Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Adducts of 1,1,1-tris(4-hydroxyphenyl)ethane with 1,2-bis(4-pyridyl)ethane and 1,2-bis(4-pyridyl)ethene: continuously interwoven structures in three dimensions

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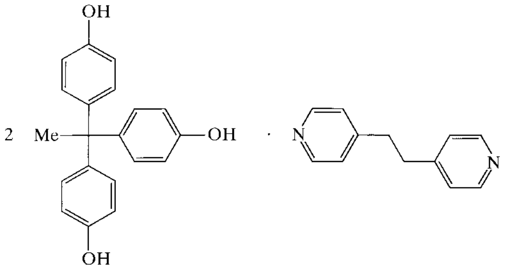
Received 11 October 2001
Accepted 12 October 2001
Online 14 December 2001

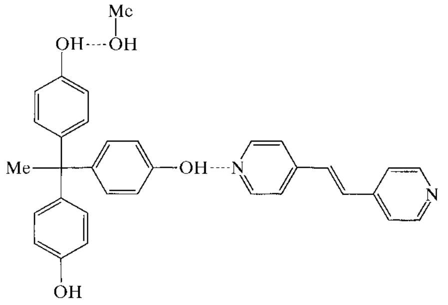
In the adduct 1,2-bis(4-pyridyl)ethane–1,1,1-tris(4-hydroxyphenyl)ethane (1/2), $C_{12}H_{12}N_2{\cdot}2C_{20}H_{18}O_3$, the bipyridyl component lies across an inversion centre in $P\overline{1}$. The tris-phenol molecules [systematic name: 4,4′,4″-(ethane-1,1,1-triyl)triphenol] are linked by O—H···O hydrogen bonds to form sheets built from $R^{4}_{4}(38)$ rings, and symmetry-related pairs of sheets are linked by the bipyridyl molecules *via* O—H···N hydrogen bonds to form open bilayers. Each bilayer is interwoven with two adjacent bilayers, forming a continuous three-dimensional structure. In the adduct 1,2-bis(4-pyridyl)ethene–1,1,1-tris(4-hydroxyphenyl)ethane–methanol (1/1/1), $C_{12}H_{10}N_2{\cdot}C_{20}H_{18}O_3{\cdot}CH_4O$, the molecules are linked by O—H···O and O—H···N hydrogen bonds into three interwoven three-dimensional frameworks, generated by single spiral chains along [010] and [001] and a triple-helical spiral along [100].

Comment

When cocrystallized with 4,4′-bipyridyl, the threefold symmetric tris-phenol 1,1,1-tris(4-hydroxyphenyl)ethane [systematic name: 4,4′,4″-(ethane-1,1,1-triyl)triphenol], $CH_3C(C_6H_4\text{-}OH)_3$, forms a hydrogen-bonded adduct of 3:2 stoichiometry, *viz*. $3C_{10}H_8N_2{\cdot}2C_{20}H_{18}O_3$, in which all the hydrogen bonds are of the O—H···N type and whose supramolecular structure consists of tenfold interwoven nets built from $R^{12}_{12}(126)$ rings (Bényei *et al.*, 1998). In a similar way, 4,4′-bipyridyl forms 3:2 adducts with both 1,3,5-benzenetricarboxylic acid (Sharma & Zaworotko, 1996) and 2,3,5,6-tetrahydroxybenzoquinone (Cowan *et al.*, 2001); in the 1,3,5-benzenetricarboxylic acid adduct, the components are linked into threefold interwoven nets built from $R^{12}_{12}(102)$ rings, while the 2,3,5,6-tetrahydroxybenzoquinone adduct has a three-dimensional supramolecular structure consisting of three interpenetrating frameworks. On the basis of the two-dimensional examples above, there seems to be no obvious impediment to the formation of nets containing yet larger rings and, accordingly, we have now investigated the cocrystallization of 1,1,1-tris(4-hydroxyphenyl)ethane with the extended bipyridyl species 1,2-bis(4-pyridyl)ethane and 1,2-bis(4-pyridyl)ethene in the hope, and expectation, of generating nets built from $R^{12}_{12}(138)$ rings. In the event, no 3:2 adducts could be found; instead, 1,2-bis(4-pyridyl)ethane yields a 1:2 adduct, $C_{12}H_{12}N_2{\cdot}2C_{20}H_{18}O_3$, (I), while 1,2-bis(4-pyridyl)ethene yields a methanol-solvated 1:1 adduct, $C_{12}H_{10}N_2{\cdot}C_{20}H_{18}O_3{\cdot}CH_4O$, (II).



