organic compounds

Hydrogen-bonding adducts of benzenepolycarboxylic acids with N,N-dimethylformamide: benzene-1,4-dicarboxylic acid N,N-dimethylformamide disolvate, benzene-1,2,4,5-tetracarboxylic acid N,N-dimethylformamide tetrasolvate and benzene-1,2,3-tricarboxylic acid N,N-dimethylformamide disolvate monohydrate

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The N,N-dimethylformamide (DMF) solvates of terephthalic acid, $H_2TA \cdot 2DMF$ ($C_8H_6O_6 \cdot 2C_3H_7NO$), pyromellitic acid, $H_4PMA \cdot 4DMF$ ($C_{10}H_6O_8 \cdot 4C_3H_7NO$), and hemimellitic acid, $H_3HMA \cdot 2DMF \cdot H_2O$ ($C_9H_6O_6 \cdot 2C_3H_7NO \cdot H_2O$), are reported. The DMF solvate of terephthalic acid is centrosymmetric, containing one complete formula unit in the asymmetric unit. Both carboxylic acid groups hydrogen bond to a DMF molecule via an $R_2^2(7)$ O—H···O/C—H···O motif. Discrete $H_2TA \cdot 2DMF$ units are observed. The DMF solvate of pyromellitic acid is centrosymmetric and the asymmetric unit contains half a formula unit. One of the unique carboxylic acid groups forms an $R_2^2(7)$ motif with a DMF molecule, while the other forms a linear O—H···O hydrogen bond to the second unique DMF molecule. Discrete $H_4PMA \cdot 4DMF$ units are observed. The DMF solvate of hemimellitic acid is non-centrosymmetric and includes a molecule of water per formula unit. Both DMF molecules form an $R_2^2(7)$ motif with the two outer carboxylic acid groups of HMA. A one-dimensional ladder structure is formed via hydrogen bonding between the central carboxylic acid group and the water molecules. The carboxylic acid $R_2^2(8)$ head-to-tail motif is not observed in any of these examples. The inclusion of DMF thereby has the effect of limiting the dimensionality of the structures.

Comment

A wide variety of solvents are available to the chemist for the dissolution and recrystallization of compounds. In the case of benzenepolycarboxylic acids, those solvents of most interest in the synthesis of solvent-inclusion clathrates must be capable of hydrogen bonding, containing donor and/or acceptor atoms. A recent study (Nangia & Desiraju, 1999), with corrections applied for the different usages of solvents in recrystallization, has found that the greater the number of donor and acceptor sites on the solvent molecule, the more likely the solvent is to be included in organic crystals. Solvents such as N,N-dimethylformamide (DMF), dimethyl sulfoxide and dioxane, while having low usage as recrystallization solvents, have an extremely high probability of inclusion through their ability to bond to the solute molecule via 'multi-point recognition' using both strong and weak hydrogen bonds.

Numerous examples of benzenepolycarboxylic acid solvent-inclusion compounds exist in the literature (for example, Dale & Elsegood, 2003b; Chatterjee et al., 2000; Herbstein & Kapon, 1978; Herbstein et al., 1978) and yet only one literature example of a single-crystal X-ray structure shows the solvation of a benzenepolycarboxylic acid by DMF, that of benzene-1,3,5-tricarboxylic acid (trimesic acid) N,N-dimethylformamide disolvate ($H_3TMA \cdot 2DMF$; Dale & Elsegood, 2003b). In the presence of DMF, the formation of the common $R_2^2(8)$ head-to-tail carboxylic acid–acid graph-set motif (Leiserowitz, 1976; Etter, 1990; Etter & MacDonald, 1990; Bernstein et al., 1995) is prevented in this structure. Instead, two of the three carboxylic acid groups interact directly with DMF molecules in an $R_2^2(7)$ graph-set pattern, with a combination of strong O—H···O and weaker C—H···O hydrogen bonds (Desiraju & Steiner, 1999), while the third carboxyl group interacts with one of these carboxyl–DMF synthons.
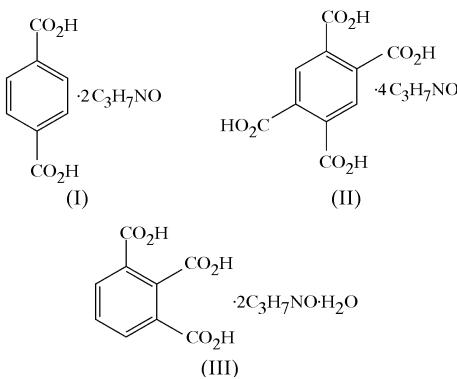
We investigate here the hydrogen-bonding arrays created by the co-crystallization of DMF with benzene-1,4-dicarboxylic acid (terephthalic acid, H_2TA), benzene-1,2,4,5-tetracarboxylic acid (pyromellitic acid, H_4PMA) and benzene-1,2,3-tricarboxylic acid (hemimellitic acid, H_3HMA). H_2TA dissolves easily in DMF, one of very few examples of organic solvents capable of dissolving this acid. X-Ray analysis of colourless crystals grown from the DMF solution at approximately 258 K showed that H_2TA co-crystallizes with two molecules of DMF, producing $H_2TA \cdot 2DMF$, (I). Because of the instability of this compound under ambient conditions, the collation of supporting evidence, such as microanalysis and IR spectra, has proven impossible. The H_2TA molecule in (I) does not possess an inversion centre because of rotational disorder

[82.8 (4):17.2 (4)%] in the carboxyl group attached to atom C1 and complementary rotational disorder in the aldehyde group of the DMF molecule hydrogen bonded to this carboxyl group. The asymmetric unit therefore comprises one complete formula unit (Fig. 1). The geometry of the H_2TA molecule (Table 1) shows good agreement with that found previously (Bailey & Brown, 1967). The H_2TA molecule is roughly planar, with the carboxyl groups only deviating slightly from coplanarity with the aromatic ring [the dihedral angles between the C1–C6 ring and the C7/O1/O2 and C8/O3/O4 planes are 0.7 (3) and 2.2 (3)°, respectively].

Both unique DMF molecules hydrogen bond to their respective carboxyl groups utilizing the same $R_2^2(7)$ synthon observed in $H_3TMA \cdot 2DMF$ (Dale & Elsegood, 2003b), with one strong O—H···O hydrogen bond and one complementary, weaker, C—H···O hydrogen bond (Table 2). Larger dihedral angles occur between the carboxyl groups and the aldehyde groups of their associated DMF molecules within the $R_2^2(7)$ motifs [the dihedral angle between C7/O1/O2 and C9/O5/H9 is 16.4 (3)°, and that between C8/O3/O4 and C12/O6/H12 is 17.3 (3)°]. No further strong hydrogen bonding exists outside the asymmetric unit.
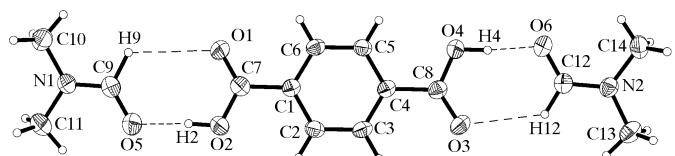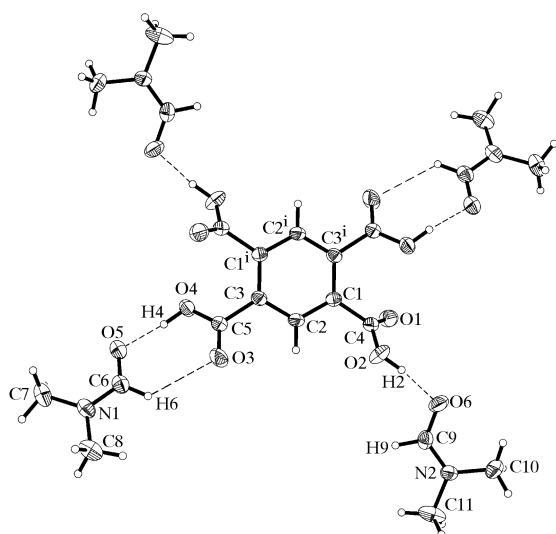
H_4PMA co-crystallizes with four molecules of DMF, yielding $H_4PMA \cdot 4DMF$, (II), which forms readily at room temperature and shows reasonable stability under ambient conditions, in contrast to (I). The H_4PMA molecule lies on a crystallographic centre of symmetry, resulting in the asymmetric unit comprising half of a formula unit (Fig. 2). The geometry of the H_4PMA molecule (Table 3) concurs with that determined previously (Dale & Elsegood, 2003c).

