organic compounds

The supramolecular structure of pyridine-2,6-dicarboxylic acid

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The structure of pyridine-2,6-dicarboxylic acid, $C_7H_5NO_4$, has been determined at 0.71 Å resolution. The molecule is located on a site with mirror symmetry. A one-dimensional supramolecular structure is stabilized in the solid state through a strong symmetric double hydrogen bond, with H···O distances of 1.86 (3) Å and O—H···O angles of 167 (3) and 171 (5)°. This arrangement is similar but not identical to that reported for the isoelectronic isophthalic acid (benzene-1,3-dicarboxylic acid).

Comment

Polycarboxylic acids, which are ubiquitous in organic chemistry and play key roles in cell metabolism, are also good organic supramolecular synthons, due to the ability of the carboxylic acid groups to form moderate to strong hydrogen bonds, with the same group acting as both donor and acceptor (Jeffrey, 1997). Within this class of compounds, benzene, pyridine and polyazine derivatives are of special interest, because they represent a unique example where a high level of predictability of potential supramolecular arrangements is achieved (Moulton & Zaworotko, 2001). For instance, terephthalic acid (benzene-1,4-dicarboxylic acid) is inherently predisposed to produce a one-dimensional supramolecular network (Lommerse *et al.*, 2000), while trimesic acid (benzene-1,3,5-tricarboxylic acid), which can be seen as a trigonal node, yields, as intuitively expected, chicken-wire two-dimensional

(I)
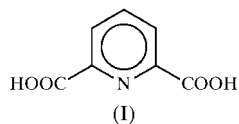
supramolecular sheets (Duchamp & Marsh, 1969). Finally, these systems based on very simple molecules are useful for a better understanding of the hydrogen-bonding-type interactions that play a central role in the molecular recognition of

more complex biological systems (Burley & Petsko, 1988). The X-ray structure of dipicolinic acid (pyridine-2,6-dicarboxylic acid), (I), a commercially available compound presenting the above-mentioned characteristics, is reported here.

The asymmetric unit of (I) (Fig. 1 and Table 1) contains one half of the molecule ($Z' = \frac{1}{2}$), with atoms N1, C4 and H4 lying on the *m* plane. The 17 torsion angles defining the conformation are close to 0 or 180° (see archived CIF), yielding a virtually planar molecule. The carboxylic H atom is clearly disordered over two positions, H1 and H2, with site-occupancy factors of 0.66 (3) and 0.34 (3), respectively, and short O—H bond lengths of 0.77 (3) Å.

The C—O bond lengths in (I) are significantly different, with C1—O1 = 1.2750 (10) Å and C1—O2 = 1.2472 (12) Å, but are in agreement with delocalized C⋯O π bonds. In contrast, localized carboxylic acid groups have been observed in two previously reported dipicolinic-acid-containing systems, namely dipicolinic acid monohydrate (Takusagawa *et al.*, 1973) and the cocrystal bis(urea) dipicolinic acid (Smith *et al.*, 1997).

The supramolecular network for (I) is built up of double hydrogen bonds involving two symmetry-related molecules around an inversion centre. The disorder observed for the H atoms produces a hydrogen-bonding scheme of the type O—($\frac{2}{3}$H)···($\frac{1}{3}$H)—O. However, from the diffraction data, it cannot be determined whether this disorder is spatial, with a random distribution on the unit cells, or results from a dynamic exchange of H atoms in the solid state.

Both hydrogen bonds present identical geometric parameters within experimental uncertainty. They can be considered as strong, first because of the short O···H distances of 1.86 (3) Å, and secondly because of the O—H···O angles, which are close to 180° (Table 2). This bridging scheme is repeated through the *m* plane, giving a ribbon-like supramolecular structure (Fig. 2). The angle of 120° between the two carboxylic acid groups is reflected in the zigzag chains running along the long [010] axis. The combination of these two main features, *i.e.* symmetrical hydrogen bonds and the one-dimensional supramolecular structure, implies that (I) is a non-polar crystal.

