

Supramolecular structures of five 5-(arylmethylene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-triones: isolated molecules, hydrogen-bonded chains and chains of fused hydrogen-bonded rings

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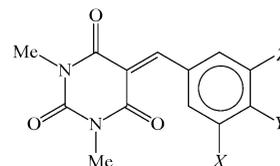
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In each of the five title compounds, namely 5-benzylidene-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione, C₁₃H₁₂N₂O₃, (I), 5-(3-methoxybenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione, C₁₄H₁₄N₂O₄, (II), 5-(4-methoxybenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione, C₁₄H₁₄N₂O₄, (III), 5-[4-(dimethylamino)benzylidene]-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione, C₁₅H₁₇N₃O₃, (IV), and 5-(3,5-di-*tert*-butyl-4-hydroxybenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione, C₂₁H₂₈N₂O₄, (V), which crystallizes with *Z'* = 2 in *P* $\bar{1}$, there is a very wide C–C–C angle at the methine C atom linking the two rings, ranging from 137.1 (2)° in (I) to 139.14 (14)° in (III). There is evidence for intramolecular charge separation in (IV) and, to a lesser degree, in (III). The molecules of (I)–(III) are linked by pairs of C–H···O hydrogen bonds into chains of edge-fused rings, with alternating *R*₂²(14) and *R*₂²(16) rings in (I), alternating *R*₂²(14) and *R*₄⁴(20) rings in (II), with two types of *R*₂²(16) rings alternating in (III). The molecules in (IV) are linked by a single C–H···O hydrogen bond into simple *C*(8) chains, but there are no direction-specific intermolecular interactions in (V).

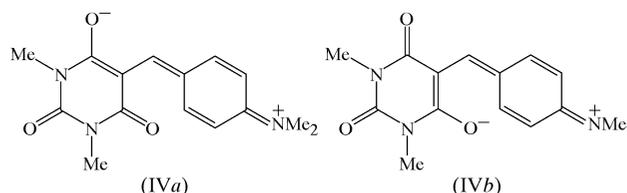
Comment

The title compounds, (I)–(V), were initially prepared as part of a study of solvatochromism (Rezende *et al.*, 2001, 2004), and it was considered necessary to determine their molecular and

supramolecular structures for subsequent comparison with their NMR and solvatochromic behaviour.



- (I) *X* = *Y* = *Z* = H
 (II) *X* = OMe, *Y* = *Z* = H
 (III) *X* = *Z* = H, *Y* = OMe
 (IV) *X* = *Z* = H, *Y* = NMe₂
 (V) *X* = *Z* = CMe₃, *Y* = OH



Compounds (I)–(IV) (Figs. 1–4) all crystallize with *Z'* = 1, but compound (V) (Fig. 5) crystallizes with *Z'* = 2 in space group *P* $\bar{1}$; the two independent molecules are very close to being mirror images of one another, but a careful search for possible additional symmetry revealed none. In each of

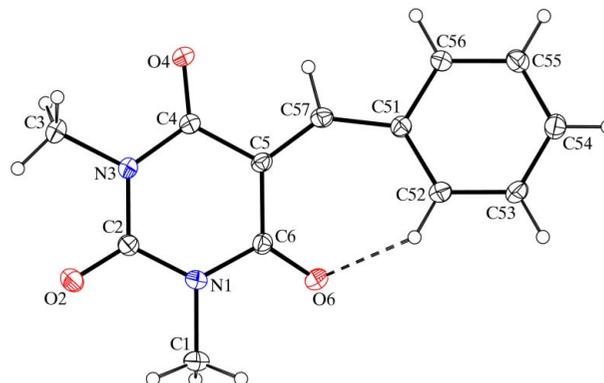


Figure 1
 The molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

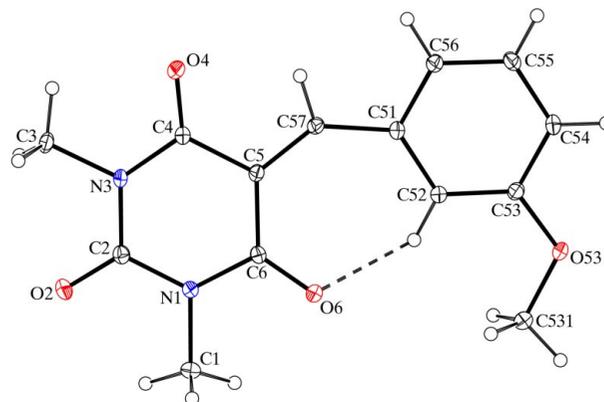


Figure 2
 The molecule of compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

