tris(4-hydroxyphenyl)ethane, $CH_3C(C_6H_4OH)_3$, the molecules are linked by O—H···O hydrogen bonds into square nets, pairs of which are interwoven and further interconnected to give a multiply interwoven three-dimensional architecture (Ferguson, Bell, Coupar & Glidewell, 1997). Fragmentation of this structure by the interpolation of 1,4-diazabicyclo[2.2.2]octane (DABCO) or piperazine molecules, which act as acceptors of hydrogen bonds, to form the adducts 1,1,1-tris(4-hydroxyphenyl)ethane–1,4-diazabicyclo[2.2.2]octane–water (1/1/1) and 1,1,1-tris(4-hydroxyphenyl)ethane–piperazine (4/3), does not change the three-dimensional character of the hydrogen bonding, but merely increases its complexity (Ferguson, Bell, Coupar & Glidewell, 1997). An even more elaborate interwoven network is formed by 1,3,5-benzenetricarboxylic acid, $C_6H_3(COOH)_3$ (trimesic acid, TMA) (Duchamp & Marsh, 1969); although interpolation of hydrogen-bond acceptors into this material generally leads to a simplification of the crystal architectures, three-dimensional hydrogen bonding often still persists (Herbstein & Kapon, 1978; Herbstein, Kapon & Wasserman, 1978; Herbstein, Kapon, Maor & Reisner, 1981). We have now prepared a 1:1 adduct from TMA and DABCO, which proves to be the salt $C_6H_{13}N_2^+.C_9H_5O_6^-$, (1), in which a single but complete proton transfer has occurred; there are three types of hydrogen bond, O—H···O, O—H···N and N—H···O, but the main structural motif is a simple strictly planar two-dimensional sheet with no interweaving.



(1)

Compound (1) crystallizes in the space group *Pnma* with a Z' of 0.5, as usually found for this space group (Brock & Dunitz, 1994). All the atoms of the TMA monoanion lie on the mirror plane, while the protonated DABCO lies across this plane with atoms N2, N3, C21 and C31 on the mirror plane. It has been pointed out (Brock & Dunitz, 1994) that mirror planes are always occupied since unoccupied ones require the occurrence of like–like interactions between adjacent molecules. Within the asymmetric unit (Fig. 1), atom O31 acts as hydrogen-bond donor to atom N3, thus generating the O—H···N-type hydrogen bond. Atom O51 in the TMA anion at (x, y, z) acts as hydrogen-bond donor to atom O12 in the anion at $(-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z)$, while atom O51 in this latter anion acts as donor to O12 in the unit at $(-1+x, y, z)$. Repetition of this O—H···O interaction thus gives rise to a chain, graph set $C(8)$ (Bernstein, Davis, Shimoni & Chang, 1995), running parallel to the [100] direction and generated by the action of the *a* glide plane (Fig. 2). In addition, atom N2 in the DABCO at (x, y, z) acts as hydrogen-bond donor to atom O11 in the TMA anion at $(-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}-z)$; this N—H···O hydrogen bond and the O—H···O and O—H···N hydrogen bonds arising from atoms O31 and O51 generate a chain running parallel to the [001] direction (Fig. 2) having graph-set descriptors $N_1 = DDD$ and $N_2 = C_3^3(17)$ (Bernstein, Davis, Shimoni & Chang, 1995). The action of the *a* glide plane causes adjacent [001] chains to run anti-parallel.

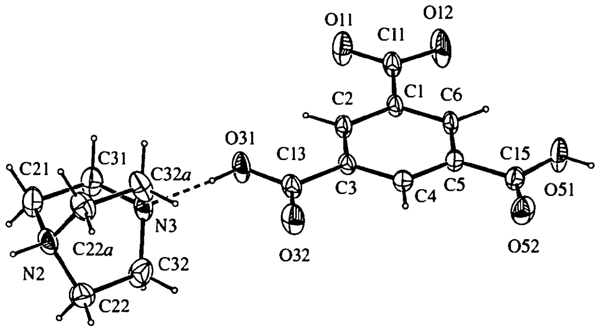


Fig. 1. A view of the asymmetric unit of (1) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