Finally, these infinite chains are stacked along the short [100] axis. No inter-chain contacts are detected, despite the short separation of 3.7663 (6) Å between the centroids of two
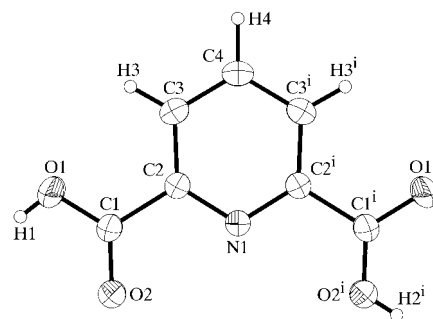
Figure 1
The structure of (I) with displacement ellipsoids at the 50% probability level. Atoms H1^i and H2, which are disordered with H1 and H2^i, have been omitted for clarity [symmetry code: (i) $x, \frac{3}{2} - y, z$].
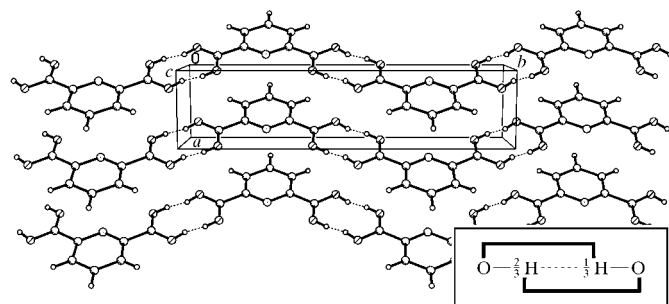
symmetry-related pyridine rings. In particular, the angle between the normal axis of a ring and the vector joining the centroids of two neighbouring rings along [100] is 27.7°, avoiding any π–π-stacking interactions.

The resulting network in (I) is thus actually one-dimensional. In spite of this low dimensionality, the packing of the structure can be considered as very efficient, as reflected in its high packing index of 75.2% (Spek, 1998). For instance, when introducing a water molecule in the lattice (Takusagawa *et al.*, 1973), the observed supramolecular network remains essentially one-dimensional, with the participation of the water molecule in the hydrogen-bonding scheme, but the calculated packing index decreases to 72.3%.

This supramolecular structure is reminiscent of that of isophthalic acid (Alcala & Martínez-Carrera, 1972), but it is not isostructural. Both compounds generate one-dimensional non-interacting zigzag chains, with classical centrosymmetric double hydrogen bonds involving the carboxylic acid groups. However, the carboxylic acid H atom is localized in the case of isophthalic acid, giving a non-disordered bridge of the type O—(H)$\cdots$O, rather than O—($\frac{2}{3}$H)$\cdots$($\frac{1}{3}$H)—O, as observed in (I). This very subtle difference is sufficient to induce a change in the crystal symmetry, changing the space group from $P2_1/m$ in (I) to $P2_1/c$ in isophthalic acid, the latter corresponding moreover to a pseudo-orthorhombic cell (β close to 90° and $Z = 4$). Another striking difference is that these isoelectronic molecules generate zigzag chains with different periodicities, 16.1667 (12) Å for (I) *versus* 16.42 Å for isophthalic acid. These small changes are probably directly controlled by the relative acidity of the molecules.

The observed one-dimensional network for (I) is consistent with the presence of two symmetry-related carboxylic acid groups. In the case of the bis(urea) dipicolinic acid cocrystal (Smith *et al.*, 1997), the presence of two components with a strong ability to form hydrogen bonds generates a three-dimensional network. The opposite case is represented by 2,6-dicarboxypyridine *N*-oxide (Rychlewska & Gdaniec, 1977). Here, the presence of the oxide drives the formation of intramolecular hydrogen bonds, which moreover stabilize the system by an entropic factor. All potential intermolecular contacts are then withdrawn and the structure can be formally described as a zero-dimensional aggregate. Similar considerations can be performed for pyridine-2,6-dicarboxylate-based systems. If this anion crystallizes with a relatively small cation, such as Ca^{2+}, a three-dimensional supramolecular structure is obtained, including water-bonded molecules (Strahs & Dickerson, 1968), and it is reduced to a one-dimensional network if a bulky cation is used (Ng, 1997).