As expected, steric repulsions force the rotation of adjacent carboxyl groups away from the plane of the aromatic ring [the dihedral angles between the C1–C3[i] ring and the C4/O1/O2 and C5/O3/O4 planes are 53.75 (12) and 38.85 (13)°, respectively; symmetry code: (i) $-x$, $2 - y$, $-z$].

The two independent DMF molecules in (II) have differing binding modes to the carboxyl groups: while one adopts the O—H···O/C—H···O $R_2^2(7)$ arrangement seen in both (I) and $H_3TMA \cdot 2DMF$ (Dale & Elsegood, 2003b), the second interacts via a simple linear O—H···O hydrogen bond utilizing the OH group of the second unique carboxyl group (Table 4). The $R_2^2(7)$ motif in this structure contains a shorter, and therefore stronger, C—H···O interaction than the same motif in (I). As with (I), no further strong hydrogen-bonding interactions occur outside the asymmetric unit of (II). The co-crystallization of commercially available $H_3HMA \cdot 2H_2O$ with DMF yields colourless crystals of $H_3HMA \cdot 2DMF \cdot H_2O$, (III) (Table 5 and Fig. 3). Compound (III) was observed to desolvate over a period of a few minutes under ambient conditions, sufficient time to allow IR spectroscopic and microanalyses to be carried out. The asymmetric unit of (III) contains a whole formula unit, in which the outer carboxyl groups of the H_3HMA molecule, at atoms C1 and C3, both hydrogen bond, via the $R_2^2(7)$ synthon, to different DMF molecules, creating $H_3HMA \cdot 2DMF$ units (Table 6). These secondary building blocks are linked into a one-dimensional ladder structure (Fig. 4) by hydrogen bonding involving the molecule of water included in the asymmetric unit.

The inner carboxyl group at atom C2 lies almost perpendicular to the plane of the aromatic ring [the dihedral angle between the C1–C6 ring and the C8/O3/O4 plane is

Figure 1
A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level, H atoms are represented by circles of arbitrary radius and hydrogen bonds are shown as dashed lines.


Figure 2
A view of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level, H atoms are represented by circles of arbitrary radius and hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $-x$, $2 - y$, $-z$.]


Figure 3
A view of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level, H atoms are represented by circles of arbitrary radius and hydrogen bonds are shown as dashed lines.

81.54 (10)°], as observed in the dihydrate of H$_3$HMA (Fornies-Marquina et al., 1972; Takusagawa & Shimada, 1973; Mo & Adman, 1975) and in its 2-methyl ester (Dale & Elsegood, 2003a). This carboxyl group, aided by its anti-planar conformation (Leiserowitz, 1976), forms a zigzag $C_2^2(6)$ chain by hydrogen bonding with one OH group of the water molecule.

A search of the Cambridge Structural Database (CSD; Version 5.25 of November 2003, plus one update; Allen, 2002) identifies 30 hits containing both carboxylic acid groups and DMF molecules, of which six are redeterminations. A more detailed search for hydrogen-bonding motifs in carboxylic acid/DMF structures [constraining the O···O contact distance to within the range 2–3.2 Å and the C···O contact distance to within the range 2.5–3.5 Å; redeterminations omitted from statistical analysis] indicates that 19 structures contain O—H···O hydrogen bonding between the CO$_2$H group and the aldehyde O atom, the mean O···O contact distance being 2.597 (15) Å (range 2.507–2.888 Å). 13 of these 19 structures also contain C—H···O hydrogen bonding, producing the $R_2^2(7)$ motif observed in (I), (II) and (III). The mean O···O contact distance within this population [containing the $R_2^2(7)$ motif] is 2.585 (13) Å (range 2.507–2.692 Å), while the mean O—H···O angle is 169.4 (17)°, indicating a slight shortening in the O—H···O hydrogen-bond distance when C—H···O interactions exist and showing good agreement with the hydrogen-bond geometry observed for the same motifs in (I), (II) and (III). C—H···O interactions within this population

have a mean C···O contact distance of 3.24 (3) Å (range 3.054–3.490 Å). It is interesting to note the structure of 1,1′-binaphthyl-2,2′-dicarboxylic acid bis(DMF) clathrate (CSD refcode CIWJIB10; Csoregh et al., 1986), in which two DMF binding modes are present, viz. one $R_2^2(7)$ motif and one simple linear O—H···O motif, just as observed in the structure of (II). The O···O contact distances within these motifs are 2.692 and 2.888 Å, respectively, considerably longer than those observed in (II) [2.5723 (12) and 2.5508 (13) Å, respectively], presumably because of the increased steric bulk of the solute molecule. While the CO$_2$H/DMF $R_2^2(7)$ synthon has relatively few examples in the CSD compared with the analogous, well studied, carboxylic acid–pyridine $R_2^2(7)$ synthon (Vishweshwar et al., 2002), the majority (15) of the 21 CSD structures containing the CO$_2$H–formyl group $R_2^2(7)$ synthon [search constraints as above; mean O···O = 2.599 (10) Å and mean C···O = 3.28 (2) Å] do involve DMF, indicating the more general carboxylic acid–formyl group as a supramolecular synthon worthy of future study.

The three examples of DMF clathrates presented here show that the presence of DMF as the co-crystallization solvent can limit the dimensionality of the resulting solid-state structure, compared with that of the parent benzenepolycarboxylic acid and its other solvent-inclusion clathrates. This limitation is due to the binding of the DMF molecules to the often extensively hydrogen-bonded carboxyl groups via the $R_2^2(7)$ synthon. While the inclusion of water molecules in (III) helps produce a more extended structure, the dimensionality of the co-crystal will, of course, also depend on the nature of the solute molecule. Comparisons with the two-dimensional structure of H$_3$TMA·2DMF imply that both the number and relative positions of the carboxyl groups in the benzenepolycarboxylic acid molecules can lead to a range of hydrogen-bonded supramolecular structures with various dimensionalities.
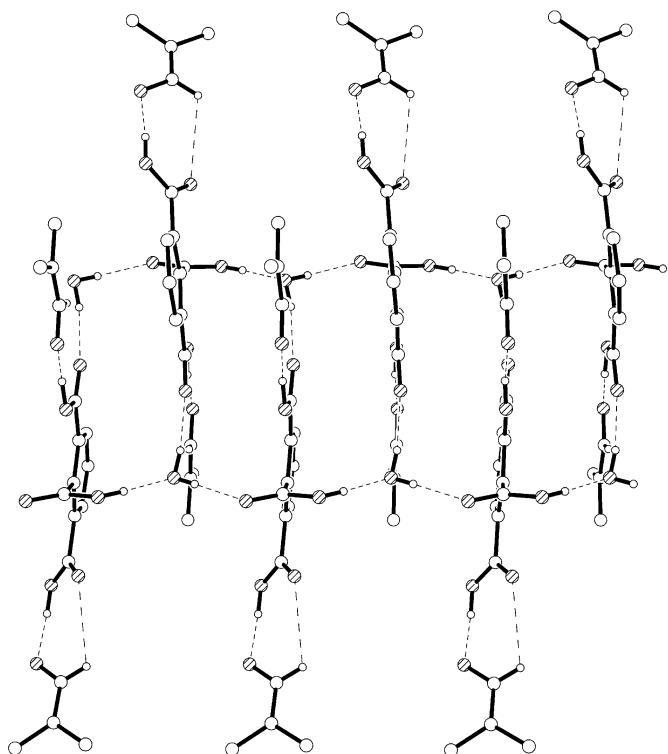
Figure 4
The one-dimensional ladder structure of (III), maintained by hydrogen bonds (shown as dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity.

