

# 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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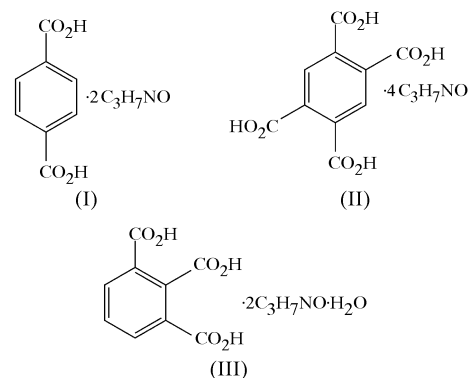
The *N,N*-dimethylformamide (DMF) solvates of terephthalic acid,  $\text{H}_2\text{TA}\cdot 2\text{DMF}$  ( $\text{C}_8\text{H}_6\text{O}_6\cdot 2\text{C}_3\text{H}_7\text{NO}$ ), pyromellitic acid,  $\text{H}_4\text{PMA}\cdot 4\text{DMF}$  ( $\text{C}_{10}\text{H}_6\text{O}_8\cdot 4\text{C}_3\text{H}_7\text{NO}$ ), and hemimellitic acid,  $\text{H}_3\text{HMA}\cdot 2\text{DMF}\cdot \text{H}_2\text{O}$  ( $\text{C}_9\text{H}_6\text{O}_6\cdot 2\text{C}_3\text{H}_7\text{NO}\cdot \text{H}_2\text{O}$ ), 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  $R_2^2(7)$   $\text{O}-\text{H}\cdots\text{O}/\text{C}-\text{H}\cdots\text{O}$  motif. Discrete  $\text{H}_2\text{TA}\cdot 2\text{DMF}$  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  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bond to the second unique DMF molecule. Discrete  $\text{H}_4\text{PMA}\cdot 4\text{DMF}$  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.

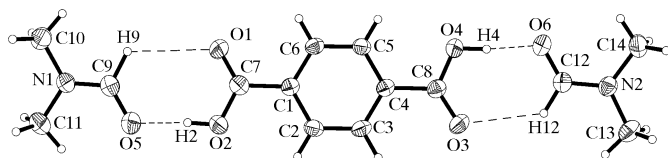
Numerous examples of benzenepolycarboxylic acid solvent-inclusion compounds exist in the literature (for example, Dale & Elsegood, 2003*b*; Chatterjee *et al.*, 2000; Herstein & Kapon, 1978; Herstein *et al.*, 1978) and yet only one literature example of a single-crystal X-ray structure shows the solvation of a benzenepolycarboxylic acid by DMF, that of benzene-1,3,5-tricarboxylic acid (trimesic acid) *N,N*-dimethylformamide disolvate ( $\text{H}_3\text{TMA}\cdot 2\text{DMF}$ ; Dale & Elsegood, 2003*b*). 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  $\text{O}-\text{H}\cdots\text{O}$  and weaker  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds (Desiraju & Steiner, 1999), while the third carboxyl group interacts with one of these carboxyl-DMF synthons.



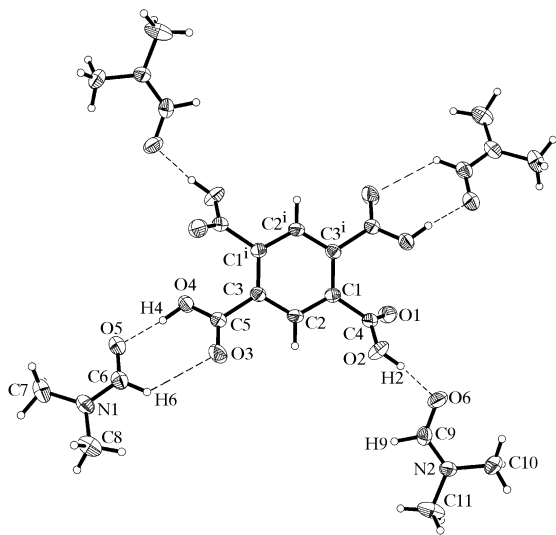
We investigate here the hydrogen-bonding arrays created by the co-crystallization of DMF with benzene-1,4-dicarboxylic acid (terephthalic acid,  $\text{H}_2\text{TA}$ ), benzene-1,2,4,5-tetracarboxylic acid (pyromellitic acid,  $\text{H}_4\text{PMA}$ ) and benzene-1,2,3-tricarboxylic acid (hemimellitic acid,  $\text{H}_3\text{HMA}$ ).  $\text{H}_2\text{TA}$  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  $\text{H}_2\text{TA}$  co-crystallizes with two molecules of DMF, producing  $\text{H}_2\text{TA}\cdot 2\text{DMF}$ , (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  $\text{H}_2\text{TA}$  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<sub>2</sub>TA molecule (Table 1) shows good agreement with that found previously (Bailey & Brown, 1967). The H<sub>2</sub>TA 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<sub>3</sub>TMA·2DMF (Dale & Elsegood, 2003*b*), 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.