In conclusion, compound (I) has been demonstrated to be a good self-complementary component for low-dimensional organic supramolecular chemistry, which can probably be extended to a wide range of related dicarboxylic acid systems.

Experimental

Single crystals of (I) were first obtained as a hydrolysis by-product of an attempt at the crystallization of a more complex ligand as a chlorhydrate, by dispersion of HCl vapour in a sealed chamber. However, the same compound was also obtained by recrystallization of dipicolinic acid from hot water, allowing a slow temperature decrease of a saturated solution in a Dewar vessel.

Crystal data

$C_7H_5NO_4$	$D_x = 1.639$ Mg m^{-3}
$M_r = 167.12$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/m$	Cell parameters from 70
$a = 3.7663$ (6) Å	reflections
$b = 16.1667$ (12) Å	$\theta = 3.9$–18.4°
$c = 5.5705$ (4) Å	$\mu = 0.14$ mm^{-1}
$\beta = 93.156$ (7)°	$T = 300$ (2) K
$V = 338.67$ (6) Å^3	Irregular, colourless
$Z = 2$	$0.7 \times 0.4 \times 0.4$ mm

Data collection

Bruker $P4$ diffractometer	$h = -5 \rightarrow 5$
ω scans	$k = -22 \rightarrow 22$
3920 measured reflections	$l = -7 \rightarrow 7$
1021 independent reflections	3 standard reflections
937 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{int} = 0.036$	intensity decay: 1%
$\theta_{max} = 30°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0827P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 0.0236P]$
$wR(F^2) = 0.121$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
1021 reflections	$\Delta\rho_{max} = 0.34$ e Å^{-3}
74 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}
All H-atom parameters refined	

Figure 2
Three one-dimensional chains in the supramolecular structure of (I). Note that all carboxylic acid H atoms have a site-occupancy factor of $\frac{2}{3}$ or $\frac{1}{3}$. Dotted lines indicate non-bonding H$\cdots$H separations. The inset describes the disorder observed for intermolecular bridges; O$\cdots$H bonds are represented with bold lines and the non-bonding H$\cdots$H contact with a dotted line.

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.2750 (10)	C2—C3	1.3973 (12)
C1—O2	1.2472 (12)	C3—C4	1.3894 (11)
C1—C2	1.4973 (11)	C4—H4	1.04 (3)
C2—N1	1.3342 (9)		
O2—C1—O1	123.81 (9)	C3—C2—C1	119.57 (7)
O2—C1—C2	119.96 (8)	C4—C3—C2	118.58 (8)
O1—C1—C2	116.23 (8)	C3—C4—C3^i	118.04 (12)
N1—C2—C3	124.29 (8)	C2^i—N1—C2	116.22 (10)
N1—C2—C1	116.14 (8)		

Symmetry code: (i) $x, \frac{3}{2} - y, z$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1$\cdots$O2^i	0.77 (3)	1.86 (3)	2.6252 (12)	167 (3)
O2—H2$\cdots$O1^i	0.77 (3)	1.86 (3)	2.6252 (12)	171 (5)

Symmetry code: (i) $-x, 1-y, 1-z$.

H atoms were found in difference maps and were refined with free coordinates. For the disordered hydroxyl H atoms, site-occupancy factors were refined, with the sum of the occupancy factors constrained to 1.0. The O1—H1 and O2—H2 distances were restrained to a unique target value, with an s.u. of 0.01 Å, while C—H distances were unrestrained. Isotropic displacement parameters for atoms H1 and H2 were constrained to a unique target value. Finally, atoms H3 and H4 were refined with free isotropic displacement parameters.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1531). Services for accessing these data are described at the back of the journal.

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