Experimental

X-Ray quality colourless crystals of (I) were obtained by diffusing Et$_2$O into a solution of terephthalic acid in DMF and then placing the resulting solution in a freezer (∼258 K) overnight. The crystalline sample proved unstable under ambient conditions and hence no further data are available. X-Ray quality colourless crystals of (II) were obtained by the slow evaporation of a DMF solution of pyromellitic acid at room temperature (m.p. 312–322 K). Analysis calculated for C$_{22}$H$_{34}$N$_4$O$_{12}$: C 48.35, H 6.27, N 10.25%; found: C 48.66, H 6.20, N 9.90%; IR (Nujol, cm^{-1}): ν_{max} 3500–2500 (br, OH), 2461 (OH), 1916, 1709, 1659 and 1642 (C=O), 1556 (C=C), 1255 and 1106 (C—O), 922, 816, 758 and 672 (aromatic C—H). X-Ray quality colourless crystals of (III) were obtained by the slow evaporation of a DMF solution of hemimellitic acid dihydrate at room temperature [m.p. 323–325 K (liquid seen), 393–397 K (desolvated) and 463 K (liquified)]. Analysis calculated for C$_{15}$H$_{22}$N$_2$O$_9$: C 48.13, H 5.92, N 7.48%; found: C 47.82, H 6.25, N 7.93%; IR (KBr, cm^{-1}): ν_{max} 3443 (br, OH), 3079 (aromatic C—H), 2976 and 2936 (Csp^3—H), 2777 (aldehyde C—H), 1704 and 1622 (s, C=O), 1583 (C=C), 1460, 1436, 1425, 1414 and 1374 (Csp^3—H), 1308, 1270, 1210, 1175, 1157, 1112, 1064, 1020 and 1008 (C—O), 905, 810, 792 and 782 (aromatic C—H), 678, 671.

Compound (I)

Crystal data

$C_8H_6O_4 \cdot 2C_3H_7NO$
$M_r = 312.32$
Monoclinic, $C2/c$
$a = 19.663 (4)$ Å
$b = 7.5404 (13)$ Å
$c = 21.929 (4)$ Å
$\beta = 104.661 (3)°$
$V = 3145.5 (10)$ Å^3
$Z = 8$
$D_x = 1.319$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 3980
  reflections
$\theta = 2.5–27.8°$
$\mu = 0.10$ mm^{-1}
$T = 150 (2)$ K
Block, colourless
$0.34 \times 0.28 \times 0.18$ mm

Data collection

Bruker SMART 1000 CCD
  diffractometer
ω scans
12 434 measured reflections
3577 independent reflections
2318 reflections with $I > 2\sigma(I)$

$R_{int} = 0.044$
$\theta_{max} = 27.5°$
$h = -25 \rightarrow 25$
$k = -9 \rightarrow 9$
$l = -28 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.144$
$S = 1.05$
3577 reflections
222 parameters
H atom; see below

$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2$
  $+ 2.6815P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Table 1
Selected interatomic distances (Å) for (I).

C1—C6	1.388 (3)	C4—C8	1.493 (3)
C1—C2	1.394 (2)	C5—C6	1.383 (3)
C1—C7	1.494 (3)	C7—O1	1.227 (2)
C2—C3	1.384 (3)	C7—O2	1.296 (2)
C3—C4	1.387 (3)	C8—O3	1.216 (2)
C4—C5	1.394 (2)	C8—O4	1.313 (2)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O5	0.93 (3)	1.64 (3)	2.563 (2)	175 (3)
O4—H4$\cdots$O6	0.93 (3)	1.63 (3)	2.554 (2)	175 (2)
O1—H1$X\cdots$O5X	0.93 (3)	1.58 (8)	2.442 (8)	152 (14)
C9—H9$X\cdots$O2	0.95	2.78	3.365 (3)	121
C9—H9$\cdots$O1	0.95	2.70	3.339 (3)	125
C12—H12$\cdots$O3	0.95	2.64	3.314 (3)	128

Compound (II)

Crystal data

$C_{10}H_6O_8 \cdot 4C_3H_7NO$
$M_r = 546.53$
Monoclinic, $P2_1/n$
$a = 12.8905 (10)$ Å
$b = 7.9398 (6)$ Å
$c = 13.8078 (10)$ Å
$\beta = 108.162 (2)°$
$V = 1342.79 (17)$ Å^3
$Z = 2$

$D_x = 1.352$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5456
  reflections
$\theta = 2.6–28.6°$
$\mu = 0.11$ mm^{-1}
$T = 150 (2)$ K
Block, colourless
$0.69 \times 0.39 \times 0.08$ mm

Table 3
Selected interatomic distances (Å) for (II).

C1—C2	1.3909 (16)	C4—O1	1.2025 (15)
C1—C3^i	1.3988 (16)	C4—O2	1.3130 (15)
C1—C4	1.5015 (16)	C5—O3	1.2097 (15)
C2—C3	1.3906 (17)	C5—O4	1.3087 (15)
C3—C5	1.5045 (16)		

Symmetry code: (i) $-x, 2 - y, -z$.

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H4$\cdots$O5	0.935 (18)	1.643 (19)	2.5723 (12)	172.4 (17)
O2—H2$\cdots$O6	0.91 (2)	1.65 (2)	2.5508 (13)	169.3 (18)
C6—H6$\cdots$O3	0.95	2.47	3.1761 (16)	132

Data collection

Bruker SMART 1000 CCD
  diffractometer
ω scans
Absorption correction: multi-scan
  (SADABS; Sheldrick, 2001)
  $T_{min} = 0.936$, $T_{max} = 0.991$
11 290 measured reflections

3213 independent reflections
2522 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 28.9°$
$h = -16 \rightarrow 17$
$k = -10 \rightarrow 10$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.100$
$S = 1.04$
3213 reflections
182 parameters
H atom: see below

$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2$
  $+ 0.3704P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Compound (III)

Crystal data

$C_9H_6O_6 \cdot 2C_3H_7NO \cdot H_2O$
$M_r = 374.35$
Orthorhombic, $P2_12_12_1$
$a = 13.8441 (15)$ Å
$b = 19.745 (2)$ Å
$c = 6.6606 (7)$ Å
$V = 1820.7 (3)$ Å^3
$Z = 4$
$D_x = 1.366$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 8092
  reflections
$\theta = 2.5–28.3°$
$\mu = 0.11$ mm^{-1}
$T = 150 (2)$ K
Block, colourless
$0.57 \times 0.16 \times 0.12$ mm

Data collection

Bruker SMART 1000 CCD
  diffractometer
ω scans
Absorption correction: multi-scan
  (SADABS; Sheldrick, 2001)
  $T_{min} = 0.929$, $T_{max} = 0.990$
16 155 measured reflections

2593 independent reflections
2297 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 29.0°$
$h = -18 \rightarrow 18$
$k = -26 \rightarrow 26$
$l = -9 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.138$
$S = 1.11$
2593 reflections
254 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0823P)^2$
  $+ 0.6452P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

Table 5
Selected interatomic distances (Å) for (III).

C1—C2	1.401 (3)	C5—C6	1.389 (3)
C1—C6	1.401 (3)	C7—O2	1.202 (3)
C1—C7	1.506 (3)	C7—O1	1.329 (3)
C2—C3	1.408 (3)	C8—O3	1.224 (3)
C2—C8	1.519 (3)	C8—O4	1.303 (3)
C3—C4	1.400 (3)	C9—O6	1.217 (3)
C3—C9	1.500 (3)	C9—O5	1.301 (3)
C4—C5	1.384 (3)		

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O8	0.95 (4)	1.62 (4)	2.561 (3)	175 (4)
O9—H9$B\cdots$O3	0.78 (4)	1.95 (4)	2.734 (3)	178 (4)
O4—H4$\cdots$O9^{ii}	0.86 (4)	1.72 (4)	2.588 (3)	178 (3)
O5—H5$\cdots$O7	0.99 (4)	1.53 (4)	2.491 (2)	162 (4)
O9—H9$A\cdots$O6^{iii}	0.87 (4)	1.90 (4)	2.749 (2)	167 (4)
C10—H10$\cdots$O6	0.95	2.67	3.353 (3)	129
C13—H13$\cdots$O2	0.95	2.80	3.329 (3)	116

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

In (I)–(III), aromatic/aldehyde (C—H = 0.95 Å) and methyl (C—H = 0.98 Å) H atoms were positioned geometrically and treated using a riding model, while the coordinates of O-bound H atoms were refined freely in (II) and (III). The U_{iso}(H) values were set at $1.2U_{eq}$(C) for aromatic and aldehyde H atoms, and at $1.5U_{eq}$(C,O) for methyl and O-bound H atoms. Geometric restraints were applied to the disordered aldehyde group and the hydroxy bond lengths in (I). Friedel pairs (1811) were merged in the refinement of (III) as a consequence of the use of Mo $K\alpha$ X-ray radiation, and hence the absolute structure was not determined.