**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.

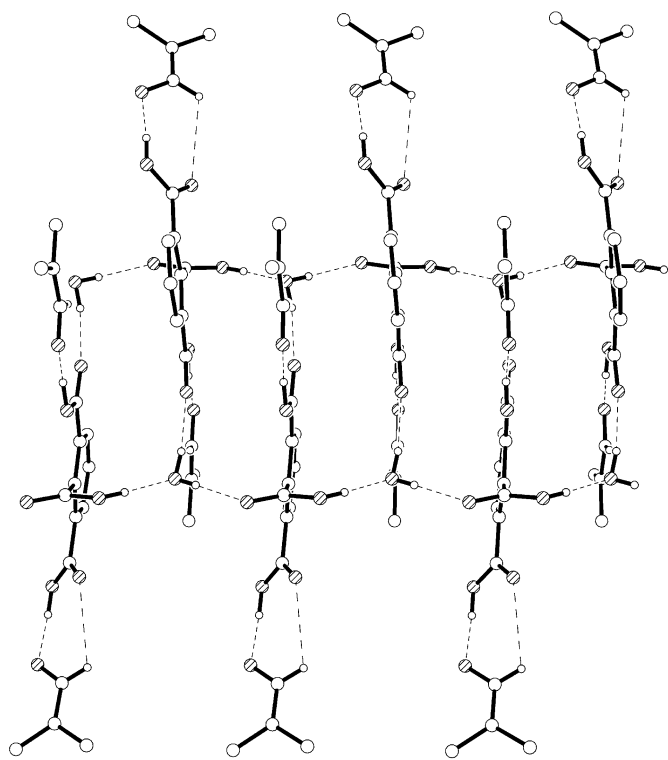


81.54 (10)°], as observed in the dihydrate of H<sub>3</sub>HMA (Fornies-Marquina *et al.*, 1972; Takusagawa & Shimada, 1973; Mo & Adman, 1975) and in its 2-methyl ester (Dale & Elsegood, 2003a). This carboxyl group, aided by its *anti*-planar conformation (Leiserowitz, 1976), forms a zigzag C<sub>2</sub>(6) 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<sub>2</sub>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<sub>2</sub><sup>2</sup>(7) motif observed in (I), (II) and (III). The mean O...O contact distance within this population [containing the R<sub>2</sub><sup>2</sup>(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<sub>2</sub><sup>2</sup>(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<sub>2</sub>H/DMF R<sub>2</sub><sup>2</sup>(7) synthon has relatively few examples in the CSD compared with the analogous, well studied, carboxylic acid–pyridine R<sub>2</sub><sup>2</sup>(7) synthon (Vishweshwar *et al.*, 2002), the majority (15) of the 21 CSD structures containing the CO<sub>2</sub>H–formyl group R<sub>2</sub><sup>2</sup>(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<sub>2</sub><sup>2</sup>(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<sub>3</sub>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<sub>2</sub>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<sub>22</sub>H<sub>34</sub>N<sub>4</sub>O<sub>12</sub>: C 48.35, H 6.27, N 10.25%; found: C 48.66, H 6.20, N 9.90%; IR (Nujol, cm<sup>-1</sup>): ν<sub>max</sub> 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<sub>15</sub>H<sub>22</sub>N<sub>2</sub>O<sub>9</sub>: C 48.13, H 5.92, N 7.48%; found: C 47.82, H 6.25, N 7.93%; IR (KBr, cm<sup>-1</sup>): ν<sub>max</sub> 3443 (*br.*, OH), 3079 (aromatic C—H), 2976 and 2936 (Csp<sup>3</sup>—H), 2777 (aldehyde C—H), 1704 and 1622 (*s.*, C=O), 1583 (C=C), 1460, 1436, 1425, 1414 and 1374 (Csp<sup>3</sup>—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<sub>8</sub>H<sub>6</sub>O<sub>4</sub>·2C<sub>3</sub>H<sub>7</sub>NO  
*M<sub>r</sub>* = 312.32  
 Monoclinic, *C*<sub>2</sub>/*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<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.319 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 3980 reflections  
 $\theta$  = 2.5–27.8°  
 $\mu$  = 0.10 mm<sup>-1</sup>  
*T* = 150 (2) K  
 Block, colourless  
 0.34 × 0.28 × 0.18 mm