(I)



(II)

In compound (I), the bis(4-pyridyl)ethane molecule lies across a centre of inversion in space group $P\overline{1}$, chosen for the sake of convenience as that at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and the tris-phenol component lies in a general position (Fig. 1). The supramolecular structure consists of continuously interwoven bilayers, giving an overall three-dimensional structure; the constitution of the bilayers, and thence of the overall structure, is most simply analysed in terms of the substructure built from just the tris-phenol component.

Atom O2 in the tris-phenol at (x, y, z) acts as a hydrogen-bond donor to O1 in the molecule at $(x, y, -1 + z)$, so generating by translation a $C(12)$ chain running parallel to the [001] direction. Atom O3 at (x, y, z) similarly acts as donor to O2 at $(x, -1 + y, z)$, producing another $C(12)$ chain, this time by translation along the [010] direction. The combination of these two simple chain motifs generates a sheet parallel to (100) built from a single type of $R^{4}_{4}(38)$ ring (Fig. 2). This reference sheet lies in the domain $0.96 < x < 1.56$, and there is a symmetry-related sheet, generated by the inversion centres at

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DOI: 10.1107/S0108270101017139

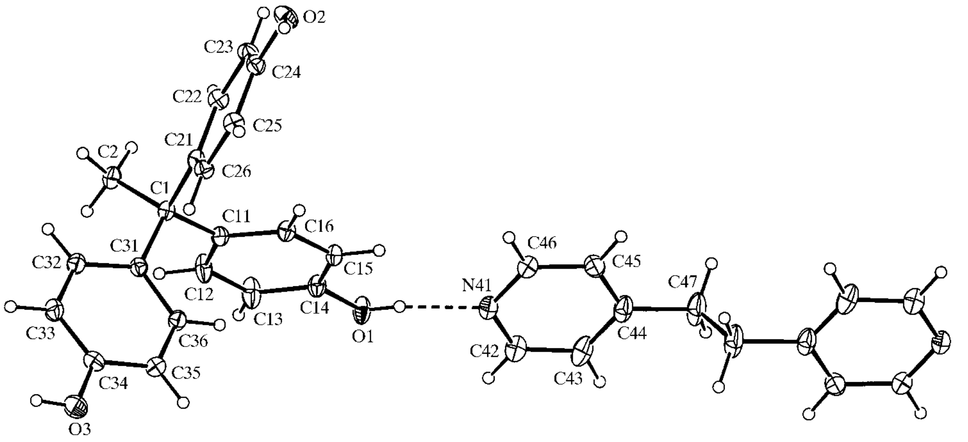

Figure 1
The molecular components of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

$(\frac{1}{2}, y, z)$, which lies in the domain $-0.56 < x < 0.04$. These two sheets are linked into a hydrogen-bonded bilayer by the amines; atoms of type O1 at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ in the domains $0.96 < x < 1.56$ and $-0.56 < x < 0.04$, respectively, act as hydrogen-bond donors to the N1 atoms at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, respectively, which both lie in the reference amine centred at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Hence, these two (100) sheets are multiply linked by the series of amines centred at $(\frac{1}{2}, m + \frac{1}{2}, n + \frac{1}{2})$, where m, n = zero or integer.