For all compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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supporting information

Hydrogen-bonding adducts of benzenepolycarboxylic acids with *N,N*-dimethylformamide: benzene-1,4-dicarboxylic acid *N,N*-dimethylformamide disolvate, benzene-1,2,4,5-tetracarboxylic acid *N,N*-dimethylformamide tetrasolvate and benzene-1,2,3-tricarboxylic acid *N,N*-dimethylformamide disolvate monohydrate

Sophie H. Dale and Mark R. J. Elsegood

Computing details

For all compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

(I) benzene-1,4-dicarboxylic acid *N,N*-dimethylformamide disolvate

Crystal data

$C_8H_6O_4 \cdot 2C_3H_7NO$	$F(000) = 1328$
$M_r = 312.32$	$D_x = 1.319$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 3980 reflections
$a = 19.663$ (4) Å	$\theta = 2.5$–27.8°
$b = 7.5404$ (13) Å	$\mu = 0.10$ mm^{-1}
$c = 21.929$ (4) Å	$T = 150$ K
$\beta = 104.661$ (3)°	Block, colourless
$V = 3145.5$ (10) Å^3	$0.34 \times 0.28 \times 0.18$ mm
$Z = 8$	

Data collection

Bruker SMART 1000 CCD diffractometer	2318 reflections with $I > 2\sigma(I)$
Radiation source: sealed tube	$R_{int} = 0.044$
Graphite monochromator	$\theta_{max} = 27.5°$, $\theta_{min} = 2.1°$
ω scans	$h = -25 \rightarrow 25$
12434 measured reflections	$k = -9 \rightarrow 9$
3577 independent reflections	$l = -28 \rightarrow 27$

Refinement

Refinement on F^2	222 parameters
Least-squares matrix: full	5 restraints
$R[F^2 > 2\sigma(F^2)] = 0.050$	Primary atom site location: structure-invariant direct methods
$wR(F^2) = 0.144$	
$S = 1.05$	Secondary atom site location: structure-invariant direct methods
3577 reflections	

Hydrogen site location: Geom except OH
  coords freely refined
H atoms treated by a mixture of independent
  and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 2.6815P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.08996 (9)	0.4816 (2)	0.12585 (8)	0.0267 (4)	
C2	0.13670 (10)	0.4234 (3)	0.18115 (8)	0.0311 (4)	
H2A	0.1455	0.4949	0.2180	0.037*	
C3	0.17034 (10)	0.2617 (3)	0.18240 (8)	0.0308 (4)	
H3	0.2021	0.2224	0.2202	0.037*	
C4	0.15803 (9)	0.1568 (3)	0.12877 (8)	0.0266 (4)	
C5	0.11138 (9)	0.2154 (3)	0.07347 (8)	0.0284 (4)	
H5	0.1026	0.1441	0.0366	0.034*	
C6	0.07778 (9)	0.3770 (3)	0.07211 (8)	0.0291 (4)	
H6	0.0462	0.4165	0.0342	0.035*	
C7	0.05241 (10)	0.6548 (3)	0.12306 (9)	0.0320 (4)	
O1	0.01091 (8)	0.7059 (2)	0.07458 (7)	0.0441 (4)	
H1X	0.004 (8)	0.827 (5)	0.069 (7)	0.066*	0.172 (4)
O2	0.06678 (8)	0.7443 (2)	0.17520 (7)	0.0476 (4)	
H2	0.0400 (16)	0.847 (4)	0.1725 (15)	0.071*	0.828 (4)
C8	0.19606 (9)	−0.0154 (3)	0.13084 (8)	0.0304 (4)	
O3	0.23846 (8)	−0.0690 (2)	0.17766 (6)	0.0412 (4)	
O4	0.17991 (8)	−0.1005 (2)	0.07687 (7)	0.0429 (4)	
H4	0.2050 (14)	−0.206 (3)	0.0783 (12)	0.064*	
C9	−0.03297 (10)	1.1015 (3)	0.12136 (10)	0.0341 (5)	
H9	−0.0294	1.0450	0.0836	0.041*	0.828 (4)
H9X	−0.0017	1.0693	0.1603	0.041*	0.172 (4)
O5	−0.00076 (9)	1.0362 (2)	0.17247 (8)	0.0405 (6)	0.828 (4)
O5X	−0.0381 (4)	1.0044 (11)	0.0715 (3)	0.038 (2)	0.172 (4)
N1	−0.07190 (8)	1.2457 (2)	0.11704 (7)	0.0314 (4)	
C10	−0.10576 (11)	1.3241 (3)	0.05625 (10)	0.0414 (5)	
H10A	−0.0944	1.2540	0.0225	0.062*	
H10B	−0.0889	1.4459	0.0546	0.062*	
H10C	−0.1568	1.3253	0.0507	0.062*	
C11	−0.07987 (12)	1.3359 (3)	0.17322 (10)	0.0426 (5)	

H11A	−0.0626	1.2593	0.2100	0.064*
H11B	−0.1296	1.3630	0.1688	0.064*
H11C	−0.0527	1.4464	0.1789	0.064*
C12	0.27680 (10)	−0.4584 (3)	0.12466 (9)	0.0320 (4)
H12	0.2723	−0.4023	0.1622	0.038*
O6	0.24528 (7)	−0.39171 (19)	0.07377 (6)	0.0393 (4)
N2	0.31611 (8)	−0.6020 (2)	0.13023 (7)	0.0323 (4)
C13	0.35034 (12)	−0.6745 (3)	0.19196 (10)	0.0432 (5)
H13A	0.3379	−0.6029	0.2248	0.065*
H13B	0.4014	−0.6724	0.1978	0.065*
H13C	0.3347	−0.7970	0.1947	0.065*
C14	0.32418 (12)	−0.6969 (3)	0.07519 (10)	0.0438 (5)
H14A	0.2984	−0.8092	0.0715	0.066*
H14B	0.3741	−0.7210	0.0793	0.066*
H14C	0.3055	−0.6248	0.0375	0.066*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0218 (9)	0.0304 (10)	0.0276 (9)	−0.0011 (7)	0.0059 (7)	0.0011 (8)
C2	0.0311 (10)	0.0363 (11)	0.0250 (9)	−0.0004 (8)	0.0057 (8)	−0.0042 (8)
C3	0.0276 (9)	0.0389 (11)	0.0236 (9)	0.0014 (8)	0.0025 (7)	0.0032 (8)
C4	0.0220 (9)	0.0315 (10)	0.0263 (9)	−0.0003 (7)	0.0062 (7)	0.0029 (8)
C5	0.0266 (9)	0.0338 (10)	0.0244 (9)	0.0007 (8)	0.0057 (7)	−0.0023 (8)
C6	0.0250 (9)	0.0365 (11)	0.0245 (9)	0.0019 (8)	0.0041 (7)	0.0023 (8)
C7	0.0264 (9)	0.0350 (11)	0.0344 (10)	−0.0021 (8)	0.0075 (8)	−0.0035 (8)
O1	0.0488 (9)	0.0397 (8)	0.0351 (8)	0.0122 (7)	−0.0057 (7)	−0.0020 (7)
O2	0.0539 (10)	0.0448 (10)	0.0354 (8)	0.0185 (8)	−0.0045 (7)	−0.0112 (7)
C8	0.0261 (9)	0.0353 (11)	0.0298 (10)	0.0007 (8)	0.0069 (8)	0.0026 (8)
O3	0.0414 (8)	0.0397 (8)	0.0351 (8)	0.0085 (7)	−0.0037 (6)	0.0033 (6)
O4	0.0479 (9)	0.0407 (9)	0.0339 (8)	0.0173 (7)	−0.0015 (7)	−0.0056 (7)
C9	0.0328 (10)	0.0326 (11)	0.0383 (11)	−0.0026 (9)	0.0115 (9)	−0.0034 (9)
O5	0.0420 (11)	0.0366 (11)	0.0424 (11)	0.0058 (8)	0.0099 (8)	0.0005 (8)
O5X	0.036 (5)	0.035 (5)	0.041 (5)	0.006 (4)	0.006 (4)	−0.004 (4)
N1	0.0293 (8)	0.0305 (9)	0.0348 (9)	−0.0024 (7)	0.0090 (7)	−0.0029 (7)
C10	0.0417 (12)	0.0381 (12)	0.0426 (12)	0.0008 (10)	0.0077 (9)	0.0031 (10)
C11	0.0442 (12)	0.0416 (13)	0.0434 (12)	0.0011 (10)	0.0139 (10)	−0.0095 (10)
C12	0.0319 (10)	0.0300 (10)	0.0349 (10)	−0.0014 (8)	0.0099 (8)	−0.0003 (8)
O6	0.0407 (8)	0.0362 (8)	0.0392 (8)	0.0093 (7)	0.0070 (6)	0.0045 (6)
N2	0.0329 (9)	0.0310 (9)	0.0332 (9)	0.0013 (7)	0.0086 (7)	0.0046 (7)
C13	0.0427 (12)	0.0436 (13)	0.0409 (11)	0.0037 (10)	0.0061 (9)	0.0118 (10)
C14	0.0475 (13)	0.0405 (12)	0.0457 (12)	0.0121 (10)	0.0159 (10)	0.0012 (10)

