organic compounds

Piperazine-2,5-dione–oxalic acid–water (1/1/2) and a redetermination of piperazine-2,5-dione, both at 120 K: hydrogen-bonded sheets containing multiple ring types

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In piperazine-2,5-dione–oxalic acid–water (1/1/2), $C_4H_6N_2O_2 \cdot C_2H_2O_4 \cdot 2H_2O$, both organic components lie across inversion centres in space group $P\overline{1}$. The molecules are linked by N—H···O and by both two-centre O—H···O and three-centre O—H···(O)$_2$ hydrogen bonds into sheets built from $R_1^2(5)$, $R_2^2(8)$, $R_4^4(8)$ and $R_5^4(15)$ rings. In piperazine-2,5-dione, $C_4H_6N_2O_2$, where the molecules lie across centres of inversion in space group $P2_1/c$, the molecules are linked by paired N—H···O hydrogen bonds into ribbons of centrosymmetric $R_2^2(8)$ rings, which are further linked into sheets by C—H···O hydrogen bonds, generating $R_4^3(14)$ rings between the ribbons.

Comment

Hydrogen-bonded adducts formed between piperazine-2,5-dione (diketopiperazine, DKP) and carboxylic acids are often characterized by the formation of ribbons of piperazine-2,5-dione molecules; these can be linked into sheets by carboxylic acids, while monocarboxylic acids can simply be pendent from these ribbons (Kartha *et al.*, 1981; Luo & Palmore, 2002). A striking exception is found in the 1:2 adduct of piperazine-2,5-dione with 2-hydroxybenzoic acid, where a finite three-component aggregate is formed (Varughese & Kartha, 1982). As part of a wider study of the supramolecular structures of systems containing piperazine-2,5-dione, which includes the study both of hydrogen-bonded systems and of metal coordination complexes, we report here the structure of piperazine-2,5-dione–oxalic acid–water (1/1/2), (I), together with a redetermination at 120 K of piperazine-2,5-dione itself, (II).

The organic components in (I) both lie across inversion centres in space group $P\overline{1}$ and the water molecule lies in a general position. While the selection of the asymmetric unit in a three-component adduct such as this provides some degree of flexibility and choice, for compound (I) it is possible to select a compact and connected asymmetric unit such that the heterocyclic and acidic components lie across the inversion centres at $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, 1, 0)$, respectively (Fig. 1).
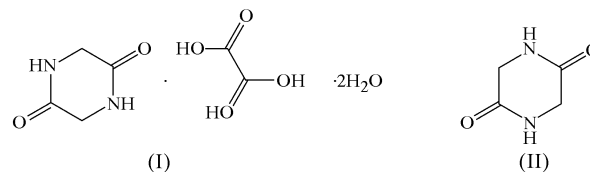
The H atoms are fully ordered and the location of the unique H atom in the acid, as deduced from a difference map, is fully consistent with the independent C—O bond distances in this component (Table 1). The bond distances in the dione are all typical of their types, but the long C—C bond in the acid is consistent with such values in simple derivatives of oxalic acid (Allen *et al.*, 1987).

The independent components are linked into sheets by a combination of one two-centre N—H···O hydrogen bond, two two-centre O—H···O hydrogen bonds and one almost planar, but asymmetric, three-centre O—H···(O)$_2$ hydrogen bond (Table 2). The formation of the sheet structure, which contains four distinct types of hydrogen-bonded ring, is readily analysed in terms of two one-dimensional substructures
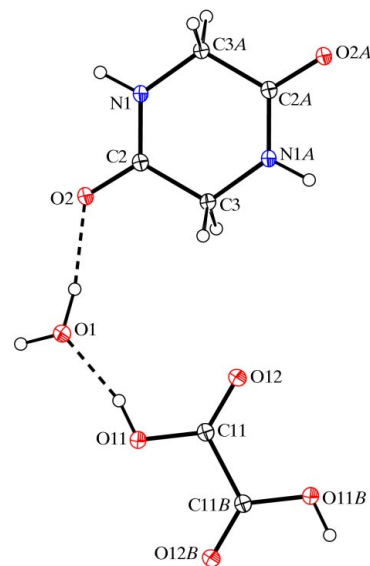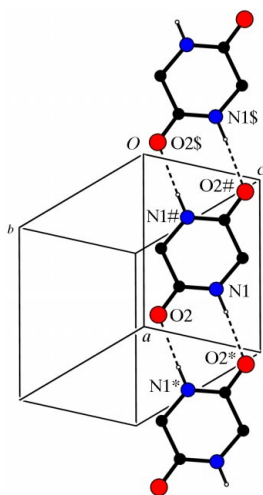

Figure 1
The independent molecular components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level, and atoms labelled with the suffixes *A* and *B* are at the symmetry positions $(1 - x, -y, 1 - z)$ and $(-x, 2 - y, -z)$, respectively.