Each bilayer is continuously interwoven with the two adjacent bilayers, as the bis(4-pyridyl)ethane linkers in one bilayer pass through the $R_4^4(38)$ rings in the adjacent sheet. In the (100) sheet containing the tris-phenol at (x, y, z), the centroids of the rings are at approximately (1.30, 0.70, 0.45), and similarly by translation along [010] and [001], and there are bis(4-pyridyl)ethane units centred close to these points, at $(\frac{3}{2}, m + \frac{1}{2}, n + \frac{1}{2})$, where m, n = zero or integer. In the other component of the reference bilayer, there is a ring centroid at approximately (−0.30, 0.30, 0.55), close to the centre of the bis(4-pyridyl)ethane molecule at $(-\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and so on. Thus, the bilayer centred at $x = \frac{1}{2}$ is interwoven with the two bilayers centred at $x = \frac{3}{2}$ and $x = -\frac{1}{2}$; with each bilayer interwoven with its two neighbouring bilayers, the overall supramolecular structure is three-dimensional (Fig. 3).

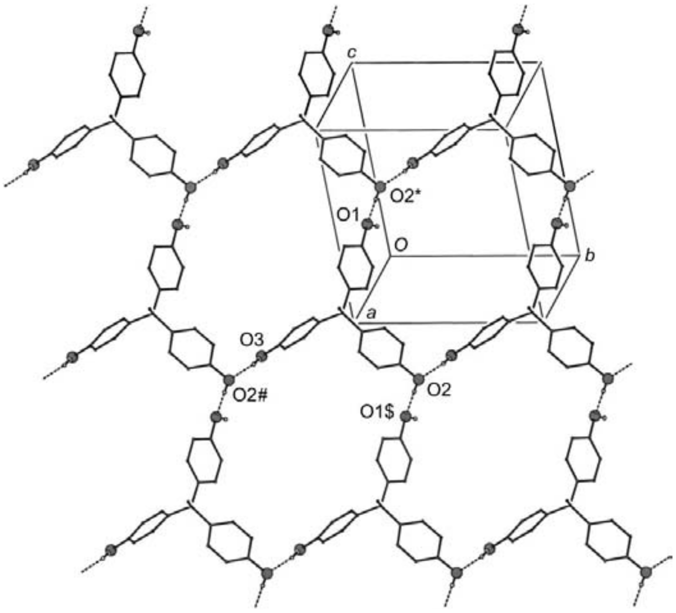

Figure 2
Part of the crystal structure of (I) showing the formation of a (100) sheet built from $R_4^4(38)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions $(x, y, 1 + z)$, $(x, -1 + y, -1 + z)$ and $(x, y, -1 + z)$, respectively.

The (100) sheets of tris-phenol molecules are generated by translation and hence are not puckered; nor are they interwoven. It is of interest to compare these sheets, built from a single tris-phenol molecule, with the analogous sheets of $R_4^4(38)$ rings in the 1:2 adduct $C_2H_8N_2{\cdot}2C_{20}H_{18}O_3$, (III), formed with 1,2-diaminoethane (Ferguson *et al.*, 1998). Here the sheets are built from two independent tris-phenol molecules and they are so deeply interwoven as to be pairwise interwoven; nonetheless the individual ring structures containing seven O atoms, but only four O—H···O hydrogen bonds, are identical in compounds (I) and (III).

The interweaving of the two-dimensional hydrogen-bonded bilayers in (I) to form an overall three-dimensional structure may be compared with the interweaving of hydrogen-bonded molecular ladders to form sheets in the 2:1 adduct of 4,4′-sulfonyldiphenol and pyrazine, (IV) (Ferguson *et al.*, 1999),

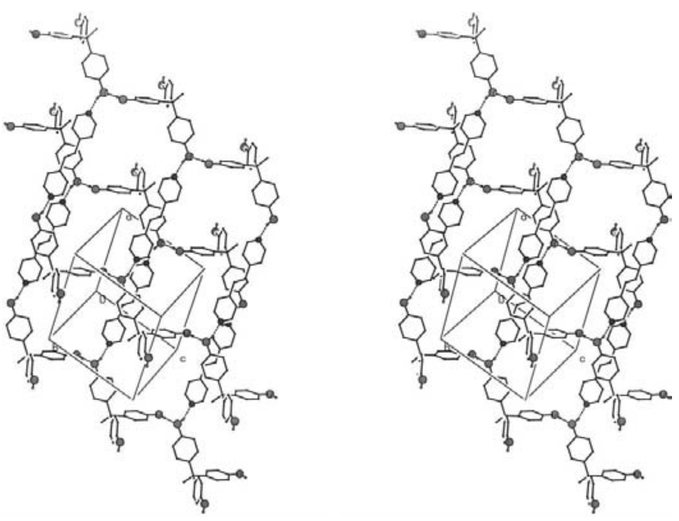

Figure 3
Stereoview of part of the crystal structure of (I) showing the interweaving of adjacent bilayers.