Geometric parameters (Å, º)

C1—C6	1.388 (3)	C9—H9	0.9500
C1—C2	1.394 (2)	C9—H9X	0.9501
C1—C7	1.494 (3)	N1—C11	1.450 (2)

C2—C3	1.384 (3)	N1—C10	1.456 (3)
C2—H2A	0.9500	C10—H10A	0.9800
C3—C4	1.387 (3)	C10—H10B	0.9800
C3—H3	0.9500	C10—H10C	0.9800
C4—C5	1.394 (2)	C11—H11A	0.9800
C4—C8	1.493 (3)	C11—H11B	0.9800
C5—C6	1.383 (3)	C11—H11C	0.9800
C5—H5	0.9500	C12—O6	1.238 (2)
C6—H6	0.9500	C12—N2	1.318 (2)
C7—O1	1.227 (2)	C12—H12	0.9500
C7—O2	1.296 (2)	N2—C14	1.446 (3)
O1—H1X	0.93 (3)	N2—C13	1.457 (2)
O2—H2	0.93 (3)	C13—H13A	0.9800
C8—O3	1.216 (2)	C13—H13B	0.9800
C8—O4	1.313 (2)	C13—H13C	0.9800
O4—H4	0.93 (3)	C14—H14A	0.9800
C9—O5	1.241 (3)	C14—H14B	0.9800
C9—O5X	1.298 (7)	C14—H14C	0.9800
C9—N1	1.319 (3)		
C6—C1—C2	119.60 (18)	H9—C9—H9X	119.8
C6—C1—C7	119.00 (16)	C9—N1—C11	120.73 (18)
C2—C1—C7	121.40 (17)	C9—N1—C10	121.52 (17)
C3—C2—C1	120.06 (17)	C11—N1—C10	117.69 (17)
C3—C2—H2A	120.0	N1—C10—H10A	109.5
C1—C2—H2A	120.0	N1—C10—H10B	109.5
C2—C3—C4	120.39 (17)	H10A—C10—H10B	109.5
C2—C3—H3	119.8	N1—C10—H10C	109.5
C4—C3—H3	119.8	H10A—C10—H10C	109.5
C3—C4—C5	119.44 (17)	H10B—C10—H10C	109.5
C3—C4—C8	119.45 (16)	N1—C11—H11A	109.5
C5—C4—C8	121.10 (16)	N1—C11—H11B	109.5
C6—C5—C4	120.25 (17)	H11A—C11—H11B	109.5
C6—C5—H5	119.9	N1—C11—H11C	109.5
C4—C5—H5	119.9	H11A—C11—H11C	109.5
C5—C6—C1	120.25 (17)	H11B—C11—H11C	109.5
C5—C6—H6	119.9	O6—C12—N2	124.43 (18)
C1—C6—H6	119.9	O6—C12—H12	117.8
O1—C7—O2	123.32 (19)	N2—C12—H12	117.8
O1—C7—C1	121.58 (17)	C12—N2—C14	120.99 (17)
O2—C7—C1	115.10 (16)	C12—N2—C13	121.11 (17)
C7—O1—C9	100.45 (13)	C14—N2—C13	117.84 (18)
C7—O1—H1X	118 (9)	N2—C13—H13A	109.5
C7—O2—H2	113 (2)	N2—C13—H13B	109.5
O3—C8—O4	123.80 (19)	H13A—C13—H13B	109.5
O3—C8—C4	123.07 (17)	N2—C13—H13C	109.5
O4—C8—C4	113.13 (15)	H13A—C13—H13C	109.5
C8—O3—C12	99.59 (13)	H13B—C13—H13C	109.5

C8—O4—H4	112.4 (16)	N2—C14—H14A	109.5
O5—C9—N1	123.10 (19)	N2—C14—H14B	109.5
O5X—C9—N1	119.0 (4)	H14A—C14—H14B	109.5
O5—C9—H9	118.4	N2—C14—H14C	109.5
N1—C9—H9	118.4	H14A—C14—H14C	109.5
O5X—C9—H9X	120.5	H14B—C14—H14C	109.5
N1—C9—H9X	120.5		
C6—C1—C2—C3	−0.4 (3)	C2—C1—C7—O2	0.1 (3)
C7—C1—C2—C3	179.54 (17)	C3—C4—C8—O3	−0.6 (3)
C1—C2—C3—C4	0.2 (3)	C5—C4—C8—O3	178.07 (18)
C2—C3—C4—C5	0.0 (3)	C3—C4—C8—O4	−179.52 (17)
C2—C3—C4—C8	178.70 (17)	C5—C4—C8—O4	−0.8 (2)
C3—C4—C5—C6	0.1 (3)	O4—C8—O3—C12	−4.0 (2)
C8—C4—C5—C6	−178.61 (17)	C4—C8—O3—C12	177.25 (15)
C4—C5—C6—C1	−0.3 (3)	O5—C9—N1—C11	−0.8 (3)
C2—C1—C6—C5	0.5 (3)	O5X—C9—N1—C11	166.2 (5)
C7—C1—C6—C5	−179.48 (16)	O5—C9—N1—C10	176.5 (2)
C6—C1—C7—O1	0.4 (3)	O5X—C9—N1—C10	−16.5 (5)
C2—C1—C7—O1	−179.54 (19)	O6—C12—N2—C14	−1.4 (3)
C6—C1—C7—O2	−179.94 (17)	O6—C12—N2—C13	−178.66 (19)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O5	0.93 (3)	1.64 (3)	2.563 (2)	175 (3)
O4—H4···O6	0.93 (3)	1.63 (3)	2.554 (2)	175 (2)
O1—H1*X*···O5*X*	0.93 (3)	1.58 (8)	2.442 (8)	152 (14)
C9—H9*X*···O2	0.95	2.78	3.365 (3)	121
C9—H9···O1	0.95	2.70	3.339 (3)	125
C12—H12···O3	0.95	2.64	3.314 (3)	128

(II) benzene-1,2,4,5-tetracarboxylic acid *N,N*-dimethylformamide tetrasolvate

Crystal data

$C_{10}H_6O_8 \cdot 4C_3H_7NO$	$F(000) = 580$
$M_r = 546.53$	$D_x = 1.352$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo *K*α radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 5456 reflections
$a = 12.8905$ (10) Å	$\theta = 2.6–28.6°$
$b = 7.9398$ (6) Å	$\mu = 0.11$ mm^{-1}
$c = 13.8078$ (10) Å	$T = 150$ K
$\beta = 108.162$ (2)°	Block, colourless
$V = 1342.79$ (17) Å^3	$0.69 \times 0.39 \times 0.08$ mm
$Z = 2$	

Data collection

Bruker SMART 1000 CCD diffractometer	11290 measured reflections
Radiation source: sealed tube	3213 independent reflections
Graphite monochromator	2522 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.017$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	$\theta_{max} = 28.9°$, $\theta_{min} = 1.9°$
$T_{min} = 0.936$, $T_{max} = 0.991$	$h = -16 \rightarrow 17$
	$k = -10 \rightarrow 10$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.035$	Hydrogen site location: Geom except OH coords freely refined
$wR(F^2) = 0.100$	
$S = 1.04$	H atoms treated by a mixture of independent and constrained refinement
3213 reflections	
182 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 0.3704P]$ where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.31$ e Å⁻³
	$\Delta\rho_{min} = -0.18$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
C1	−0.02936 (9)	1.15687 (14)	0.02955 (8)	0.0237 (2)
C2	0.07958 (9)	1.11810 (15)	0.04362 (9)	0.0253 (2)
H2A	0.1343	1.1992	0.0738	0.030*
C3	0.10990 (9)	0.96287 (15)	0.01433 (8)	0.0240 (2)
C4	−0.05675 (10)	1.33162 (15)	0.05531 (9)	0.0267 (3)
O1	−0.11925 (7)	1.42163 (12)	−0.00569 (8)	0.0390 (2)
O2	−0.00097 (9)	1.37265 (12)	0.14924 (7)	0.0381 (2)
H2	−0.0168 (15)	1.481 (3)	0.1616 (14)	0.057*
C5	0.22954 (9)	0.93294 (16)	0.03142 (9)	0.0275 (3)
O3	0.29836 (7)	0.98649 (16)	0.10621 (8)	0.0494 (3)
O4	0.25066 (7)	0.85283 (12)	−0.04312 (7)	0.0332 (2)
H4	0.3257 (15)	0.832 (2)	−0.0226 (13)	0.050*
C6	0.51767 (10)	0.84451 (16)	0.07839 (10)	0.0309 (3)
H6	0.4884	0.9216	0.1156	0.037*
O5	0.45481 (7)	0.78348 (12)	−0.00169 (7)	0.0346 (2)