compounds (I)–(V), the molecules are nearly planar, as shown by the leading torsion angles (Table 1), and there are short intramolecular C–H···O contacts to both O4 and O6 (Table 2). Of these, the dimensions of that involving O6 are suggestive of a genuine hydrogen bond. However, the bond angles at C5 and C57 give a strong indication that the H57···O4 contact is repulsive: the C–C–C angles at C57 are, in all cases, particularly large for fragments of this type. Similarly, the bond angles at C51 are more consistent with a repulsive H52···O6 contact than with a significantly attractive contact. However, it is noteworthy that these repulsive contacts are accommodated by distortion of the skeletal bond angles in preference to an evasive rotation around the C51–C57 bond, which would appear at first sight to represent a far less energy-costly resolution. In each of the methoxy compounds, *viz.* (II) and (III), the methoxy C atom is nearly coplanar with the adjacent aryl ring and the exocyclic bond angles at the aryl C atom *ipso* to the methoxy substituent, *viz.* C53 in (II) and C54 in (III), show the usual deviations from 120°.

Whereas in compounds (I) and (II), the C–C distances in the aryl rings are consistent with classically delocalized π electrons, in compounds (III) and, particularly, (IV), there is evidence for a significant contribution from polarized charge-separated forms. Thus in (IV), the C52–C53 and C55–C56

distances are significantly less than the remaining distances in the aryl ring. Likewise, the C51–C57 bond in (IV) is the shortest such bond observed in this series, while C57–C5 is the longest. The C4–O4 and C6–O6 bonds are also longer in (IV) than in (I)–(III). Finally, the C54–N54 distance is less than the quartile value (1.363 Å; Allen *et al.*, 1987) for bonds of this type. Taken all together, these observations provide evidence for the contribution of the polarized forms (IVa) and (IVb) to the overall molecular–electronic structure. There are similar, although weaker, indications for the contribution of similar forms in (III), not only from the distances within the aryl ring but also, in particular, the fact that the C51–C57 bond is shorter in (III) than in the isomeric compound (II), while C57–C5 is longer in (III) than in (II). In addition, the C54–O54 bond in (III) is somewhat shorter than the C53–O53 bond in (II). In compound (V), the indications for charge-separation are very weak, at best.

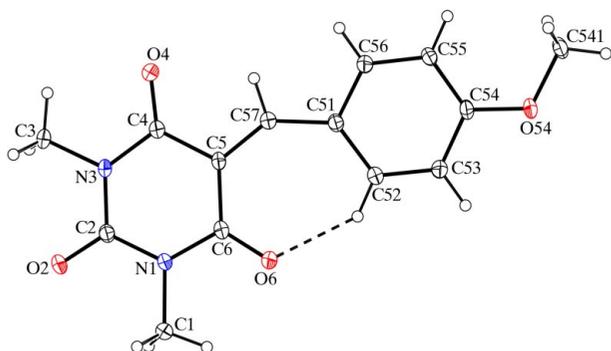


Figure 3
The molecule of compound (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

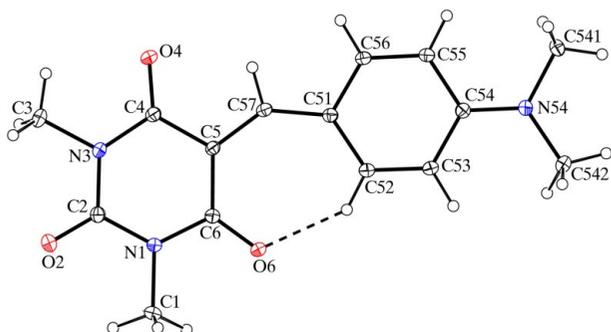


Figure 4
The molecule of compound (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

