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# Pyrazine-2,3-dicarboxamide

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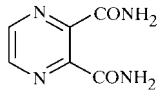
In the crystal structure of the title diamide, $C_6H_6N_4O_2$, linear tapes of carboxamide N—H···O and pyrazine C—H···N hydrogen-bond dimers are connected by N—H···O bonds to form a staircase-like pattern.

## Comment

The role of the carboxamide functional group in crystal packing and molecular recognition is well studied (Leiserowitz & Schmidt, 1969; Desiraju, 1989; Palmore & MacDonald, 2000). A common feature in the crystal structures of amides is the short 5.1 Å axis, a consequence of translation-related centrosymmetric amide dimers connected by N—H···O bonds. While benzamide [Cambridge Structural Database (CSD; 2000) refcode BZAMID; Penfold & White, 1959] has the archetypical amide structure, pyrazine carboxamide (CSD refcode PYRZIN; Takaki *et al.*, 1960) is quite different and exists in five different polymorphic forms. This shows that the isoelectronic CH → N replacement in the molecule has a profound effect on the crystal structure. The role of N—H···O and C—H···N mediated supramolecular synthons in the polymorphs of pyrazine carboxamide has been discussed recently by Desiraju (1997). With this background, and given our interest in understanding crystal structures with strong and weak hydrogen bonds (Kumar & Nangia, 2000), we report here the crystal structure of pyrazine-2,3-dicarboxamide, (I), which exhibits an interesting staircase-like architecture. Compound (I) has also been used as a ligand in metal complexes showing magnetic properties (Klein *et al.*, 1983).




(I)

The molecular geometry of (I) in the crystal is shown in Fig. 1. One of the carboxamide groups (C10) is in the plane of the heterocyclic ring while the other (C7) is out of plane (see Table 1 for torsion angles). The coplanar conformation of the C10 carboxamide in the crystal is stabilized by the intramolecular N5—H5*B*···N6 hydrogen bond (Table 2).

The carboxamide group that is coplanar with the heterocyclic ring (C10) forms centrosymmetric N—H···O dimers [N5—H5*A*···O2$^{iii}$; symmetry code: (iii) $-x, 1-y, -z$] which extend in a linear tape along [201] *via* C—H···N dimers [C11—H11···N3$^{vi}$; symmetry code: (vi) $2-x, 1-y, 1-z$]. Such C—H···N dimers were noted recently in the crystal structures of some pyrazines (Thalladi *et al.*, 2000). In the normal 5.1 Å packing, translation-related amide dimers are connected by N—H···O bonds to produce a sheet-like structure, as in benzamide (Desiraju, 1989). In (I), however, the N—H of the C10 carboxamide is bonded to the O atom of the out-of-plane C7 carboxamide group [N5—H5*B*···O1$^{iv}$; symmetry code: (iv) $x, y-1, z$], connecting the tapes mentioned above by translation along **b**. This produces a staircase-like pattern, with the tape along [201] constituting the flat step and the N—H···O bond along [010] giving the

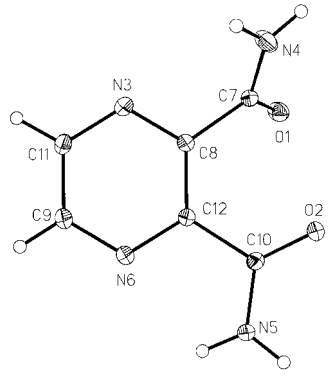



**Figure 1**
The *ORTEP*II (Johnson, 1976) diagram and atom-numbering scheme for (I). The C10 carboxamide is in the plane of the heterocyclic pyrazine ring and the C7 carboxamide is out-of-plane. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

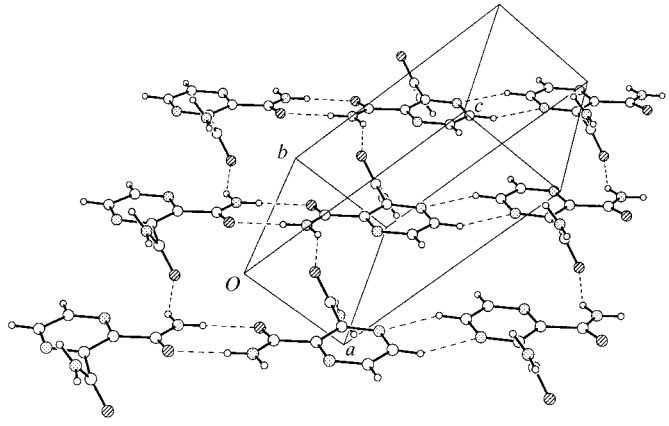



**Figure 2**
The crystal structure of (I), showing the molecular staircase. The linear tapes of N—H···O and C—H···N dimers [the hydrogen bonds with symmetry codes (iii) and (vi)] along [201] form the steps of the staircase and the N—H···O bonds [the hydrogen bond with symmetry code (iv)] along [010] build the network upwards. Symmetry codes are given in Table 2.

height to the staircase (Fig. 2). Such staircase networks are in turn connected by N4—H4*A*···O2$^{i}$, N4—H4*B*···O1$^{ii}$, N4—H4*B*···O2$^{ii}$ and C9—H9···N6$^{v}$ hydrogen bonds (Fig. 3) [symmetry codes: (i) $1-x, 2-y, -z$; (ii) $1+x, y, z$; (v) $1-x, -y, 1-z$]. A molecular staircase motif was also identified recently in the crystal structure of the complex of benzene-1,2,4,5-tetracarboxylic acid and hexamethylenetetramine (Lough *et al.*, 2000).