N1	0.62271 (9)	0.80804 (15)	0.11438 (9)	0.0336 (3)
C7	0.67272 (12)	0.6921 (2)	0.06036 (13)	0.0451 (4)
H7A	0.6494	0.5768	0.0683	0.068*
H7B	0.7524	0.6998	0.0886	0.068*
H7C	0.6500	0.7216	−0.0122	0.068*
C8	0.69038 (12)	0.8810 (2)	0.21002 (12)	0.0462 (4)
H8A	0.6466	0.9597	0.2358	0.069*
H8B	0.7518	0.9414	0.1985	0.069*
H8C	0.7182	0.7912	0.2600	0.069*
C9	0.06223 (11)	1.75010 (17)	0.22678 (10)	0.0322 (3)
H9	0.1213	1.6993	0.2103	0.039*
O6	−0.02586 (8)	1.67321 (12)	0.20340 (8)	0.0402 (2)
N2	0.07929 (8)	1.89666 (14)	0.27270 (8)	0.0308 (2)
C10	−0.00745 (13)	1.9791 (2)	0.30094 (14)	0.0483 (4)
H10A	−0.0405	2.0668	0.2509	0.072*
H10B	0.0226	2.0301	0.3685	0.072*
H10C	−0.0631	1.8960	0.3024	0.072*
C11	0.18364 (13)	1.9831 (2)	0.29769 (13)	0.0537 (4)
H11A	0.2338	1.9184	0.2714	0.081*
H11B	0.2145	1.9938	0.3719	0.081*
H11C	0.1730	2.0954	0.2667	0.081*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0246 (6)	0.0242 (6)	0.0208 (5)	−0.0013 (4)	0.0048 (4)	0.0000 (4)
C2	0.0222 (5)	0.0265 (6)	0.0250 (6)	−0.0047 (4)	0.0042 (4)	−0.0032 (4)
C3	0.0210 (5)	0.0278 (6)	0.0213 (5)	−0.0013 (4)	0.0039 (4)	−0.0002 (4)
C4	0.0246 (6)	0.0242 (6)	0.0310 (6)	−0.0033 (4)	0.0082 (5)	−0.0017 (5)
O1	0.0317 (5)	0.0301 (5)	0.0462 (6)	0.0051 (4)	−0.0009 (4)	−0.0006 (4)
O2	0.0552 (6)	0.0244 (5)	0.0296 (5)	0.0024 (4)	0.0058 (4)	−0.0056 (4)
C5	0.0230 (5)	0.0288 (6)	0.0290 (6)	−0.0012 (5)	0.0056 (5)	−0.0020 (5)
O3	0.0228 (5)	0.0757 (8)	0.0434 (6)	0.0007 (5)	0.0010 (4)	−0.0262 (6)
O4	0.0231 (4)	0.0435 (5)	0.0326 (5)	−0.0004 (4)	0.0082 (4)	−0.0086 (4)
C6	0.0284 (6)	0.0288 (6)	0.0375 (7)	0.0008 (5)	0.0131 (5)	0.0078 (5)
O5	0.0274 (4)	0.0382 (5)	0.0385 (5)	0.0029 (4)	0.0108 (4)	0.0020 (4)
N1	0.0256 (5)	0.0371 (6)	0.0386 (6)	0.0006 (4)	0.0108 (5)	0.0091 (5)
C7	0.0318 (7)	0.0540 (9)	0.0529 (9)	0.0098 (6)	0.0179 (7)	0.0079 (7)
C8	0.0327 (7)	0.0575 (10)	0.0440 (8)	−0.0058 (7)	0.0057 (6)	0.0060 (7)
C9	0.0325 (6)	0.0339 (7)	0.0299 (6)	0.0087 (5)	0.0091 (5)	−0.0002 (5)
O6	0.0440 (6)	0.0277 (5)	0.0448 (6)	−0.0034 (4)	0.0079 (4)	−0.0111 (4)
N2	0.0254 (5)	0.0314 (6)	0.0328 (6)	−0.0035 (4)	0.0050 (4)	−0.0032 (4)
C10	0.0438 (8)	0.0341 (8)	0.0655 (10)	0.0038 (6)	0.0148 (7)	−0.0185 (7)
C11	0.0383 (8)	0.0701 (11)	0.0449 (9)	−0.0239 (8)	0.0015 (7)	0.0045 (8)

Geometric parameters (Å, º)

C1—C2	1.3909 (16)	C7—H7A	0.9800
C1—C3[i]	1.3988 (16)	C7—H7B	0.9800
C1—C4	1.5015 (16)	C7—H7C	0.9800
C2—C3	1.3906 (17)	C8—H8A	0.9800
C2—H2A	0.9500	C8—H8B	0.9800
C3—C5	1.5045 (16)	C8—H8C	0.9800
C4—O1	1.2025 (15)	C9—O6	1.2400 (16)
C4—O2	1.3130 (15)	C9—N2	1.3105 (17)
O2—H2	0.91 (2)	C9—H9	0.9500
C5—O3	1.2097 (15)	N2—C10	1.4499 (18)
C5—O4	1.3087 (15)	N2—C11	1.4527 (17)
O4—H4	0.935 (18)	C10—H10A	0.9800
C6—O5	1.2471 (16)	C10—H10B	0.9800
C6—N1	1.3208 (16)	C10—H10C	0.9800
C6—H6	0.9500	C11—H11A	0.9800
N1—C7	1.4560 (19)	C11—H11B	0.9800
N1—C8	1.4569 (19)	C11—H11C	0.9800
C2—C1—C3[i]	119.40 (11)	H7B—C7—H7C	109.5
C2—C1—C4	118.24 (10)	N1—C8—H8A	109.5
C3[i]—C1—C4	122.21 (10)	N1—C8—H8B	109.5
C3—C2—C1	121.24 (10)	H8A—C8—H8B	109.5
C3—C2—H2A	119.4	N1—C8—H8C	109.5
C1—C2—H2A	119.4	H8A—C8—H8C	109.5
C2—C3—C1[i]	119.37 (10)	H8B—C8—H8C	109.5
C2—C3—C5	117.49 (10)	O6—C9—N2	124.41 (12)
C1[i]—C3—C5	123.14 (11)	N2—C9—O2	168.49 (10)
O1—C4—O2	125.83 (12)	O6—C9—H9	117.8
O1—C4—C1	122.61 (11)	N2—C9—H9	117.8
O2—C4—C1	111.50 (10)	C9—N2—C10	120.24 (11)
C4—O2—H2	109.5 (12)	C9—N2—C11	122.54 (13)
O3—C5—O4	124.42 (11)	C10—N2—C11	117.22 (13)
O3—C5—C3	121.44 (11)	N2—C10—H10A	109.5
O4—C5—C3	114.07 (10)	N2—C10—H10B	109.5
C5—O4—H4	107.4 (11)	H10A—C10—H10B	109.5
O5—C6—H6	118.1	N2—C10—H10C	109.5
N1—C6—H6	118.1	H10A—C10—H10C	109.5
C6—N1—C7	120.77 (12)	H10B—C10—H10C	109.5
C6—N1—C8	120.52 (12)	N2—C11—H11A	109.5
C7—N1—C8	118.71 (12)	N2—C11—H11B	109.5
N1—C7—H7A	109.5	H11A—C11—H11B	109.5
N1—C7—H7B	109.5	N2—C11—H11C	109.5
H7A—C7—H7B	109.5	H11A—C11—H11C	109.5
N1—C7—H7C	109.5	H11B—C11—H11C	109.5
H7A—C7—H7C	109.5		