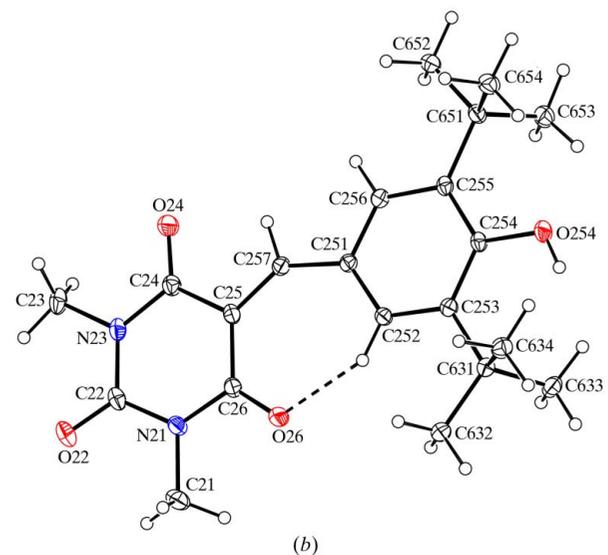
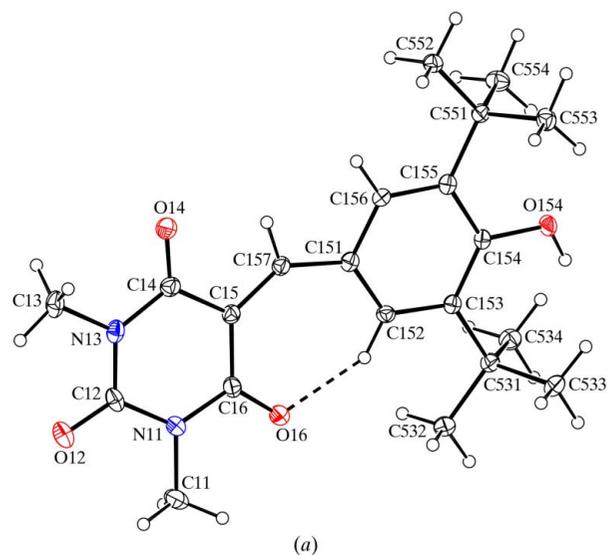


Figure 5
The independent molecules of compound (V), showing the atom-labelling schemes for (a) molecule 1 and (b) molecule 2. Displacement ellipsoids are drawn at the 30% probability level.

In each of compounds (I) and (II), the heterocyclic ring shows a small but significant deviation from planarity, with a total puckering amplitude Q (Cremer & Pople, 1975) of 0.105 (2) Å in (I) and 0.075 (2) Å in (II). The ring-puckering parameters for the atom sequence N1–C2–N3–C4–C5–C6 are $\theta = 51.9$ (11)° and $\varphi = 276.7$ (16)° for (I), and $\theta = 137.2$ (11)° and $\varphi = 45.9$ (17)° for (II). The best single description for both of these rings is thus as half-chair conformers (Evans & Boeyens, 1989). In the two independent molecules in compound (V), the heterocyclic rings have effectively identical total puckering amplitudes, *viz.* 0.115 (3) Å in molecule 1 (Fig. 5a) and 0.114 (3) Å in molecule 2 (Fig. 5b). The ring-puckering parameters for the atom sequences Nn1–Cn2–Nn3–Cn4–Cn5–Cn6 (where $n = 1$ or 2) are $\theta = 70.0$ (15)° and $\varphi = 16.7$ (14)° when $n = 1$, and $\theta = 109.5$ (15)° and $\varphi = 193.5$ (14)°