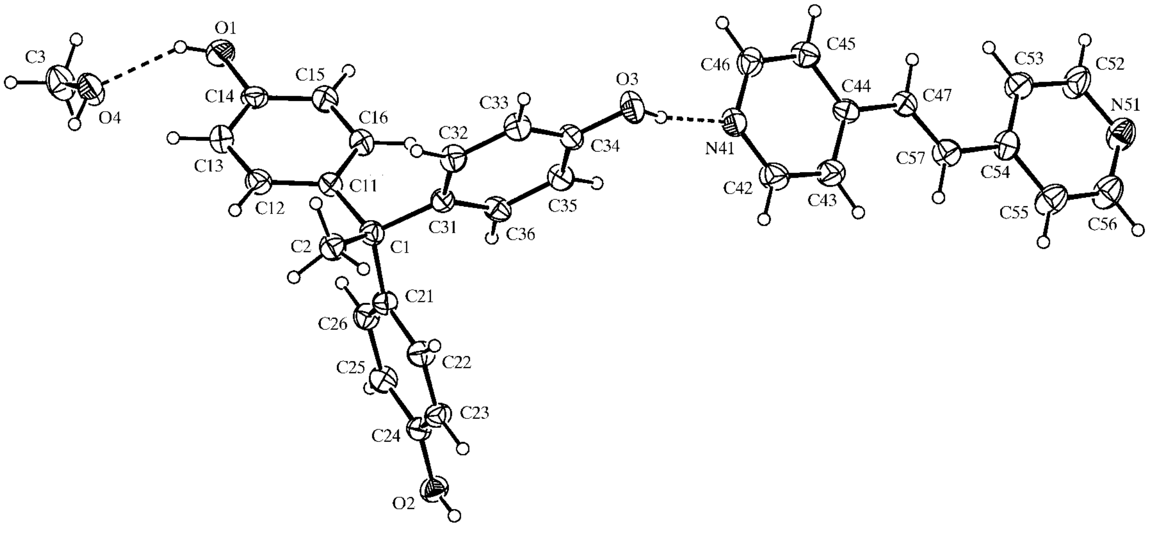

Figure 4
The molecular components of (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

where the ladders have $R_6^6(50)$ rings between the rungs and each ladder is interwoven with two adjacent ladders. We have previously noted (Ferguson *et al.*, 1999) that for systems of this type based on substituted aryl components and containing interwoven substructures, ring types such as $R_4^4(32)$ and $R_4^4(38)$ can permit just one strand of an interwoven substructure to pass through each ring, while larger types, such as $R_6^6(48)$, can accommodate up to three strands; the number apparently depends upon the extent to which the rings are puckered. Consistent with this, in compounds (I) and (III), the $R_4^4(38)$ rings can accommodate either part of another tris-phenol molecule, as in (III), or part of a bipyridyl, as in (I), but these choices are mutually exclusive. The larger $R_6^6(50)$ rings in the interwoven ladders of (IV) can readily accommodate two strands from adjacent ladders.

