organic compounds

Threefold interweaving of (4,4) nets built from $R_{10}^{10}(58)$ rings in the hydrogen-bonded adduct 1,4-diazabicyclo[2.2.2]octane–5-hydroxyisophthalic acid (1/1)

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The 1:1 adduct of 1,4-diazabicyclo[2.2.2]octane and 5-hydroxyisophthalic acid is a salt, $[H(C_6H_{12}N_2)]^+ \cdot [HOC_6H_3(COOH)COO]^-$ or $C_6H_{13}N_2^+ \cdot C_8H_5O_5^-$. The ions are linked by three types of hydrogen bond, i.e. $N-H \cdots O$, $O-H \cdots O$ and $O-H \cdots N$, into continuous two-dimensional (4,4) nets built from a single type of $R_{10}^{10}(58)$ ring. Six independent sheets of this type make up the structure and these are interwoven in sets of three.

Comment

The aromatic dicarboxylic acid 5-hydroxyisophthalic acid, $C_8H_6O_5$, (I), is a potentially versatile building block for supramolecular chemistry in that it contains three substituents, each capable of acting as both hydrogen-bond donors and
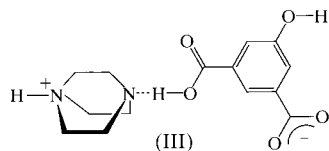
hydrogen-bond acceptors. The mutual disposition of these substituents, however, prevents the formation of intramolecular $O-H \cdots O$ hydrogen bonds of the type found, for example, in the 2-isomer, (II) (Solari *et al.*, 1996). Isomer (I) forms a 1:1 salt with the extended diamine 4,4′-trimethylenedipyridine (Wheatley *et al.*, 1999), in which the supramolecular structure consists of four identical but independent interpenetrating three-dimensional frameworks. Developing the use of building block (I), we have now prepared and structurally characterized a 1:1 adduct, (III), of the acid (I) with the cage diamine 1,4-diazabicyclo[2.2.2]octane (DABCO), $C_6H_{12}N_2$, in which there are again multiply interpenetrating arrays, this time two-dimensional in nature.

The constitution of compound (III) is that of a 1:1 salt, $[H(C_6H_{12}N_2)]^+ \cdot [HOC_6H_3(COOH)COO]^-$; difference maps clearly showed the complete transfer of an H atom from one carboxyl group of the acid to one of the N atoms of the diamine and, further, that all H atoms occupy fully ordered sites. There are only three independent hydrogen bonds in the crystal structure, one each of the $O-H \cdots N$, $O-H \cdots O$ and $N-H \cdots O$ types (Table 2), but these are sufficient to generate a series of threefold interwoven nets. For ease of descriptive analysis, it is convenient to consider the effects first of just one type of hydrogen bond, then of two, and finally the combined effect of all three types.

Compound (III) crystallizes in space group $C2/c$ with $Z = 8$ and the asymmetric unit thus contains one ion of each type, both lying in general positions. The selection of the asymmetric unit, and thus the mutual disposition of the components within it, is to some extent flexible, but the most convenient choice (Fig. 1) is that in which the components are linked by an $O-H \cdots N$ hydrogen bond involving the un-ionized carboxyl group of the anion as the hydrogen-bond donor and the unprotonated N atom of the cation as the acceptor.

These ion-pair units are then linked into centrosymmetric pairs by means of $O-H \cdots O$ hydrogen bonds: hydroxyl O5 at (x, y, z) acts as a hydrogen-bond donor to anionic O4 at $(\frac{1}{2} - x, \frac{1}{2} - y, z)$, while O5 at $(\frac{1}{2} - x, \frac{1}{2} - y, z)$ in turn acts as donor to O4 at (x, y, z). Hence, the dimeric unit is based upon the rather unusual $R_2^2(14)$ motif (Fig. 2) centred at $(\frac{1}{4}, \frac{1}{4}, 0)$. There are three other such dimeric units within the unit cell, centred at $(\frac{3}{4}, \frac{3}{4}, 0)$, $(\frac{1}{4}, \frac{3}{4}, \frac{1}{2})$ and $(\frac{3}{4}, \frac{1}{4}, \frac{1}{2})$. Similar $R_2^2(14)$ rings are found in the two-dimensional anion sheets formed by 3,5-dihydroxybenzoate ions in the salt with $[(tet-a)H_2]^{2+}$ (tet-a is *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane); although in this case, the $R_2^2(14)$ rings alternate with $R_6^4(30)$ rings in a continuous array (Gregson *et al.*, 2000).