C3ⁱ—C1—C2—C3	0.38 (19)	C2—C3—C5—O3	37.22 (18)
C4—C1—C2—C3	−175.22 (11)	C1ⁱ—C3—C5—O3	−143.11 (14)
C1—C2—C3—C1ⁱ	−0.38 (19)	C2—C3—C5—O4	−139.67 (11)
C1—C2—C3—C5	179.30 (11)	C1ⁱ—C3—C5—O4	40.01 (16)
C2—C1—C4—O1	122.73 (13)	O5—C6—N1—C7	0.6 (2)
C3ⁱ—C1—C4—O1	−52.74 (17)	O5—C6—N1—C8	−178.33 (12)
C2—C1—C4—O2	−54.62 (14)	O6—C9—N2—C10	0.8 (2)
C3ⁱ—C1—C4—O2	129.91 (12)	O6—C9—N2—C11	−179.32 (13)

Symmetry code: (i) −x, −y+2, −z.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O5	0.935 (18)	1.643 (19)	2.5723 (12)	172.4 (17)
O2—H2···O6	0.91 (2)	1.65 (2)	2.5508 (13)	169.3 (18)
C6—H6···O3	0.95	2.47	3.1761 (16)	132

(III) benzene-1,2,3-tricarboxylic acid *N*,*N*-dimethylformamide disolvate monohydrate

Crystal data

$C_9H_6O_6·2C_3H_7NO·H_2O$	$F(000) = 792$
$M_r = 374.35$	$D_x = 1.366$ Mg m⁻³
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 8092 reflections
$a = 13.8441$ (15) Å	$\theta = 2.5–28.3°$
$b = 19.745$ (2) Å	$\mu = 0.11$ mm⁻¹
$c = 6.6606$ (7) Å	$T = 150$ K
$V = 1820.7$ (3) Å³	Block, colourless
$Z = 4$	$0.57 \times 0.16 \times 0.12$ mm

Data collection

Bruker SMART 1000 CCD diffractometer	16155 measured reflections
Radiation source: sealed tube	2593 independent reflections
Graphite monochromator	2297 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.022$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	$\theta_{max} = 29.0°$, $\theta_{min} = 1.8°$
	$h = -18 \rightarrow 18$
	$k = -26 \rightarrow 26$
$T_{min} = 0.929$, $T_{max} = 0.990$	$l = -9 \rightarrow 8$

Refinement

Refinement on F^2	Secondary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.049$	Hydrogen site location: Geom except OH coords freely refined
$wR(F^2) = 0.138$	
$S = 1.11$	H atoms treated by a mixture of independent and constrained refinement
2593 reflections	
254 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0823P)^2 + 0.6452P]$ where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.66$ e Å⁻³
	$\Delta\rho_{min} = -0.22$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.70722 (16)	0.22164 (11)	0.4858 (4)	0.0215 (5)
C2	0.76594 (14)	0.16416 (10)	0.5032 (4)	0.0174 (4)
C3	0.72210 (16)	0.09996 (11)	0.5152 (4)	0.0204 (4)
C4	0.62119 (17)	0.09517 (12)	0.5166 (4)	0.0246 (5)
H4A	0.5917	0.0519	0.5265	0.030*
C5	0.56364 (16)	0.15232 (12)	0.5038 (4)	0.0262 (5)
H5A	0.4953	0.1483	0.5077	0.031*
C6	0.60639 (16)	0.21563 (12)	0.4852 (4)	0.0243 (5)
H6	0.5672	0.2549	0.4721	0.029*
C7	0.75213 (17)	0.29089 (11)	0.4701 (4)	0.0237 (5)
O1	0.69869 (14)	0.33449 (9)	0.3663 (4)	0.0355 (5)
H1	0.728 (3)	0.378 (2)	0.359 (7)	0.053*
O2	0.82946 (13)	0.30466 (9)	0.5413 (3)	0.0334 (5)
C8	0.87487 (15)	0.17298 (10)	0.4967 (4)	0.0197 (4)
O3	0.91671 (12)	0.18029 (9)	0.3363 (3)	0.0246 (4)
O4	0.92184 (12)	0.17362 (9)	0.6663 (3)	0.0238 (4)
H4	0.888 (3)	0.1673 (17)	0.774 (6)	0.036*
C9	0.77795 (18)	0.03485 (11)	0.5189 (4)	0.0239 (5)
O5	0.87118 (12)	0.04261 (8)	0.5093 (4)	0.0347 (5)
H5	0.900 (3)	−0.003 (2)	0.505 (7)	0.052*
O6	0.73742 (15)	−0.01970 (8)	0.5300 (4)	0.0363 (5)
C10	0.93429 (19)	−0.11833 (12)	0.5068 (4)	0.0286 (5)
H10	0.8658	−0.1204	0.5147	0.034*
O7	0.97352 (14)	−0.06117 (9)	0.5093 (4)	0.0354 (5)
N1	0.98230 (15)	−0.17588 (10)	0.4940 (3)	0.0258 (4)
C11	1.08763 (19)	−0.17693 (13)	0.4816 (5)	0.0341 (6)
H11A	1.1118	−0.1305	0.4680	0.051*
H11B	1.1075	−0.2036	0.3646	0.051*
H11C	1.1142	−0.1974	0.6038	0.051*
C12	0.9320 (2)	−0.24081 (12)	0.4907 (5)	0.0319 (5)
H12A	0.8621	−0.2330	0.4894	0.048*
H12B	0.9495	−0.2670	0.6104	0.048*
H12C	0.9507	−0.2661	0.3701	0.048*
C13	0.83670 (19)	0.47076 (13)	0.4570 (5)	0.0332 (6)
H13	0.8410	0.4455	0.5780	0.040*

O8	0.78043 (15)	0.44991 (10)	0.3228 (4)	0.0391 (5)
N2	0.89063 (18)	0.52613 (12)	0.4398 (4)	0.0348 (6)
C14	0.8855 (3)	0.56746 (18)	0.2587 (7)	0.0565 (10)
H14A	0.8639	0.5394	0.1458	0.085*
H14B	0.9495	0.5862	0.2290	0.085*
H14C	0.8396	0.6046	0.2795	0.085*
C15	0.9484 (2)	0.55029 (17)	0.6057 (6)	0.0428 (8)
H15A	0.9494	0.5160	0.7121	0.064*
H15B	0.9204	0.5923	0.6580	0.064*
H15C	1.0145	0.5589	0.5595	0.064*
O9	0.82103 (14)	0.15198 (10)	−0.0129 (3)	0.0300 (4)
H9B	0.848 (3)	0.160 (2)	0.088 (7)	0.045*
H9A	0.808 (3)	0.110 (2)	0.019 (6)	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0205 (9)	0.0206 (10)	0.0233 (11)	−0.0003 (8)	0.0000 (10)	−0.0011 (10)
C2	0.0173 (9)	0.0178 (9)	0.0171 (10)	−0.0021 (7)	−0.0007 (9)	−0.0009 (9)
C3	0.0221 (9)	0.0173 (9)	0.0219 (11)	−0.0023 (8)	0.0008 (10)	−0.0001 (9)
C4	0.0231 (10)	0.0252 (10)	0.0255 (12)	−0.0082 (8)	0.0008 (10)	−0.0015 (11)
C5	0.0177 (9)	0.0326 (11)	0.0284 (12)	−0.0032 (9)	0.0036 (11)	−0.0007 (12)
C6	0.0190 (9)	0.0269 (11)	0.0270 (12)	0.0032 (8)	−0.0001 (10)	−0.0022 (11)
C7	0.0235 (10)	0.0191 (10)	0.0285 (12)	0.0008 (8)	−0.0006 (10)	−0.0020 (10)
O1	0.0325 (10)	0.0200 (8)	0.0539 (13)	−0.0006 (8)	−0.0123 (10)	0.0061 (9)
O2	0.0266 (8)	0.0230 (8)	0.0506 (13)	−0.0042 (7)	−0.0115 (9)	0.0017 (9)
C8	0.0176 (9)	0.0142 (8)	0.0273 (11)	−0.0010 (7)	−0.0003 (10)	0.0008 (10)
O3	0.0217 (8)	0.0268 (9)	0.0252 (9)	−0.0029 (7)	0.0041 (7)	0.0005 (7)
O4	0.0198 (8)	0.0255 (8)	0.0261 (9)	−0.0038 (7)	−0.0035 (7)	0.0031 (7)
C9	0.0275 (10)	0.0185 (9)	0.0257 (12)	−0.0014 (8)	−0.0006 (10)	−0.0012 (10)
O5	0.0250 (8)	0.0171 (7)	0.0621 (14)	0.0021 (6)	−0.0013 (10)	−0.0003 (10)
O6	0.0391 (10)	0.0180 (8)	0.0518 (13)	−0.0065 (7)	0.0025 (10)	0.0013 (9)
C10	0.0308 (11)	0.0254 (10)	0.0296 (13)	0.0082 (9)	−0.0038 (13)	−0.0003 (11)
O7	0.0358 (9)	0.0224 (8)	0.0479 (12)	0.0067 (7)	−0.0021 (11)	−0.0037 (9)
N1	0.0322 (10)	0.0225 (9)	0.0228 (10)	0.0062 (8)	0.0014 (10)	−0.0008 (10)
C11	0.0326 (12)	0.0300 (12)	0.0397 (15)	0.0094 (10)	−0.0015 (13)	−0.0015 (13)
C12	0.0385 (13)	0.0230 (11)	0.0343 (14)	0.0031 (10)	0.0018 (15)	0.0006 (11)
C13	0.0294 (12)	0.0230 (11)	0.0472 (17)	0.0008 (9)	−0.0022 (12)	0.0039 (12)
O8	0.0406 (10)	0.0257 (9)	0.0508 (13)	−0.0079 (8)	−0.0102 (10)	0.0046 (10)
N2	0.0299 (11)	0.0256 (10)	0.0490 (16)	−0.0032 (9)	−0.0023 (11)	−0.0007 (11)
C14	0.064 (2)	0.0409 (17)	0.064 (2)	−0.0229 (17)	−0.005 (2)	0.0161 (18)
C15	0.0322 (14)	0.0375 (14)	0.059 (2)	0.0001 (12)	−0.0034 (14)	−0.0132 (15)
O9	0.0340 (9)	0.0241 (8)	0.0320 (10)	−0.0073 (7)	−0.0023 (10)	0.0013 (9)