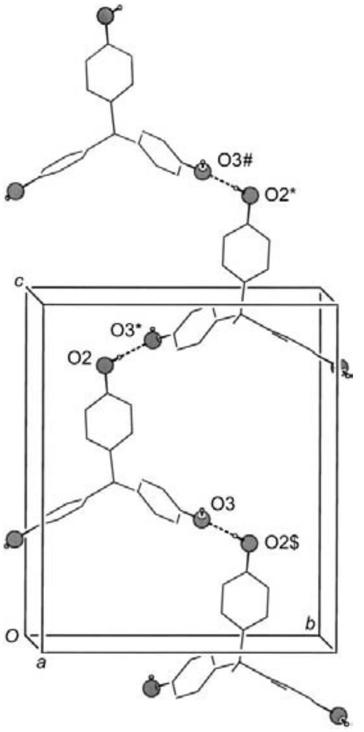

Figure 5
Part of the crystal structure of (II) showing the formation of a $C(12)$ chain along [100]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions $(\frac{1}{2}-x, 1-y, \frac{1}{2}+z)$, $(x, y, 1+z)$ and $(\frac{1}{2}-x, 1-y, -\frac{1}{2}+z)$, respectively.

In the methanol solvate (II), atoms O1 and O3 in the tris-phenol component act as hydrogen-bond donors to the methanol O4 and bipyridyl N41 atoms, respectively, within the asymmetric unit (Fig. 4). The two remaining hydrogen bonds (Table 4) serve to link the molecules in three dimensions; the hydrogen bonds having O2 and O4 as donors independently generate spiral chains along [001] and [100], respectively, while their combined action generates a spiral chain long [010].

The tris-phenol O2 atom at (x, y, z) acts as hydrogen-bond donor to O3 at $(\frac{1}{2}-x, 1-y, \frac{1}{2}+z)$, while O2 at $(\frac{1}{2}-x, 1-y, \frac{1}{2}+z)$ acts as donor to O3 at $(x, y, 1+z)$, so producing a $C(12)$ chain running parallel to [001] and generated by the 2_1 screw axis along $(\frac{1}{4},\frac{1}{2},z)$ (Fig. 5). The methanol O4 atom at (x, y, z) acts as donor to N51 at $(-\frac{3}{2}+x, \frac{1}{2}-y, 1-z)$, while O4 at $(-\frac{3}{2}+x, \frac{1}{2}-y, 1-z)$, in turn, acts as donor to N51 at $(-3+x, y, z)$. The resulting $C_3^3(25)$ chain parallel to [100] (Fig. 6) is generated by the 2_1 axis along $(x,\frac{1}{4},\frac{1}{2})$ and it has a repeat vector along [100] of three unit-cell lengths; there are thus three such spiral chains, related by translation, forming a triple helix along [100]. Each of these chains along [001] and [100] involves just one hydrogen bond outside the asymmetric unit; the combination of these two spiral chains generates a third spiral, along [010], involving both of the hydrogen bonds outside the asymmetric unit,

Just as O4 at (x, y, z) acts as donor to N51 at $(-\frac{3}{2}+x, \frac{1}{2}-y, 1-z)$ to generate the [100] chain, so O4 at $(\frac{1}{2}-x, 1-y, \frac{1}{2}+z)$ in the [001] chain acts as donor to N51 at $(2-x, \frac{1}{2}+y, \frac{3}{2}-z)$;

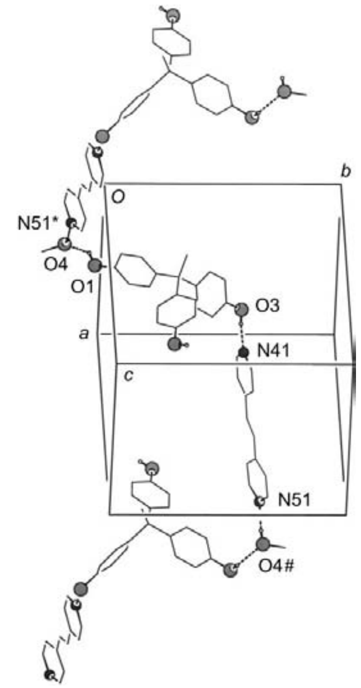

Figure 6
Part of the crystal structure of (II) showing one component of the triple helix along [001]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions ($-\frac{3}{2}+x$, $\frac{1}{2}-y$, $1-z$) and ($\frac{3}{2}+x$, $\frac{1}{2}-y$, $1-z$), respectively.