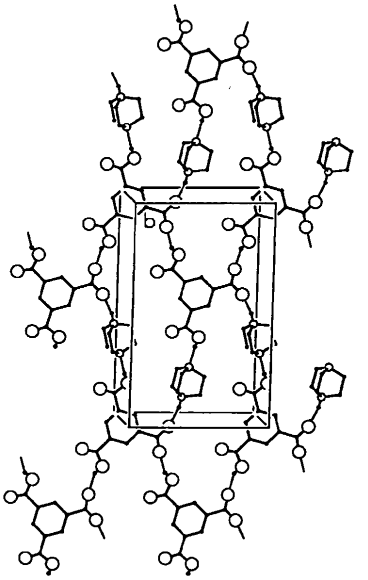


Fig. 2. A view of one sheet of hydrogen-bonded species in the crystal structure. H atoms are not shown except for those involved in the O—H···O, O—H···N and N—H···O hydrogen bonding. The cell origin is at the bottom left, with the *a* axis vertical and the *c* axis horizontal.

The TMA anion thus participates in two orthogonal chain motifs with two of its O atoms, O31 and O51, acting as hydrogen-bond donors and two, O11 and O12, acting as acceptors. In turn, the entire asymmetric unit of protonated DABCO and TMA anion is both a double donor and a double acceptor of hydrogen bonds, and this leads to the formation of a continuous two-dimensional sheet built from $R_6^6(38)$ rings (Fig. 2). The action of the *a* glide plane ensures that all the rings are identical, so that the rings are fitted together on the mirror plane in a two-dimensional tiling pattern having plane group *pg*. Since all the atoms generating the ring lie on the mirror plane, there is no possibility of interweaving of neighbouring sheets, as this would require some degree of folding of the individual sheets.

Although the TMA monoanion retains two unionized COOH groups, it is noteworthy that the hydrogen-bonding scheme contains neither the $R_2^2(8)$ $(COOH)_2$ rings characteristic of many carboxylic acid structures, such as those of benzoic acid (Sim, Robertson & Goodwin, 1955; Bruno & Randaccio, 1980) and TMA itself (Duchamp & Marsh, 1969), nor the $C(4)$ O—H···O═C chains found in some aliphatic carboxylic acids, such as acetic acid (Jones & Templeton, 1958; Nahringbauer, 1970; Jonsson, 1971). In the 2:3 adduct formed between TMA and 4,4′-bipyridyl (Sharma & Zaworotko, 1996), no proton transfer from acid to base occurs. There is an excess of hydrogen-bond acceptors over donors in the 1:1 adduct (1) and two of the O atoms of the TMA anion, O32 and O52, participate in no O—H···O or N—H···O hydrogen bonds (Table 3). Atom O52 in fact acts as acceptor in two soft (Braga, Grepioni, Biradha, Pedireddi & Desiraju, 1995) C—H···O hydrogen bonds, in which one DABCO C—H bond in each of the adjacent layers acts as donor; atom O52 in the anion at (x, y, z) acts as acceptor from the atoms C22 in each of the two units at $(-\frac{1}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}+z)$ and $(-\frac{1}{2}-x, -y, -\frac{1}{2}+z)$. Similarly, atom O51 in the anion at (x, y, z), as well as acting as a donor in an O—H···O hydrogen bond, acts as acceptor in C—H···O hydrogen bonds formed by the C32 atoms in the two units at $(-x, -y, -z)$ and $(-x, \frac{1}{2}+y, -z)$ (Table 3). These C—H···O interactions are propagated along the [010] direction by the action of the mirror planes and serve to link all the layers together, albeit weakly.

All the hydrogen bonds (O—H···O, O—N···N, N—H···O and C—H···O) are short (Table 3); it is noteworthy that both the N—H···O and the O—H···O hydrogen bonds involve one charged component and these N···O and O···O distances support the view that hydrogen bonds involving ionic components are generally significantly shorter than those involving only neutral species (Aakeröy & Seddon, 1993; Gilli, Bertolasi, Ferreti & Gilli, 1994). Similarly, it is notable that both the O atoms, O11 and O12, of the ionized carboxyl group act as acceptors of hydrogen bonds, whereas none of the O atoms in the unionized carboxyl groups acts as an acceptor of hard (Braga, Grepioni, Biradha, Pedireddi & Desiraju, 1995) hydrogen bonds.