*Data collection*

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

*R*<sub>int</sub> = 0.044  
 $\theta_{\max}$  = 27.5°  
*h* = -25 → 25  
*k* = -9 → 9  
*l* = -28 → 27

*Refinement*

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.050  
*wR*(*F*<sup>2</sup>) = 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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.27 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{Å}^{-3}$

**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).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
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—H1X...O5X	0.93 (3)	1.58 (8)	2.442 (8)	152 (14)
C9—H9X...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

**Compound (II)***Crystal data*

C<sub>10</sub>H<sub>6</sub>O<sub>8</sub>·4C<sub>3</sub>H<sub>7</sub>NO  
*M<sub>r</sub>* = 546.53  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*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<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 1.352 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 5456 reflections  
 $\theta$  = 2.6–28.6°  
 $\mu$  = 0.11 mm<sup>-1</sup>  
*T* = 150 (2) K  
 Block, colourless  
 0.69 × 0.39 × 0.08 mm

**Table 3**

Selected interatomic distances (Å) for (II).

C1—C2	1.3909 (16)	C4—O1	1.2025 (15)
C1—C3 <sup>i</sup>	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).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
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

*Data collection*

Bruker SMART 1000 CCD diffractometer  
 $\omega$  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* > 2σ(*I*)  
 $R_{\text{int}} = 0.017$   
 $\theta_{\max} = 28.9^\circ$   
*h* = -16 → 17  
*k* = -10 → 10  
*l* = -18 → 18

*Refinement*

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.035  
*wR*(*F*<sup>2</sup>) = 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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{Å}^{-3}$

**Compound (III)***Crystal data*

C<sub>9</sub>H<sub>6</sub>O<sub>6</sub>·2C<sub>3</sub>H<sub>7</sub>NO·H<sub>2</sub>O  
*M<sub>r</sub>* = 374.35  
 Orthorhombic, *P*<sub>2</sub><sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
*a* = 13.8441 (15) Å  
*b* = 19.745 (2) Å  
*c* = 6.6606 (7) Å  
*V* = 1820.7 (3) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.366 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 8092 reflections  
 $\theta$  = 2.5–28.3°  
 $\mu$  = 0.11 mm<sup>-1</sup>  
*T* = 150 (2) K  
 Block, colourless  
 0.57 × 0.16 × 0.12 mm

*Data collection*

Bruker SMART 1000 CCD diffractometer  
 $\omega$  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* > 2σ(*I*)  
 $R_{\text{int}} = 0.022$   
 $\theta_{\max} = 29.0^\circ$   
*h* = -18 → 18  
*k* = -26 → 26  
*l* = -9 → 8

*Refinement*

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.049  
*wR*(*F*<sup>2</sup>) = 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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.66 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.22 \text{ e } \text{Å}^{-3}$

**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...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...O9 <sup>ii</sup>	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...O6 <sup>iii</sup>	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: (ii)  $x, y, 1 + z$ ; (iii)  $\frac{1}{2} - x, -y, z - \frac{1}{2}$ .

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  $U_{\text{iso}}(\text{H})$  values were set at  $1.2U_{\text{eq}}(\text{C})$  for aromatic and aldehyde H atoms, and at  $1.5U_{\text{eq}}(\text{C}, \text{O})$  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: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1747). Services for accessing these data are described at the back of the journal.

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