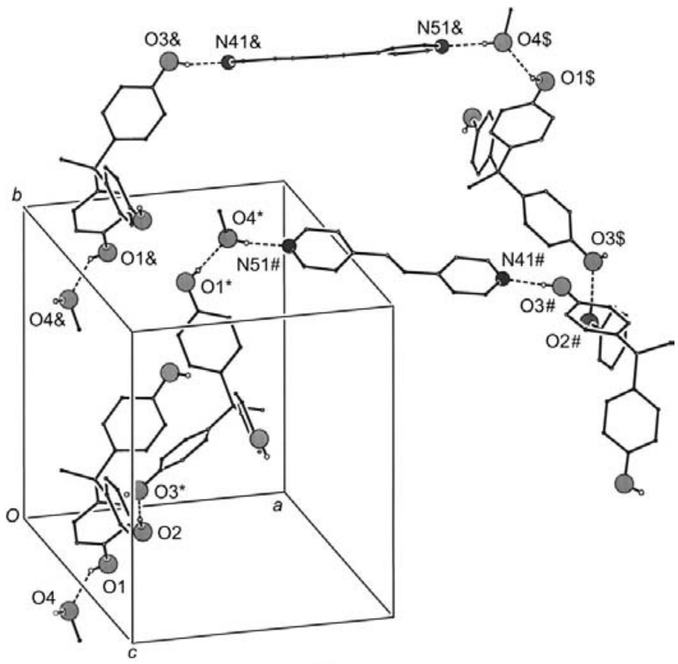

Figure 7
Part of the crystal structure of (II) showing the formation of a $C_4^4(35)$ chain along [010]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions ($\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$), ($2-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$), ($\frac{3}{2}+x$, $\frac{3}{2}-y$, $1-z$) and (x, $1+y$, z), respectively.

O2 at ($2-x, \frac{1}{2}+y, \frac{3}{2}-z$), in turn, acts as donor to O3 at ($\frac{3}{2}+x$, $\frac{3}{2}-y$, $1-z$), and O4 at ($\frac{3}{2}+x$, $\frac{3}{2}-y$, $1-z$) acts as donor to N51 at (x, $1+y$, z). In this way, a $C_4^4(35)$ chain is generated parallel to [010] (Fig. 7), which links the [100] and [001] spirals, so forming a three-dimensional framework. Since there are three unconnected chains in the triple helix along [100], there are three interwoven frameworks in the structure.

In both (I) and (II), the tris-phenol component shows significant deviations from the idealized C_3 molecular symmetry (Tables 1 and 2). While the bipyridyl component in (II) is almost flat, in (I), the bipyridyl skeleton is very far from being planar. The bond lengths and angles present no unusual features.

Experimental

Equimolar quantities of 1,1,1-tris(4-hydroxyphenyl)ethane and the appropriate bipyridyl were separately dissolved in methanol. For each compound, solutions of the tris-phenol and the appropriate bipyridyl were mixed and set aside to crystallize, providing (I) and (II), respectively. Analyses, (I): found C 77.8, H 6.2, N 3.5%; $C_{52}H_{48}N_2O_6$ requires C 77.7, H 6.3, N 3.6%; (II): found C 76.0, H 6.7, N 5.4%; $C_{33}H_{32}N_2O_4$ requires C 76.1, H 6.2, N 5.4%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

Compound (I)

Crystal data

$C_{12}H_{12}N_2{\cdot}2C_{20}H_{18}O_3$
$M_r = 796.92$
Triclinic, $P\overline{1}$
$a = 10.2076$ (2) Å
$b = 10.6559$ (2) Å
$c = 10.9341$ (2) Å
$\alpha = 100.9920$ (16)°
$\beta = 109.4530$ (14)°
$\gamma = 101.6700$ (11)°
$V = 1054.49$ (3) Å^3
$Z = 1$
$D_x = 1.255$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4446 reflections
$\theta = 3.1$–27.5°
$\mu = 0.08$ mm^{-1}
$T = 150$ (2) K
Block, colourless
0.30 × 0.20 × 0.18 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.976$, $T_{\max} = 0.985$
13 679 measured reflections
4797 independent reflections
3886 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 12$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.123$
$S = 1.09$
4797 reflections
276 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.196P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.074 (8)

Table 1
Selected torsion angles (°) for (I).