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generated, respectively, by the piperazinedione component on the one hand and by the acid and water molecules on the other; the linking of these substructures generates the sheet.

In the first substructure, amide atoms N1 at (x, y, z) and $(1 - x, -y, 1 - z)$ are both components of the reference piperazinedione molecule centred at $(\frac{1}{2}, 0, \frac{1}{2})$; these atoms act as hydrogen-bond donors to amide atoms O2 at $(2 - x, -y, 1 - z)$ and $(-1 + x, y, z)$, respectively, which are themselves components of the dione molecules centred at $(\frac{3}{2}, 0, \frac{1}{2})$ and $(-\frac{1}{2}, 0, \frac{1}{2})$. Propagation by inversion of this hydrogen bond then generates a $C(6)[R_2^2(8)]$ chain of rings (Bernstein et al., 1995) running parallel to the [100] direction, in which dione molecules centred at $(n + \frac{1}{2}, 0, \frac{1}{2})$ (n = zero or integer) alternate with $R_2^2(8)$ rings centred at $(n, 0, \frac{1}{2})$ (n = zero or integer) (Fig. 2).

In the second substructure, carboxyl atom O11 at (x, y, z), which forms part of the acid molecule centred across $(0, 1, 0)$, acts as a hydrogen-bond donor to water atom O1, also at (x, y, z). This water atom in turn acts as a donor, via H1B, to carbonyl atom O12 at $(1 + x, y, z)$ and to carboxyl atom O11 at $(1 - x, 2 - y, -z)$, both of which lie in the acid molecule centred across $(1, 1, 0)$. Although the three-centre hydrogen bond involving H1B is asymmetric (Table 2), the sum of the angles at H1B is 358°; while the longer, weaker, component may be an adventitious consequence of the other, shorter, O—H⋯O interactions in the structure, its presence or absence does not affect the overall supramolecular structure, only the details of the hydrogen-bonded ring systems. Propagation of these two hydrogen-bonding interactions generates a chain of edge-fused $R_1^2(5)$ and $R_4^4(8)$ rings running parallel to the [100] direction, in which acid molecules centred at $(n, 1, 0)$ (n = zero or integer) alternate with $R_4^4(8)$ rings centred at $(n + \frac{1}{2}, 1, 0)$ (n = zero or integer) (Fig. 3).

The final O—H⋯O hydrogen bond links the two types of [100] chain into a sheet. The water molecule at (x, y, z), which lies in the acid–water chain along $(x, 1, 0)$, acts as a hydrogen-bond donor, via H1A, to amide atom O2, also at (x, y, z), which lies in the piperazinedione chain along $(x, 0, \frac{1}{2})$. Propagation by inversion of this final hydrogen bond then links the chains into a (012) sheet in which piperazinedione chains alternate with acid–water chains (Fig. 4). The hydrogen-bonded rings that link the two types of chain are of $R_5^4(15)$ type so that there are, in fact, four types of ring embedded within the sheet, of $R_1^2(5)$, $R_2^2(8)$, $R_4^4(8)$ and $R_5^4(15)$ types. There are no direction-specific interactions between adjacent sheets.

The two substructures observed in the structure of (I) may usefully be compared with the hydrogen-bonded structures of piperazine-2,5-dione and oxalic acid dihydrate. Two poly-

Figure 3
Part of the crystal structure of (I), showing the formation of a [100] chain of edge-fused rings built from acid and water molecules only. Atoms marked with an asterisk (*), a hash (#) or a dollar sign ($) are at the symmetry positions $(1 - x, 2 - y, -z)$, $(-x, 2 - y, -z)$ and $(1 + x, y, z)$, respectively.
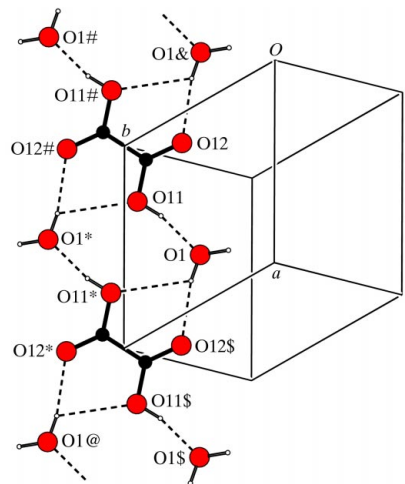