In (I), hydrogen bonding in both the amide groups is satisfied because the number of strong donors (four, two $NH_2$ groups) and acceptors (four, two C=O groups) are matched. The weak C—H donors are bonded to the heterocyclic N atoms. The crystal structure may therefore be rationalized *via* the preferred combinations of hydrogen-bond donors and acceptors (Etter, 1990). It may be noted that each atom in (I) is either a donor (N—H, C$sp^2$—H) or an acceptor (C=O, ring N) and, further, that all these groups are involved in hydrogen bonding. The title crystal structure may be compared with that of pyrazine-2,3-dicarboxylic acid, which crystallizes as a dihydrate (Takusagawa & Shimada, 1973); the imbalance of the donor–acceptor ratio in the diacid (2:4) is compensated for by the inclusion of the two water molecules.

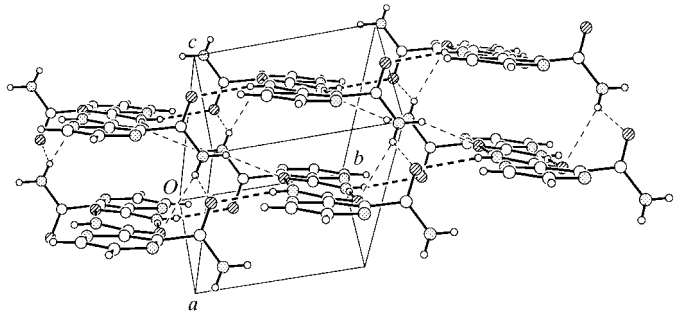



**Figure 3**
A side view of the molecular staircase networks in (I). The hydrogen bonds with symmetry codes (iii) and (iv) are shown as thick dotted lines. The C7 carboxamide $NH_2$ group connects these staircase networks *via* the hydrogen bonds with symmetry codes (i) and (ii), shown as thin dotted lines. The C—H···N interaction with symmetry code (v) has been omitted for clarity. Symmetry codes are given in Table 2.

In a recent survey of the CSD for bimolecular motifs in organic crystal structures, Allen *et al.* (1999) noted that the eight-membered carboxamide dimer synthon occurs in the maximum number of structures (627) and tops the list of 75 different ring motifs analysed. We have discussed this crystal structure in terms of robust amide dimer and pyrazine dimer supramolecular synthons (Desiraju, 1997), although larger hydrogen-bond patterns involving both the amide groups are present in the structure. The identification of robust, in other words recurring, supramolecular synthons is a current theme in crystal engineering.

## Experimental

Colourless crystals of (I) were obtained by crystallization of pyrazine-2,3-dicarboxamide from water (m.p. 541 K). The compound was purchased from Acros Chemicals and used as received.

*Crystal data*

$C_6H_6N_4O_2$
$M_r$ = 166.15
Triclinic, $P\overline{1}$
$a$ = 5.0250 (3) Å
$b$ = 7.0977 (3) Å
$c$ = 10.1196 (5) Å
$\alpha$ = 70.826 (3)°
$\beta$ = 81.868 (3)°
$\gamma$ = 81.163 (3)°
$V$ = 335.25 (3) Å$^3$
$Z$ = 2
$D_x$ = 1.646 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1868 reflections
$\theta$ = 3.14–30.02°
$\mu$ = 0.129 mm$^{-1}$
$T$ = 153 (2) K
Cubic, colourless
0.32 × 0.30 × 0.30 mm

*Data collection*

Nonius KappaCCD diffractometer
$\omega$ scans
2623 measured reflections
1868 independent reflections
1754 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.015
$\theta_{max}$ = 30.02°
$h = -7 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -14 \rightarrow 13$
Intensity decay: <1%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.101
$S$ = 1.058
1835 reflections
133 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 0.0906P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.50 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.20 e Å$^{-3}$

**Table 1**
Selected torsion angles (°).

| | | | |
|---|---|---|---|
| O1—C7—C8—N3 | −114.85 (9) | O2—C10—C12—N6 | −173.24 (8) |
| N4—C7—C8—N3 | 62.39 (10) | N5—C10—C12—N6 | 6.84 (11) |
| O1—C7—C8—C12 | 60.71 (12) | O2—C10—C12—C8 | 6.00 (13) |
| N4—C7—C8—C12 | −122.06 (9) | N5—C10—C12—C8 | −173.92 (8) |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N4—H4*A*···O2$^{i}$ | 0.873 (15) | 2.282 (15) | 3.097 (1) | 155.3 (14) |
| N4—H4*B*···O1$^{ii}$ | 0.871 (15) | 2.393 (15) | 3.080 (1) | 136.0 (13) |
| N4—H4*B*···O2$^{ii}$ | 0.871 (15) | 2.373 (15) | 3.153 (1) | 149.1 (13) |
| N5—H5*A*···O2$^{iii}$ | 0.882 (16) | 2.037 (16) | 2.919 (1) | 177.5 (15) |
| N5—H5*B*···O1$^{iv}$ | 0.874 (15) | 2.108 (15) | 2.876 (1) | 146.4 (14) |
| N5—H5*B*···N6 | 0.874 (15) | 2.271 (15) | 2.657 (1) | 106.6 (12) |
| C9—H9···N6$^{v}$ | 0.964 (15) | 2.725 (15) | 3.545 (1) | 143.3 (12) |
| C11—H11···N3$^{vi}$ | 0.993 (15) | 2.470 (15) | 3.325 (1) | 144.0 (11) |

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* in *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTON* (Spek, 1992); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1424). Services for accessing these data are described at the back of the journal.

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