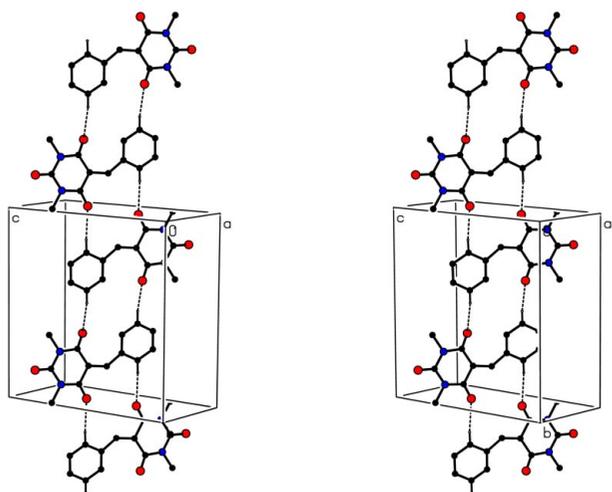


Figure 6
A stereoview of part of the crystal structure of compound (I), showing the formation of a [010] chain of alternating $R_2^2(14)$ and $R_2^2(16)$ rings. For the sake of clarity, the H atoms not involved in these motifs have been omitted.

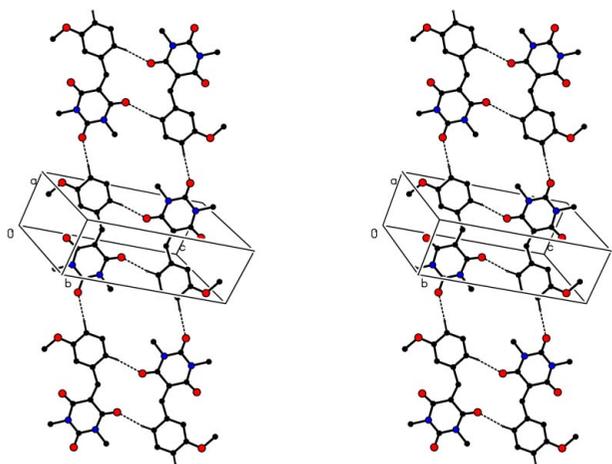


Figure 7
A stereoview of part of the crystal structure of compound (II), showing the formation of a $[210]$ chain of alternating $R_2^2(14)$ and $R_1^2(20)$ rings. For the sake of clarity, the H atoms not involved in these motifs have been omitted.

when $n = 2$, emphasizing the nearly enantiomorphous character of the two molecules in the selected asymmetric unit. The best single descriptor for these ring conformations is screw-boat, for which ideally $\theta = 67.5^\circ$ and $\varphi = (60k + 30)^\circ$. By contrast, the heterocyclic rings in compounds (III) and (IV) are effectively planar.

In compounds (I)–(III), the molecules are linked by pairs of C–H...O hydrogen bonds (Table 2) into chains of edge-fused rings, but the details of these interactions are different in each case, as are the structures of the resulting chains. In compound (I) (Fig. 1), aryl atoms C53 and C56 in the molecule at (x, y, z) act as hydrogen-bond donors to, respectively, atom O6 in the molecule at $(1 - x, 1 - y, 1 - z)$ and O4 in the molecule at $(1 - x, -y, 1 - z)$, so generating by inversion a chain of edge-fused rings running parallel to the [010] direction. There are $R_2^2(16)$ (Bernstein *et al.*, 1995) rings centred at $(\frac{1}{2}, \frac{1}{2} + n, \frac{1}{2})$ ($n =$ zero or integer) and $R_2^2(14)$ rings centred at $(\frac{1}{2}, n, \frac{1}{2})$ ($n =$ zero or integer) (Fig. 6). Two chains of this type pass through each unit cell, centred along the lines $(\frac{1}{2}, y, \frac{1}{2})$ and $(0, y, 0)$, but there are no direction-specific interactions between adjacent chains.

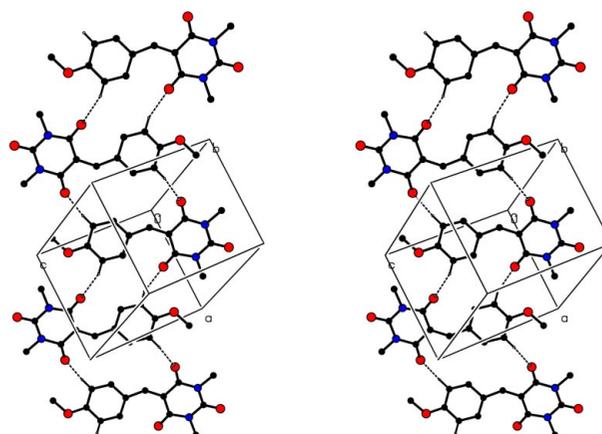


Figure 8
A stereoview of part of the crystal structure of compound (III), showing the formation of a $[110]$ chain containing two types of $R_2^2(16)$ ring. For the sake of clarity, the H atoms not involved in these motifs have been omitted.