Within the molecular fragments, the C—O bond lengths (Table 2) provide corroborative evidence for the state of deprotonation of the carboxyl groups; similarly, the C—N bond lengths reflect the protonation of N2. The other bond lengths are unexceptional.

Examination of the structure with *PLATON* (Spek, 1996*a*) showed that there were no solvent-accessible voids in the crystal lattice.

Experimental

Samples of trimesic acid and DABCO (0.005 mol of each) were separately dissolved in methanol/water (6:1 *v*/*v*) (100 ml). The solutions were mixed and the mixture set aside to crystallize. The product consisted of two distinct crystalline phases, needles and prisms. These were separated mechanically and the needles proved to be the trimethyl ester of trimesic acid, while the prisms were compound (1). Analysis of (1): found C 55.9, H 5.9, N 8.7%; $C_{15}H_{18}N_2O_6$ requires C 55.9, H 5.6, N 8.7%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$C_6H_{13}N_2^+.C_9H_5O_6^-$
$M_r = 322.31$
Orthorhombic
Pnma
$a = 11.2525\,(11)$ Å
$b = 7.0950\,(12)$ Å
$c = 18.612\,(2)$ Å
$V = 1485.9\,(3)$ Å^3
$Z = 4$
$D_x = 1.441$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 12.49$–$23.84°$
$\mu = 0.113$ mm^{-1}
$T = 294\,(1)$ K
Block
0.42 × 0.35 × 0.24 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2522 measured reflections
2323 independent reflections
1380 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.041$
$\theta_{\rm max} = 29.94°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 120 min
intensity variation: 0.5%

Refinement

Refinement on F^2
$R(F) = 0.0489$
$wR(F^2) = 0.1531$
$S = 1.060$
2323 reflections
134 parameters
H atoms riding (C—H 0.93–0.97, N—H 0.91 and O—H 0.82 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0786P)^2 + 0.1098P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.297$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.185$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0028 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O11	0.36766 (14)	1/4	0.04558 (9)	0.0658 (6)
O12	0.3068 (2)	1/4	0.15685 (8)	0.0808 (8)
O31	0.06421 (15)	1/4	−0.14622 (8)	0.0586 (6)
O32	−0.12986 (15)	1/4	−0.12160 (9)	0.0607 (6)
O51	−0.0974 (2)	1/4	0.22150 (9)	0.0691 (7)
O52	−0.24720 (15)	1/4	0.14437 (10)	0.0580 (5)
C1	0.1591 (2)	1/4	0.06806 (10)	0.0330 (5)
C2	0.1266 (2)	1/4	−0.00392 (10)	0.0353 (5)
C3	0.0080 (2)	1/4	−0.02431 (10)	0.0329 (5)
C4	−0.0801 (2)	1/4	0.02778 (11)	0.0348 (5)
C5	−0.0488 (2)	1/4	0.09995 (11)	0.0353 (5)
C6	0.0709 (2)	1/4	0.11970 (10)	0.0363 (5)
C11	0.2874 (2)	1/4	0.09149 (11)	0.0424 (6)
C13	−0.0273 (2)	1/4	−0.10201 (11)	0.0408 (6)
C15	−0.1431 (2)	1/4	0.15625 (11)	0.0396 (5)
N2	−0.0466 (2)	1/4	−0.41345 (10)	0.0478 (5)
N3	0.0018 (2)	1/4	−0.28219 (10)	0.0512 (6)
C21	0.0856 (2)	1/4	−0.40488 (14)	0.0599 (8)
C22	−0.0970 (2)	0.0775 (3)	−0.37995 (9)	0.0575 (5)
C31	0.1124 (2)	1/4	−0.32443 (13)	0.0559 (7)
C32	−0.0683 (2)	0.0818 (3)	−0.30032 (10)	0.0614 (6)