The formation of these four-ion units (Fig. 2) utilizes the $O-H \cdots N$ and $O-H \cdots O$ hydrogen bonds. The remaining hydrogen bond, of the $N-H \cdots O$ type, serves to link these centrosymmetric aggregates into continuous two-dimensional sheets. Each dimeric unit (Fig. 2) acts as a twofold donor and a twofold acceptor in $N-H \cdots O$ hydrogen bonds, so that each is linked to four others. Atom N2 at (x, y, z) acts as a hydrogen-bond donor to anionic O3 at $(x, -1 - y, \frac{1}{2} + z)$; this O3 is a component of the dimer centred at $(\frac{1}{4}, -\frac{5}{4}, \frac{1}{2})$. The symmetry-related N2 in the original dimer, centred at $(\frac{1}{4}, \frac{1}{4}, 0)$, is at $(\frac{1}{2} - x,$
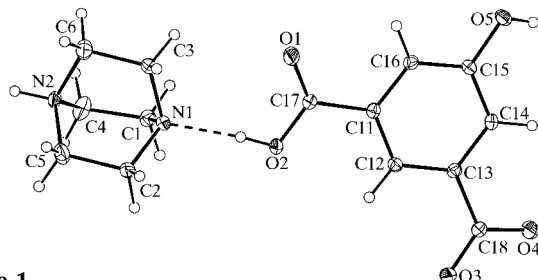

Figure 1
The molecular components of (III) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii.
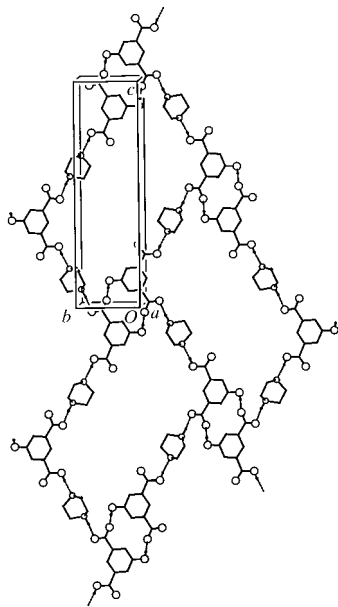
Figure 2
Part of the crystal structure of (III) showing formation of the $R_2^2(14)$ and $R_{10}^{10}(58)$ rings comprising the (100) net.

$\frac{1}{2} - y, -z$) and this acts as a hydrogen-bond donor to O3 at $(\frac{1}{2} - x, \frac{3}{2} + y, -\frac{1}{2} - z)$, which is a component of the dimer centred at $(\frac{1}{4}, \frac{7}{4}, -\frac{1}{2})$. At the same time, the two O3 atoms in the original dimer at (x, y, z) and $(\frac{1}{2} - x, \frac{1}{2} - y, -z)$, respectively, accept N—H···O hydrogen bonds from the atoms N2 at $(x, -1 - y, -\frac{1}{2} + z)$ and $(\frac{1}{2} - x, \frac{3}{2} + y, \frac{1}{2} - z)$, respectively; these two atoms lie in dimers centred at $(\frac{1}{4}, -\frac{5}{4}, -\frac{1}{2})$ and $(\frac{1}{4}, \frac{7}{4}, \frac{1}{2})$, respectively. Hence, the four-ion dimer centred at $(\frac{1}{4}, \frac{1}{4}, 0)$ is directly linked by the N—H···O hydrogen bonds to those centred at $(\frac{1}{4}, -\frac{5}{4}, \frac{1}{2})$, $(\frac{1}{4}, -\frac{5}{4}, -\frac{1}{2})$, $(\frac{1}{4}, \frac{7}{4}, \frac{1}{2})$ and $(\frac{1}{4}, \frac{7}{4}, -\frac{1}{2})$; propagation of these hydrogen bonds by translation generates a continuous two-dimensional sheet parallel to (100) and built from $R_{10}^{10}(58)$ rings (Fig. 2).

The repeat period of this net (Fig. 2) is one unit cell in the [001] direction, but three unit cells in the [010] direction. Moreover, the formation of one such net utilizes only $\frac{4}{3}$ ion pairs per unit cell, and hence there must be six independent nets making up the entire structure. The net built around the dimeric unit centred at $(\frac{1}{4}, \frac{1}{4}, 0)$ lies entirely within the domain $0 < x < \frac{1}{2}$ (Fig. 3). Because of the repeat period along [010], there must be three such nets within the domain $0 < x < \frac{1}{2}$, related by translation and based upon dimers centred at $(\frac{1}{4}, \frac{1}{4}, 0)$, $(\frac{1}{4}, \frac{5}{4}, 0)$ and $(\frac{1}{4}, -\frac{3}{4}, 0)$. There are three further nets in the domain $\frac{1}{2} < x < 1$, related to one another by translation and to the first set by the action of the C-centring operation of the space group.