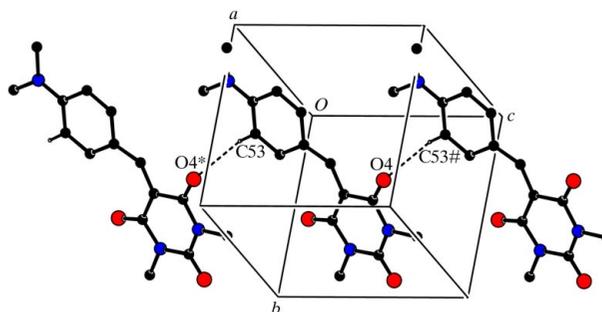


Figure 9
Part of the crystal structure of compound (IV), showing the formation of a C(8) chain along [001]. For the sake of clarity, the H atoms not involved in this motif have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, y, z - 1)$ and $(x, y, 1 + z)$, respectively.

In compound (II) (Fig. 2), aryl atom C56 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom O4 in the molecule at $(1 - x, 1 - y, 1 - z)$, so generating by inversion an $R_2^2(14)$ ring analogous to that in compound (I), although now centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 6). At the same time, atom C54 at (x, y, z) acts as donor to atom O2 in the molecule at $(x - 2, 1 + y, z)$, so generating by translation a $C(11)$ chain running parallel to the $[\bar{2}10]$ direction. The combination of the two hydrogen bonds then generates a $[\bar{2}10]$ chain of centrosymmetric edge-fused $R_2^2(14)$ and $R_4^4(20)$ rings. Of the four molecules which participate in the formation of an $R_4^4(20)$ ring, two act as double donors and two as double acceptors of hydrogen bonds (Fig. 7). Again, there are no direction-specific interactions between adjacent chains.

The chain formation in compound (III) is rather different from that in the isomeric compound, (II). In (III), aryl atoms C53 and C55 in the molecule at (x, y, z) act as hydrogen-bond donors to, respectively, atoms O6 and O4 in the molecules at $(1 - x, -y, 1 - z)$ and $(-x, 1 - y, 1 - z)$, so generating by inversion a chain of edge-fused rings along $[1\bar{1}0]$ in which there are two distinct types of centrosymmetric $R_2^2(16)$ ring (Fig. 8), one involving O4 as the sole hydrogen-bond acceptor and the other involving O6 only.

In contrast with the chain formation in compounds (I)–(III), that in compound (IV) (Fig. 4) depends upon just one intermolecular C–H...O hydrogen bond. Atom C53 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom O4 in the molecule at $(x, y, z - 1)$, thereby generating by translation a simple $C(8)$ chain running parallel to the $[001]$ direction (Fig. 9). Two such chains, antiparallel to one another, pass through each unit cell, but there are no direction-specific interactions between adjacent chains.

In compound (V), there are no direction-specific intermolecular interactions. In particular, neither of the hydroxyl groups participates in hydrogen-bond formation, because of the steric shielding provided by the two adjacent *tert*-butyl substituents. The nearest plausible donor/acceptor atoms to O154 and O254 are, respectively, O154 at $(1 - x, -y, 1 - z)$, with O...Oⁱ and O...Hⁱ distances of 3.391 (2) and 3.56 Å, respectively, and O254 at $(2 - x, 1 - y, 1 - z)$, with O...Oⁱⁱ and O...Hⁱⁱ distances of 3.010 (2) and 2.91 Å, respectively [symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $2 - x, 1 - y, 1 - z$].