Table 2. *Selected geometric parameters (Å, °)*

O11—C11	1.243 (3)	C5—C15	1.491 (3)
O12—C11	1.236 (2)	N2—C22	1.486 (2)
O31—C13	1.318 (3)	N2—C21	1.495 (3)
O32—C13	1.210 (3)	N3—C32	1.470 (2)
O51—C15	1.319 (3)	N3—C31	1.472 (3)
O52—C15	1.192 (3)	C21—C31	1.528 (4)
C1—C11	1.508 (3)	C22—C32	1.517 (3)
C3—C13	1.500 (3)		
O11—C11—O12	123.3 (2)	O32—C13—C3	122.9 (2)
O11—C11—C1	119.8 (2)	O51—C15—O52	123.6 (2)
O12—C11—C1	116.9 (2)	O51—C15—C5	111.7 (2)
O31—C13—O32	123.8 (2)	O52—C15—C5	124.7 (2)
O31—C13—C3	113.3 (2)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O11$^{\rm i}$	0.91	1.75	2.642 (3)	167
O31—H3···N3	0.82	1.81	2.626 (2)	175
O51—H5···O12$^{\rm ii}$	0.82	1.78	2.508 (2)	148
C2—H2A···O31	0.93	2.42	2.740 (2)	100
C6—H6···O51	0.93	2.35	2.679 (3)	101
C22—H22B···O52$^{\rm iii}$	0.97	2.50	2.946 (2)	108
C32—H32B···O51$^{\rm iv}$	0.97	2.41	3.342 (3)	162

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, -\frac{1}{2} - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$; (iii) $-\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (iv) $-x, -y, -z$.

All H atoms were clearly visible in difference-density maps which showed that one of the carboxyl-group H atoms had been transferred to one of the N atoms of the diamine. The carboxyl O atoms are anisotropic in a direction normal to the mirror plane and it is possible that the O atoms are very slightly disordered on either side of the mirror plane. Refinement was attempted in the non-centrosymmetric $Pna2_1$ space group, removing the requirement for mirror symmetry, but as the refinement was completely unstable even with heavy damping, this was abandoned.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *CAD-4-PC Software*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*96. Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1996*a*) and *PLUTON* (Spek 1996*b*). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*93 and *WordPerfect* macro *PREPCIF* (Ferguson, 1996).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1456). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-(*n*-Butyl)-3,4-dibromomaleimide

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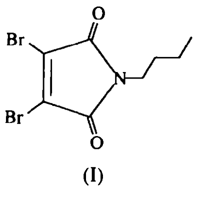
Abstract

The X-ray structure analysis of the title compound, $C_8H_9Br_2NO_2$, was carried out. In the unit cell, the molecules are stacked with their C═C double bonds at close intermolecular distances of approximately 3.6 Å. Conjugation in the imide ring is not significant.

Comment

The (2+2) photodimerization of maleic anhydride in the solid state is completely inhibited at 278 K and the crystal structure analysis of the monomer indicates that no parallel double bonds or intermolecular distances are adequate for photodimerization (Marsh, Ubell & Wilcox, 1962). In contrast, however, photodimerization of maleimide derivatives in the crystalline state takes place readily (Boens, De Schryver & Smets, 1975).

N-(*n*-Butyl)-3,4-dibromomaleimide, (I), was obtained as a by-product during the synthesis of *N*-(*n*-butyl)-3,4-dibromo-2-oxopyrrolium 5-oxide. The packing of compound (I) shows that the distance between C═C double bonds of neighbouring maleimide rings is similar to the sum of the van der Waals radii of carbon (1.7 Å). It seems likely that the packing may facilitate polymerization parallel to the *a* axis [C2···C2^{i} 3.51 (2) and C3···O1^{i} 3.66 (2) Å; symmetry code: (i) $1-x$, $2-y$, $1-z$].



(I)

The *ORTEP* (Johnson, 1965) plot of the title molecule with the numbering scheme is shown in Fig. 1. The C2—C3 distance of 1.305 (8) Å is comparable to that in maleic anhydride [1.303 Å; Marsh, Ubell & Wilcox, 1962]. The mean length of the single C—C bond in the maleimide ring [1.441 (8) Å] is comparable

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