Figure 2
Part of the crystal structure of (I), showing the formation of a [100] chain of rings built from piperazinedione molecules only. For clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), a hash (#) or a dollar sign ($) are at the symmetry positions $(2 - x, -y, 1 - z)$, $(1 - x, -y, 1 - z)$ and $(-1 + x, y, z)$, respectively.
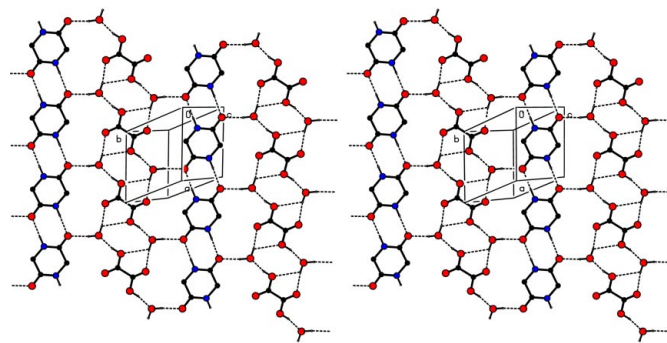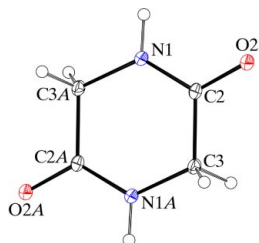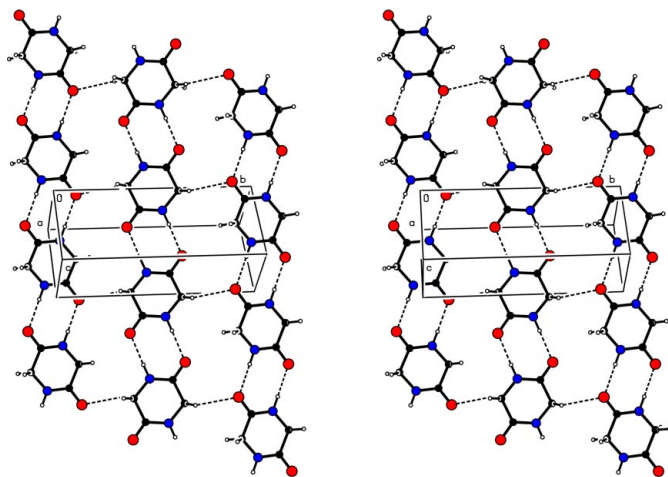

Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of a (012) sheet containing $R_1^2(5)$, $R_2^2(8)$, $R_4^4(8)$ and $R_5^4(15)$ rings. For clarity, H atoms bonded to C atoms have been omitted.

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Figure 5
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and atoms labelled with the suffix *A* are at the symmetry position $(2 - x, 1 - y, 2 - z)$.

Figure 6
A stereoview of part of the crystal structure of (II), showing the formation of a $(11\bar{1})$ sheet of $R_2^2(8)$ and $R_4^3(14)$ rings.

morphs of oxalic acid dihydrate have been reported (Iwasaki *et al.*, 1967; Delaplane & Ibers, 1969); in each form, the oxalic acid molecules lie across centres of inversion, but the hydrogen-bonded network is three-dimensional in each polymorph, as opposed to the two-dimensional acid–water substructure found in (I). The structure of piperazine-2,5-dione, (II), was reported many years ago (Degeilh & Marsh, 1959) to consist of hydrogen-bonded ribbons of centrosymmetric molecules. We have now reinvestigated this structure at 120 K (Fig. 5) and we find that these [101] ribbons are in fact linked by a C—H···O hydrogen bond (Table 3) into $(11\bar{1})$ sheets containing both $R_2^2(8)$ and $R_4^3(14)$ rings (Fig. 6). In the formation of adduct (I), the C—H···O hydrogen bonds in (II) have been displaced by much stronger O—H···O hydrogen bonds, while the N—H···O hydrogen bonds are all preserved.

Experimental

Oxalic acid (0.5 g, 3.96 mmol) was dissolved in hot water. To the resulting clear solution was added a solution of piperazine-2,5-dione (0.45 g, 3.96 mmol) in hot water. The mixture was heated over a water bath for 5 h to obtain a clear solution. This solution was allowed to cool to room temperature and crystals of (I) suitable for single-crystal X-ray diffraction were obtained after 2 d [m.p. 473 K; IR: 1681 cm^{-1}

(C=O)]. Crystals of (II) were also obtained from aqueous solution [IR: 1702 cm^{-1} (C=O)].