Experimental

For the preparation of compounds (I)–(V), mixtures of *N,N*-dimethylbarbituric acid (0.50 g, 3.2 mmol) and the appropriate aryl-aldehyde (3.2 mmol) in glacial acetic acid (4 ml) were heated under reflux for 2 h, cooled and filtered. The resulting solids were washed with diethyl ether (5 ml). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in acetic acid for (I) and (II), in acetonitrile for (III) and (IV), or in ethanol for (V). For (I), m.p. 430–432 K (literature value 430–431 K; Suzuki *et al.*, 1976); for (II), m.p. 406–408 K; for (III), m.p. 416–418 K (literature value 417–418 K; Suzuki *et al.*, 1976); for (IV), m.p. 497–499 K (literature value 497–499 K; Rezende *et al.*, 2001); for (V), m.p. 467–469 K.

Compound (I)

Crystal data

$C_{13}H_{12}N_2O_3$
 $M_r = 244.25$
 Monoclinic, $P2_1/n$
 $a = 6.1293$ (3) Å
 $b = 13.9633$ (8) Å
 $c = 13.2727$ (8) Å
 $\beta = 97.688$ (4)°
 $V = 1125.74$ (11) Å³
 $Z = 4$

$D_x = 1.441$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2573 reflections
 $\theta = 2.9$ – 27.6 °
 $\mu = 0.10$ mm⁻¹
 $T = 120$ (2) K
 Plate, colourless
 $0.34 \times 0.25 \times 0.09$ mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.954$, $T_{\max} = 0.991$
 12 444 measured reflections

2573 independent reflections
 1885 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$
 $\theta_{\max} = 27.6$ °
 $h = -7 \rightarrow 7$
 $k = -18 \rightarrow 16$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.069$
 $wR(F^2) = 0.201$, $S = 1.05$
 2573 reflections
 165 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1092P)^2 + 0.6873P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.47$ e Å⁻³
 $\Delta\rho_{\min} = -0.30$ e Å⁻³

Compound (II)

Crystal data

$C_{14}H_{14}N_2O_4$
 $M_r = 274.27$
 Triclinic, $P\bar{1}$
 $a = 5.6946$ (2) Å
 $b = 8.2994$ (3) Å
 $c = 14.0411$ (5) Å
 $\alpha = 73.5580$ (17)°
 $\beta = 87.393$ (2)°
 $\gamma = 77.037$ (2)°
 $V = 620.13$ (4) Å³

$Z = 2$
 $D_x = 1.469$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2847 reflections
 $\theta = 3.0$ – 27.5 °
 $\mu = 0.11$ mm⁻¹
 $T = 120$ (2) K
 Block, colourless
 $0.52 \times 0.34 \times 0.16$ mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.953$, $T_{\max} = 0.983$
 14 859 measured reflections

2847 independent reflections
 2331 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\max} = 27.5$ °
 $h = -7 \rightarrow 7$
 $k = -10 \rightarrow 10$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.132$, $S = 1.11$
 2847 reflections
 184 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0732P)^2 + 0.1975P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.40$ e Å⁻³
 $\Delta\rho_{\min} = -0.40$ e Å⁻³

Compound (III)

Crystal data

$C_{14}H_{14}N_2O_4$
 $M_r = 274.27$
 Triclinic, $P\bar{1}$
 $a = 7.5906$ (6) Å
 $b = 8.2989$ (7) Å
 $c = 10.3010$ (10) Å
 $\alpha = 92.544$ (6)°
 $\beta = 93.074$ (5)°
 $\gamma = 104.456$ (6)°
 $V = 626.33$ (10) Å³

$Z = 2$
 $D_x = 1.454$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2860 reflections
 $\theta = 3.1$ – 27.5 °
 $\mu = 0.11$ mm⁻¹
 $T = 120$ (2) K
 Block, yellow
 $0.48 \times 0.44 \times 0.34$ mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.947$, $T_{\max} = 0.964$
 10 553 measured reflections

2860 independent reflections
 2173 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -9 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.136$, $S = 1.06$
 2860 reflections
 184 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0773P)^2 + 0.1359P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.27 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{Å}^{-3}$

Compound (IV)