C2—C1—C11—C12	−42.87 (17)	C2—C1—C31—C32	−35.04 (15)
C2—C1—C21—C22	−52.93 (14)	C43—C44—C47—C47$^{\rm i}$	−104.0 (3)

Symmetry code: (i) $1-x, 1-y, 1-z$.

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
O1—H1···N41	0.84	1.81	2.6145 (18)	159
O2—H2···O1$^{\mathrm{i}}$	0.84	1.83	2.6671 (13)	175
O3—H3···O2$^{\mathrm{ii}}$	0.84	1.98	2.8039 (17)	168

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

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
O1—H1···O4	0.84	2.03	2.652 (6)	131
O2—H2···O3$^{\mathrm{i}}$	0.84	1.85	2.684 (6)	172
O3—H3···N41	0.84	1.81	2.631 (6)	166
O4—H4···N51$^{\mathrm{ii}}$	0.84	1.87	2.696 (6)	166

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

Compound (II)

Crystal data

$C_{12}H_{10}N_2 \cdot C_{20}H_{18}O_3 \cdot CH_4O$
$M_r = 520.61$
Orthorhombic, $P2_12_12_1$
$a = 11.8264\ (9)$ Å
$b = 14.2158\ (9)$ Å
$c = 16.8109\ (12)$ Å
$V = 2826.3\ (3)$ Å^3
$Z = 4$
$D_x = 1.223$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2663 reflections
$\theta = 2.6$–$25.0°$
$\mu = 0.08$ mm^{-1}
$T = 150\ (2)$ K
Block, colourless
$0.30 \times 0.26 \times 0.16$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.976$, $T_{\max} = 0.987$
11 922 measured reflections
2795 independent reflections
1859 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.082$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 20$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.149$
$S = 1.08$
2795 reflections
359 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0458P)^2 + 1.5250P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0144 (17)

Table 3
Selected torsion angles (°) for (II).

C2—C1—C11—C12	−28.0 (6)	C43—C44—C47—C57	1.2 (9)
C2—C1—C21—C22	−57.8 (6)	C53—C54—C57—C47	−6.8 (10)
C2—C1—C31—C32	−30.6 (7)		

Compound (I) crystallized in the triclinic system; space group $P\overline{1}$ was assumed and subsequently confirmed by the analysis. For compound (II), space group $P2_12_12_1$ was uniquely assigned from the systematic absences. The refined value of the Flack (1983) parameter [2 (3)] was inconclusive (Flack & Bernardinelli, 2000), hence Friedel equivalents were merged prior to the final refinements. All H atoms were treated as riding atoms, with C—H distances in the range 0.95–0.99 Å and O—H distances of 0.84 Å.

For compounds (I) and (II), data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC Canada. CMZ thanks the Association of Commonwealth Universities for the award of a Commonwealth Fellowship 2000–2001.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1516). Services for accessing these data are described at the back of the journal.

References

Bényei, A. C., Coupar, P. I., Ferguson, G., Glidewell, C., Lough, A. J. & Meehan, P. R. (1998). *Acta Cryst.* C**54**, 1515–1519.
Cowan, J. A., Howard, J. A. K. & Leech, M. A. (2001). *Acta Cryst.* C**57**, 1196–1198.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Ferguson, G., Glidewell, C., Gregson, R. M. & Lavender, E. S. (1999). *Acta Cryst.* B**55**, 573–590.
Ferguson, G., Glidewell, C., Gregson, R. M. & Meehan, P. R. (1998). *Acta Cryst.* B**54**, 330–338.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Flack, H. D. & Bernardinelli, G. (2000). *J. Appl. Cryst.* **33**, 1143–1148.
Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.
Sharma, C. V. K. & Zaworotko, M. J. (1996). *Chem. Commun.* pp. 2655–2656.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Spek, A. L. (2001). *PLATON*. August 2001 Version. University of Utrecht, The Netherlands.