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Pyrazine-2,3-dicarboxylic acid

Thathan Premkumar,[a] Subbiah Govindarajan,[a] Wojciech Starosta[b] and Janusz Leciejewicz[b]*

[a]Department of Chemistry, Bharathiar University, Coimbatore 641 046, Tamilnadu, India, and [b]Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warszawa, Poland

Correspondence e-mail: jlec@orange.ichtj.waw.pl

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.031
wR factor = 0.110
Data-to-parameter ratio = 9.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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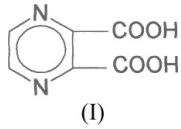
The title compound, $C_6H_4N_2O_4$, is a new unsolvated form of pyrazine-2,3-dicarboxylic acid. The asymmetric unit contains two independent molecules with different geometry. The planes of the carboxylic groups make dihedral angles with the planar pyrazine rings of 22.7 (2) and 50.0 (2)° in one molecule, and 9.7 (2) and 79.1 (2)° in the other. The molecules form layers in which hydrogen bonds occur, with O···O distances ranging from 2.728 (2) to 2.773 (2) Å. The shortest distance between two adjacent layers is 3.5 Å, indicating van der Waals interactions.

Comment

The structures of three isomers of pyrazinedicarboxylic acid have been reported, all as dihydrates: pyrazine-2,3-dicarboxylic acid (Takusagawa & Shimada, 1973), pyrazine-2,5-dicarboxylic acid (Ptasiewicz-Bąk & Leciejewicz, 1998) and pyrazine-2,6-dicarboxylic acid (Ptasiewicz-Bąk & Leciejewicz, 2003). The crystal structures of the last two compounds contain sheets composed of acid molecules in which the carboxylate groups are coplanar with the pyrazine rings. By contrast, in the structure of pyrazine-2,3-dicarboxylic acid dihydrate, only one carboxylic group is coplanar with the pyrazine ring, and the other makes a dihedral angle of *ca* 90° with it. This geometry has also been observed in the structures of metal complexes with pyrazine-2,3-dicarboxylate and water ligands, for example, in a magnesium(II) complex (Ptasiewicz-Bąk & Leciejewicz, 1997*a*) and in calcium(II) complexes (Ptasiewicz-Bąk & Leciejewicz, 1997*b*; Starosta & Leciejewicz, 2004).



(I)

The asymmetric unit of the unsolvated title compound, (I), contains two independent acid molecules (Fig. 1). Both pyrazine rings are almost planar, with r.m.s. deviations from the mean plane of 0.019 and 0.003 Å. The dihedral angles between the planes of the pyrazine rings and the planes of the carboxylic acid groups are 22.7 (2) (O11—C17—O12) and 50.0 (2)° (O13—C18—O14) in molecule 1, and 9.7 (2) (O21—C27—O22) and 79.1 (2)° (O23—C28—O24) in molecule 2.

The molecules of (I) form layers. The lack of water molecules simplifies the network of hydrogen bonds, which occur only within a sheet, linking the O atoms of carboxyl OH groups as donors with N atoms as well as carboxylate O atoms, all belonging to adjacent acid molecules. The observed O···O

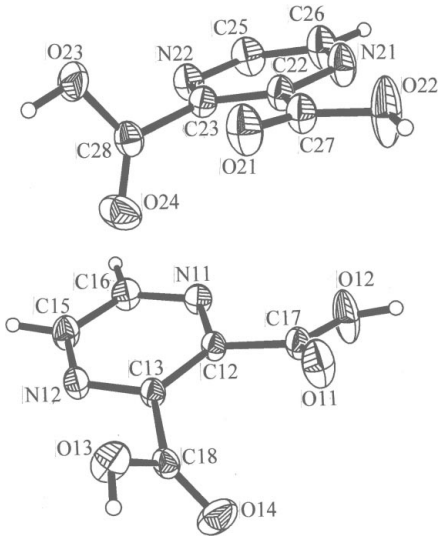


Figure 1
The asymmetric unit of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

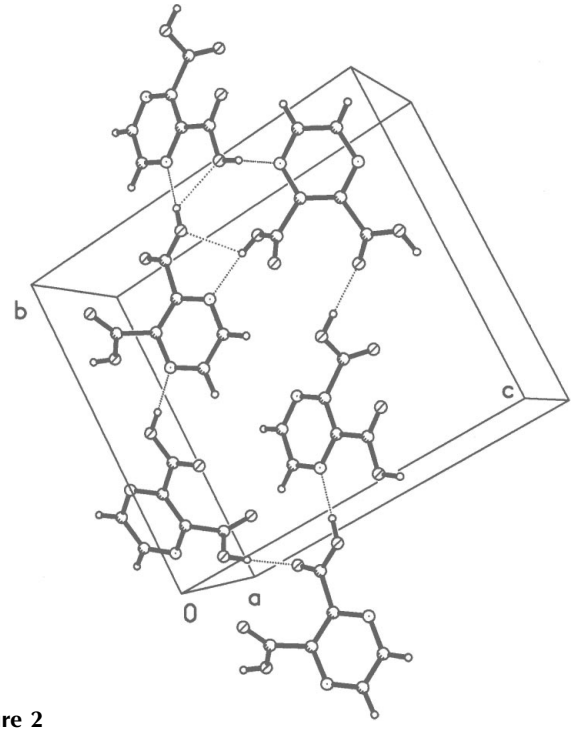


Figure 2
A fragment of a layer of (I) in the crystal structure. Hydrogen bonds are shown as dotted lines.

distances fall in the range 2.726 (2)–2.773 (2) Å (Table 1). Fig. 2 shows a fragment of a layer with the hydrogen bonds represented by dotted lines. Van der Waals contacts operate between adjacent layers, as the shortest distance between two atoms belonging to different layers is *ca* 3.5 Å.

Experimental

Single crystals of the title compound, in the form of colourless needles, were extracted from a mass of polycrystalline material obtained after evaporation to dryness at room temperature of an aqueous solution containing a mixture of pyrazine-2,3-dicarboxylic acid dihydrate (Aldrich) and lanthanum nitrate hexahydrate (Aldrich) in the molar ratio 1.5:1.

Crystal data

$C_6H_4N_2O_4$
M_r = 168.11
Monoclinic, $P2_1/c$
a = 7.9690 (16) Å
b = 11.952 (2) Å
c = 14.336 (3) Å
β = 101.69 (3)°
V = 1337.1 (5) Å^3
Z = 8
D_x = 1.670 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 6–15°
μ = 0.14 mm^{-1}
T = 293 (2) K
Block (cut from a needle), colourless
0.24 × 0.22 × 0.20 mm

Data collection

Kuma KM-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2528 measured reflections
2423 independent reflections
1612 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 25.2°
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 0$
$l = -17 \rightarrow 0$
2 standard reflections
every 200 reflections
intensity decay: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.110
S = 1.03
2423 reflections
249 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0769P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O23—H23···O11^{i}	0.85 (3)	1.92 (3)	2.763 (2)	169 (3)
O13—H13···N11^{ii}	0.81 (3)	1.97 (3)	2.776 (2)	172 (2)
O13—H13···O12^{ii}	0.81 (3)	2.54 (3)	2.935 (2)	112 (2)
O12—H12···N21^{iii}	0.90 (3)	1.83 (3)	2.730 (2)	176 (3)
O22—H22···N12^{iv}	0.93 (3)	1.84 (3)	2.772 (2)	175 (3)

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

Data collection: *KM*-4 *Software* (Kuma, 1996); cell refinement: *KM*-4 *Software*; data reduction: *DATAPROC* (Kuma, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1992); software used to prepare material for publication: *SHELXL*97.

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