Geometric parameters (Å, º)

C1—C2	1.401 (3)	C10—H10	0.9500
C1—C6	1.401 (3)	N1—C12	1.459 (3)

C1—C7	1.506 (3)	N1—C11	1.461 (3)
C2—C3	1.408 (3)	C11—H11A	0.9800
C2—C8	1.519 (3)	C11—H11B	0.9800
C3—C4	1.400 (3)	C11—H11C	0.9800
C3—C9	1.500 (3)	C12—H12A	0.9800
C4—C5	1.384 (3)	C12—H12B	0.9800
C4—H4A	0.9500	C12—H12C	0.9800
C5—C6	1.389 (3)	C13—O8	1.255 (4)
C5—H5A	0.9500	C13—N2	1.329 (3)
C6—H6	0.9500	C13—H13	0.9500
C7—O2	1.202 (3)	N2—C15	1.445 (4)
C7—O1	1.329 (3)	N2—C14	1.458 (5)
O1—H1	0.95 (4)	C14—H14A	0.9800
C8—O3	1.224 (3)	C14—H14B	0.9800
C8—O4	1.303 (3)	C14—H14C	0.9800
O4—H4	0.86 (4)	C15—H15A	0.9800
C9—O6	1.217 (3)	C15—H15B	0.9800
C9—O5	1.301 (3)	C15—H15C	0.9800
O5—H5	0.99 (4)	O9—H9B	0.78 (4)
C10—O7	1.253 (3)	O9—H9A	0.87 (4)
C10—N1	1.319 (3)		
C2—C1—C6	120.7 (2)	C10—N1—C12	121.1 (2)
C2—C1—C7	120.12 (19)	C10—N1—C11	121.3 (2)
C6—C1—C7	119.2 (2)	C12—N1—C11	117.6 (2)
C1—C2—C3	118.96 (18)	N1—C11—H11A	109.5
C1—C2—C8	118.75 (18)	N1—C11—H11B	109.5
C3—C2—C8	122.20 (18)	H11A—C11—H11B	109.5
C4—C3—C2	119.4 (2)	N1—C11—H11C	109.5
C4—C3—C9	117.1 (2)	H11A—C11—H11C	109.5
C2—C3—C9	123.39 (19)	H11B—C11—H11C	109.5
C5—C4—C3	121.3 (2)	N1—C12—H12A	109.5
C5—C4—H4A	119.4	N1—C12—H12B	109.5
C3—C4—H4A	119.4	H12A—C12—H12B	109.5
C4—C5—C6	119.6 (2)	N1—C12—H12C	109.5
C4—C5—H5A	120.2	H12A—C12—H12C	109.5
C6—C5—H5A	120.2	H12B—C12—H12C	109.5
C5—C6—C1	120.0 (2)	O8—C13—N2	123.9 (3)
C5—C6—H6	120.0	O8—C13—H13	118.1
C1—C6—H6	120.0	N2—C13—H13	118.1
O2—C7—O1	123.7 (2)	C13—N2—C15	121.1 (3)
O2—C7—C1	123.1 (2)	C13—N2—C14	120.3 (3)
O1—C7—C1	113.2 (2)	C15—N2—C14	118.4 (3)
C7—O1—H1	112 (3)	N2—C14—H14A	109.5
O3—C8—O4	121.29 (18)	N2—C14—H14B	109.5
O3—C8—C2	120.6 (2)	H14A—C14—H14B	109.5
O4—C8—C2	118.1 (2)	N2—C14—H14C	109.5
C8—O4—H4	116 (2)	H14A—C14—H14C	109.5

O6—C9—O5	124.4 (2)	H14B—C14—H14C	109.5
O6—C9—C3	121.5 (2)	N2—C15—H15A	109.5
O5—C9—C3	114.2 (2)	N2—C15—H15B	109.5
C9—O5—H5	107 (2)	H15A—C15—H15B	109.5
O7—C10—N1	123.9 (2)	N2—C15—H15C	109.5
N1—C10—O6	155.89 (18)	H15A—C15—H15C	109.5
O7—C10—H10	118.0	H15B—C15—H15C	109.5
N1—C10—H10	118.0	H9B—O9—H9A	94 (4)
C6—C1—C2—C3	1.6 (4)	C6—C1—C7—O2	151.2 (3)
C7—C1—C2—C3	−179.3 (2)	C2—C1—C7—O1	150.7 (3)
C6—C1—C2—C8	178.1 (3)	C6—C1—C7—O1	−30.1 (4)
C7—C1—C2—C8	−2.7 (4)	C1—C2—C8—O3	−79.5 (3)
C1—C2—C3—C4	−2.2 (4)	C3—C2—C8—O3	97.0 (3)
C8—C2—C3—C4	−178.7 (3)	C1—C2—C8—O4	99.4 (3)
C1—C2—C3—C9	175.3 (2)	C3—C2—C8—O4	−84.1 (3)
C8—C2—C3—C9	−1.1 (4)	C4—C3—C9—O6	−2.6 (4)
C2—C3—C4—C5	0.8 (4)	C2—C3—C9—O6	179.8 (3)
C9—C3—C4—C5	−176.9 (2)	C4—C3—C9—O5	177.4 (3)
C3—C4—C5—C6	1.3 (4)	C2—C3—C9—O5	−0.2 (4)
C4—C5—C6—C1	−2.0 (4)	O7—C10—N1—C12	−179.6 (3)
C2—C1—C6—C5	0.5 (4)	O7—C10—N1—C11	0.1 (5)
C7—C1—C6—C5	−178.6 (2)	O8—C13—N2—C15	175.2 (3)
C2—C1—C7—O2	−28.0 (4)	O8—C13—N2—C14	1.1 (5)

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O8	0.95 (4)	1.62 (4)	2.561 (3)	175 (4)
O9—H9B···O3	0.78 (4)	1.95 (4)	2.734 (3)	178 (4)
O4—H4···O9ⁱ	0.86 (4)	1.72 (4)	2.588 (3)	178 (3)
O5—H5···O7	0.99 (4)	1.53 (4)	2.491 (2)	162 (4)
O9—H9A···O6ⁱⁱ	0.87 (4)	1.90 (4)	2.749 (2)	167 (4)
C10—H10···O6	0.95	2.67	3.353 (3)	129
C13—H13···O2	0.95	2.80	3.329 (3)	116

Symmetry codes: (i) $x, y, z+1$; (ii) $-x+3/2, -y, z-1/2$.