Crystal data

$\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_3$
 $M_r = 287.32$
 Triclinic, $P\bar{1}$
 $a = 8.6187(2) \text{ Å}$
 $b = 8.8451(3) \text{ Å}$
 $c = 9.0566(3) \text{ Å}$
 $\alpha = 82.2980(18)^\circ$
 $\beta = 84.465(2)^\circ$
 $\gamma = 82.365(2)^\circ$
 $V = 675.94(4) \text{ Å}^3$

$Z = 2$
 $D_x = 1.412 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 3073 reflections
 $\theta = 3.1\text{--}27.5^\circ$
 $\mu = 0.10 \text{ mm}^{-1}$
 $T = 120(2) \text{ K}$
 Block, orange
 $0.40 \times 0.30 \times 0.20 \text{ mm}$

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.955$, $T_{\max} = 0.980$
 13 410 measured reflections

3073 independent reflections
 2698 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -11 \rightarrow 11$
 $k = -11 \rightarrow 11$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.108$, $S = 1.05$
 3073 reflections
 194 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 0.2209P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.009$
 $\Delta\rho_{\text{max}} = 0.28 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{Å}^{-3}$

Compound (V)

Crystal data

$\text{C}_{21}\text{H}_{28}\text{N}_2\text{O}_4$
 $M_r = 372.45$
 Triclinic, $P\bar{1}$
 $a = 9.6040(3) \text{ Å}$
 $b = 11.6691(4) \text{ Å}$
 $c = 17.2905(6) \text{ Å}$
 $\alpha = 97.4860(16)^\circ$
 $\beta = 92.5540(18)^\circ$
 $\gamma = 90.006(2)^\circ$
 $V = 1919.29(11) \text{ Å}^3$

$Z = 4$
 $D_x = 1.289 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 8856 reflections
 $\theta = 3.1\text{--}27.7^\circ$
 $\mu = 0.09 \text{ mm}^{-1}$
 $T = 120(2) \text{ K}$
 Plate, colourless
 $0.15 \times 0.10 \times 0.03 \text{ mm}$

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.967$, $T_{\max} = 0.997$
 39 965 measured reflections
 8856 independent reflections

6116 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.068$
 $\theta_{\text{max}} = 27.7^\circ$
 $h = -12 \rightarrow 12$
 $k = -15 \rightarrow 15$
 $l = -22 \rightarrow 22$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.070$
 $wR(F^2) = 0.179$, $S = 1.05$
 8856 reflections
 503 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2 + 1.5268P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.47 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.42 \text{ e } \text{Å}^{-3}$

Table 1
 Selected bond distances (Å) for compounds (I)–(V).