Within each domain of x, the three highly puckered nets (Fig. 3) are mutually interwoven. The approximate area of each $R_{10}^{10}(58)$ ring, taking due account of the van der Waals radii of the molecular components forming the ring, is *ca* 100 Å^2 (Fig. 2). As in all interwoven systems, the number of mutually interwoven nets depends upon the number of strands of each which can pass through the rings; for rings of the size observed here, passage of two strands is an entirely reasonable outcome (Ferguson *et al.*, 1998). In the notation developed by Ferguson *et al.* (1998), the molecular weaving in compound

(III) is of the {6,3,2} type, indicating the requirement for six nets to define the structure completely, interwoven in sets of three with two strands passing through each ring of the net. In the 2:3 adduct formed between 1,3,5-benzenetricarboxylic acid and 4,4′-bipyridyl (Sharma & Zaworotko, 1996), the weaving is of the {18,3,2} type, again with two-dimensional sheets interwoven in sets of three. However, there is a significant difference between the sheets in this latter adduct and those in (III). In the 1,3,5-benzenetricarboxylic acid–4,4′-bipyridyl adduct, the individual nets are of the (6,3) type, where in the notation (*n,p*), *p* is the number of connections at each node and *n* is the number of nodes in the shortest circuit (Batten & Robson, 1998). In contrast, in compound (II), the nets are of the (4,4) type. In both cases, the interpenetration is of parallel nets. While twofold parallel interpenetration of (4,4) nets is reasonably common, threefold parallel interpenetration of such nets, as in compound (III), appears to be rather rare, with no examples recorded by Batten & Robson (1998).

The C—O distances in the ionized and unionized carboxylate groups (Table 1) are fully consistent with the location of the H atoms. However, the difference between the mean values of the C—N distances associated with the protonated and unprotonated N atoms in the cation is scarcely significant. For the ionized –CO$_2^-$ substituent, the two O—C—C angles are essentially identical. However, for the neutral –COOH substituent, the O=C—C angle is very much larger than the (H)O—C—C angle. The two O—C—O angles, on the other hand, are rather similar. As usual, the two O—C—C angles associated with the hydroxyl group are significantly different, with the larger being *cisoid* to the H atom, which is effectively diagnostic of the site of this H atom.

The conformational properties of the DABCO molecule have been extensively investigated, both in the solid state (Weiss *et al.*, 1964; Nimmo & Lucas, 1976; Mak *et al.*, 1984) and in the gas phase (Yokozeki & Kuchitsu, 1971). The principal point of interest is the extent of any twist of the molecule from ideal D_{3h} symmetry by internal rotation about the N···N vector; in the D_{3h} conformation, the neighbouring CH$_2$ groups are necessarily eclipsed. For isolated molecules in the gas phase (Yokozeki & Kuchitsu, 1971), the internal dynamics indicated a very broad potential well for the twist motion, best
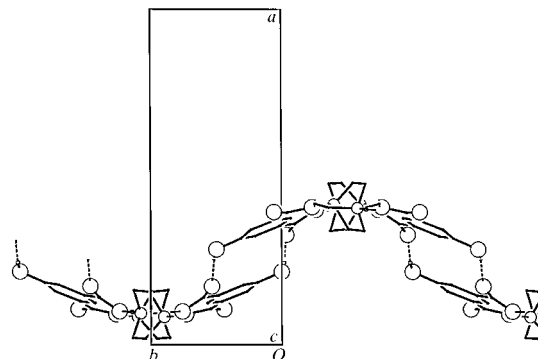

Figure 3
Projection of part of the crystal structure of (III) showing the repeat period in the [010] direction and the puckering of a (100) net, which together lead to threefold interweaving of the nets.

fitted by an harmonic quartic potential function having an energy minimum corresponding to a twist of *ca* 10° from D_{3h} geometry. In compound (III), the N—C—C—N torsion angles range from 5.7 (2) to 7.9 (2)°, indicative of a small but real distortion of the DABCO skeleton from the fully eclipsed conformation. Somewhat larger distortions have been observed in the 2:1 adduct of 2,2′-biphenol with DABCO (Glidewell *et al.*, 1999), while rather smaller distortions were found in the 2:1 adduct of phenol itself with DABCO (Mak *et al.*, 1984).