Compound (I)

Crystal data

$C_4H_6N_2O_2 \cdot C_2H_2O_4 \cdot 2H_2O$	$Z = 1$
$M_r = 240.18$	$D_x = 1.583$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.1494\ (7)$ Å	Cell parameters from 1073
$b = 6.1984\ (8)$ Å	reflections
$c = 7.3642\ (9)$ Å	$\theta = 3.0–27.5°$
$\alpha = 83.486\ (6)°$	$\mu = 0.15$ mm^{-1}
$\beta = 82.580\ (8)°$	$T = 120\ (2)$ K
$\gamma = 65.067\ (7)°$	Plate, colourless
$V = 251.86\ (6)$ Å^3	$0.42 \times 0.18 \times 0.08$ mm

Data collection

Nonius KappaCCD diffractometer	1043 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.048$
Absorption correction: multi-scan	$\theta_{max} = 27.6°$
(*SADABS*; Sheldrick, 2003)	$h = -7 \rightarrow 7$
$T_{min} = 0.931$, $T_{max} = 0.988$	$k = -8 \rightarrow 8$
4586 measured reflections	$l = -9 \rightarrow 9$
1143 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0795P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 0.0483P]$
$wR(F^2) = 0.136$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.20$	$(\Delta/\sigma)_{max} < 0.001$
1143 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
74 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
H-atom parameters constrained	

Compound (II)

Crystal data

$C_4H_6N_2O_2$	$D_x = 1.646$ Mg m^{-3}
$M_r = 114.11$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 508
$a = 3.8967\ (10)$ Å	reflections
$b = 11.527\ (3)$ Å	$\theta = 4.4–27.5°$
$c = 5.159\ (2)$ Å	$\mu = 0.13$ mm^{-1}
$\beta = 96.46\ (2)°$	$T = 120\ (2)$ K
$V = 230.26\ (12)$ Å^3	Plate, colourless
$Z = 2$	$0.58 \times 0.26 \times 0.06$ mm

Table 1
Selected geometric parameters (Å) for (I).

N1—C2	1.3192 (18)	C11—O11	1.2982 (16)
N1—C3^i	1.4510 (19)	C11—O12	1.2107 (17)
C2—O2	1.2497 (17)	C11—C11^{ii}	1.545 (3)
C2—C3	1.5042 (19)		

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

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O2	0.91	1.80	2.6971 (14)	168
O1—H1B···O12^{iii}	0.85	1.99	2.8208 (15)	167
O1—H1B···O11^{iv}	0.85	2.46	2.9565 (15)	118
O11—H11···O1	0.84	1.69	2.5040 (14)	164
N1—H1···O2^v	0.88	2.01	2.8807 (16)	170

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

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan
  (*SORTAV*; Blessing, 1995, 1997)
  $T_{min} = 0.935$, $T_{max} = 0.992$
2525 measured reflections
508 independent reflections

490 reflections with $I > 2\sigma(I)$
$R_{int} = 0.105$
$\theta_{max} = 27.5°$
$h = -4 \rightarrow 4$
$k = -14 \rightarrow 14$
$l = -6 \rightarrow 6$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.206$
$S = 1.25$
508 reflections
37 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1311P)^2 + 0.0775P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

Table 3
Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1$\cdots$O2^{vi}	0.88	1.96	2.840 (2)	176
C3—H3$B\cdots$O2^{vii}	0.99	2.51	3.266 (3)	133

Symmetry codes: (vi) $-x + 1, -y + 1, -z + 1$; (vii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.

Crystals of (I) are triclinic; space group $P\bar{1}$ was selected and confirmed by the subsequent analysis. For (II), the space group $P2_1/c$ was uniquely assigned from the systematic absences. All H atoms were located from difference maps. H atoms in the organic components were subsequently treated as riding atoms, with C—H distances of 0.99 Å, N—H distances of 0.88 Å and an O—H distance of 0.84 Å, and with $U_{iso}(H)$ values of $1.2U_{eq}(C,N)$ or $1.5U_{eq}(O)$. H atoms in the water molecule were permitted to ride at the distances found from the difference maps (O—H = 0.85 and 0.91 Å), with $U_{iso}(H)$ values of $1.5U_{eq}(O)$. For both structures, several very intense low-angle reflections were rejected during the data processing because of incomplete profiles and/or detector saturation.

For (I), data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*. For (II), data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*. For both compounds, structure solution: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); structure refinement: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); publication software: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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