Parameter	(I)	(II)	(III)	(IV)	(V), molecule 1	(V), molecule 2
<i>n</i>	nil	nil	nil	nil	1	2
Cn2—On2	1.211 (3)	1.2160 (18)	1.2166 (18)	1.2189 (14)	1.219 (3)	1.216 (3)
Cn4—On4	1.219 (3)	1.2235 (17)	1.2204 (18)	1.2273 (14)	1.217 (3)	1.224 (3)
Cn6—On6	1.211 (3)	1.2234 (18)	1.2157 (19)	1.2250 (14)	1.223 (3)	1.217 (3)
Cn5—Cn57	1.362 (3)	1.3627 (19)	1.366 (2)	1.3814 (16)	1.364 (3)	1.367 (3)
Cn57—Cn51	1.447 (3)	1.4658 (19)	1.449 (2)	1.4295 (15)	1.457 (3)	1.453 (3)
Cn51—Cn52	1.403 (3)	1.4065 (19)	1.410 (2)	1.4179 (15)	1.396 (3)	1.397 (3)
Cn52—Cn53	1.391 (3)	1.390 (2)	1.378 (2)	1.3751 (16)	1.396 (3)	1.393 (3)
Cn53—Cn54	1.387 (3)	1.396 (2)	1.402 (2)	1.4191 (16)	1.406 (3)	1.406 (3)
Cn54—Cn55	1.383 (4)	1.385 (2)	1.388 (2)	1.4211 (15)	1.414 (3)	1.412 (3)
Cn55—Cn56	1.397 (3)	1.392 (2)	1.384 (2)	1.3709 (16)	1.382 (3)	1.385 (3)
Cn56—Cn51	1.405 (3)	1.404 (2)	1.404 (2)	1.4202 (16)	1.401 (3)	1.400 (3)
Cn53—On53		1.3679 (17)				
Cn54—On54			1.3578 (17)		1.367 (3)	1.369 (3)
Cn54—Nn54				1.3545 (14)		
Cn5—Cn4—On4	123.6 (2)	122.83 (13)	123.49 (13)	123.61 (11)	127.7 (2)	123.5 (2)
Cn5—Cn6—On6	124.5 (2)	124.95 (13)	124.00 (14)	125.54 (10)	124.6 (2)	125.1 (2)
Cn4—Cn5—Cn57	115.23 (19)	114.14 (12)	114.26 (13)	114.20 (10)	113.2 (2)	113.4 (2)
Cn6—Cn5—Cn57	125.99 (19)	127.41 (13)	126.71 (13)	126.83 (10)	128.0 (2)	127.7 (2)
Cn5—Cn57—Cn51	137.1 (2)	137.62 (13)	139.14 (14)	138.79 (10)	138.5(2)	138.5 (2)
Cn57—Cn51—Cn52	127.2 (2)	126.34 (13)	128.25 (14)	128.58 (10)	127.1 (2)	127.2 (2)
Cn52—Cn53—On53		123.31 (13)				
Cn54—Cn53—On53		115.69 (13)				
Cn53—Cn54—On54			115.72 (13)		121.2 (2)	118.9 (2)
Cn55—Cn54—On54			124.18 (14)		115.8 (2)	118.3 (2)
Cn5—Cn57—Cn51—Cn52	−14.6 (2)	4.1 (3)	6.1 (3)	0.9 (2)	4.5 (5)	−4.6 (5)
Cn52—Cn53—On53—Cn531		−2.1 (2)				
Cn53—Cn54—On54—Cn541			176.86 (13)			

Table 2

Hydrogen bonds and short intramolecular contacts (Å, °) for compounds (I)–(V).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
Compound (I)				
C52—H52...O6	0.95	2.17	2.867 (3)	130
C53—H53...O6 ⁱ	0.95	2.47	3.399 (3)	167
C56—H56...O4 ⁱⁱ	0.95	2.40	3.310 (3)	159
C57—H57...O4	0.95	2.28	2.751 (3)	110
Compound (II)				
C52—H52...O6	0.95	2.07	2.855 (2)	139
C54—H54...O2 ⁱⁱⁱ	0.95	2.38	3.334 (2)	178
C56—H56...O4 ⁱ	0.95	2.38	3.313 (2)	168
C57—H57...O4	0.95	2.24	2.727 (2)	111
Compound (III)				
C52—H52...O6	0.95	2.11	2.889 (2)	138
C53—H53...O6 ⁱⁱ	0.95	2.52	3.387 (2)	152
C55—H55...O4 ^{iv}	0.95	2.39	3.261 (2)	152
C57—H57...O4	0.95	2.23	2.729 (2)	112
Compound (IV)				
C52—H52...O6	0.95	2.09	2.895 (2)	141
C53—H53...O4 ^v	0.95	2.53	3.381 (2)	149
C57—H57...O4	0.95	2.24	2.731 (2)	111
Compound (V)				
C152—H152...O16	0.95	2.08	2.889 (3)	143
C157—H157...O14	0.95	2.21	2.709 (3)	112
C252—H252...O26	0.95	2.08	2.892 (3)	143
C257—H257...O24	0.95	2.22	2.716 (3)	112

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

For compound (I), the space group $P2_1/n$ was uniquely assigned from the systematic absences. Crystals of compounds (II)–(IV) are triclinic and for each compound, the space group $P\bar{1}$ was selected and then confirmed by the structure analysis. All H atoms were located in difference maps and subsequently treated as riding atoms, with C—H distances of 0.95 (aromatic) or 0.98 Å (methyl) and O—H distances of 0.84 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{O})$ or $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$. There are several short intramolecular H...H contacts in both molecules of (V); these all involve contacts between a hydroxyl H atom and a H atom in a *tert*-butyl group.

For all compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1828). Services for accessing these data are described at the back of the journal.

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