Experimental

Equimolar quantities of 1,4-diazabicyclo[2.2.2]octane and 5-hydroxyisophthalic acid were dissolved separately in methanol. The solutions were mixed and the mixture was set aside to crystallize, providing analytically pure crystalline (III). Analysis found: C 57.3, H 6.1, N 9.4%; $C_{14}H_{18}N_2O_5$ requires: C 57.1, H 6.1, N 9.5%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$C_6H_{13}N_2^+\cdot C_8H_5O_5^-$	$D_x = 1.403$ Mg m^{-3}
$M_r = 294.30$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 3119
$a = 17.3820\ (7)$ Å	reflections
$b = 6.7257\ (3)$ Å	$\theta = 2.78$–27.48°
$c = 23.9374\ (9)$ Å	$\mu = 0.107$ mm^{-1}
$\beta = 95.368\ (2)$°	$T = 100\ (2)$ K
$V = 2786.2\ (2)$ Å^3	Block, colourless
$Z = 8$	$0.25 \times 0.25 \times 0.23$ mm

Data collection

KappaCCD diffractometer	2441 reflections with $I > 2\sigma(I)$
φ and ω scans with κ offsets	$R_{int} = 0.022$
Absorption correction: multi-scan	$\theta_{max} = 27.48$°
(*DENZO-SMN*; Otwinowski &	$h = 0 \rightarrow 22$
Minor, 1997)	$k = 0 \rightarrow 8$
$T_{min} = 0.974$, $T_{max} = 0.976$	$l = -29 \rightarrow 30$
3374 measured reflections	Intensity decay: negligible
3119 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$+ 2.4139P]$
$wR(F^2) = 0.121$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.095$	$(\Delta/\sigma)_{max} < 0.001$
3119 reflections	$\Delta\rho_{max} = 0.30$ e Å^{-3}
193 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.0025 (7)

Compound (III) crystallized in the monoclinic system and space group $C2/c$ or Cc was suggested from the systematic absences; $C2/c$ was assumed and confirmed by the analysis. H atoms were treated as riding, with C—H = 0.95 (aromatic) or 0.99 (aliphatic), N—H = 0.93 and O—H = 0.84 Å. Examination of the structure with *PLATON* (Spek, 2000) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

Table 1
Selected geometric parameters (Å, °).

O1—C17	1.220 (2)	N1—C1	1.481 (2)
O2—C17	1.310 (2)	N1—C2	1.482 (2)
O3—C18	1.2654 (19)	N1—C3	1.483 (2)
O4—C18	1.2518 (19)	N2—C6	1.487 (2)
O5—C15	1.3609 (18)	N2—C5	1.487 (2)
C11—C17	1.504 (2)	N2—C4	1.489 (2)
C13—C18	1.513 (2)		
O5—C15—C14	122.67 (14)	O5—C15—C16	117.75 (14)
O1—C17—O2	123.82 (15)	O3—C18—O4	124.45 (15)
O1—C17—C11	122.12 (15)	O3—C18—C13	117.66 (13)
O2—C17—C11	114.06 (13)	O4—C18—C13	117.86 (14)
C12—C11—C17—O1	173.96 (15)	N1—C1—C4—N2	6.2 (2)
C12—C11—C17—O2	−6.7 (2)	N1—C2—C5—N2	7.9 (2)
C12—C13—C18—O3	−13.9 (2)	N1—C3—C6—N2	5.7 (2)
C12—C13—C18—O4	168.04 (15)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$N1	0.84	1.78	2.6175 (17)	172
O5—H5$\cdots$O4^{i}	0.84	1.85	2.6628 (17)	162
N2—H2$A\cdots$O3^{ii}	0.93	1.71	2.6365 (17)	173

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

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC, Canada.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1007). Services for accessing these data are described at the back of the journal.

References

Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed. Engl.* **37**, 1460–1494.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Ferguson, G., Glidewell, C., Gregson, R. M. & Meehan, P. R. (1998). *Acta Cryst.* B**54**, 330–338.
Glidewell, C., Ferguson, G., Gregson, R. M. & Lough, A. J. (1999). *Acta Cryst.* C**55**, 2136–2140.
Gregson, R. M., Glidewell, C., Ferguson, G. & Lough, A. J. (2000). *Acta Cryst.* B**56**, 39–57.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Mak, T. C. W., Yip, W.-H. & Book, L. (1984). *J. Crystallogr. Spectrosc. Res.* **14**, 457–465.
Nimmo, J. K. & Lucas, B. W. (1976). *Acta Cryst.* B**32**, 348–353.
Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sharma, C. V. K. & Zaworotko, M. J. (1996). *J. Chem. Soc. Chem. Commun.* pp. 2655–2656.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Solari, E., Klose, A., Floriani, C., Re, N., Chiesi-Villa, A. & Rizzoli, C. (1996). *Polyhedron*, **15**, 4103–4108.
Spek, A. L. (2000). *PLATON*. Version of March 2000. University of Utrecht, The Netherlands.
Weiss, G. S., Parkes, A. S., Nixon, E. R. & Hughes, R. E. (1964). *J. Chem. Phys.* **41**, 3759–3767.
Wheatley, P. S., Lough, A. J., Ferguson, G. & Glidewell, C. (1999). *Acta Cryst.* C**55**, 1486–1489.
Yokozeki, A. & Kuchitsu, K. (1971). *Bull. Chem. Soc. Jpn*, **44**, 72–77.