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Concomitant polymorphism and conformational isomerism in 4-acetylresorcinol

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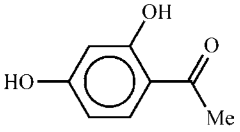
Two polymorphs of the title compound [systematic name: 1-(2,4-dihydroxyphenyl)ethanone], $C_8H_8O_3$, were investigated. The known structure [designated (I-M); $P2_1/c$, $Z = 4$; previously investigated at room temperature by Robert, Moore, Eichhorn & Rillema (2007). *Acta Cryst.* E**63**, o4252] was redetermined at low temperature, and a new form [(I-O); $P2_12_12_1$, $Z = 12$] was discovered in the same sample. In both forms, the molecules are planar (apart from the methyl H atoms) and they contain intramolecular O—H···O═C hydrogen bonds. In polymorph (I-M), molecules are linked into chains by a single intermolecular O—H···O hydrogen bond, and the chains are linked into sheets by two C—H···O hydrogen bonds. Three O—H···O hydrogen bonds link the molecules of polymorph (I-O) into chains and neighbouring chains are connected by one C—H···O interaction to form an offset layer structure. Two weak methyl C—H···O interactions link the layers.

Comment

In the course of synthetic approaches to coronand systems, the title compound was obtained in crystalline form as an unexpected product. The sample consisted of two types of crystal, large blocks and a smaller quantity of fine needles. Data were measured for a block and corresponded to the known structure of 4-acetylresorcinol, (I) (monoclinic, space group $P2_1/c$, $Z = 4$; Robert *et al.*, 2007). The needles were also measured and it was clear that the asymmetric unit was much larger, but it proved to contain three independent molecules of the same compound ($P2_12_12_1$, $Z = 12$). This is a new polymorph of (I). In view of our interest in the structures of polymorphs (see *e.g.* Jones & Lozano, 2003*a*,*b*; Ossowski *et al.*, 2006; Kuś *et al.*, 2009), and because the structure of Robert *et al.* (2007) was based on room-temperature data, we retained the low-temperature data of the known polymorph and present here a comparison of the two forms.

The molecule of the monoclinic form, henceforth form (I-M), is shown in Fig. 1. Except for the methyl H atoms, it is planar (r.m.s. deviation = 0.03 Å). The bond lengths and angles may be regarded as normal. There is an intramolecular O2—H12···O3 hydrogen bond.



(I)

The three molecules of the orthorhombic polymorph, henceforth form (I-O), connected within the asymmetric unit by hydrogen bonds, are shown in Fig. 2. The molecules are again planar (r.m.s. deviations excluding methyl H atoms = 0.03, 0.03 and 0.02 Å) and approximately parallel [the interplanar angle between molecules 1 and 2 is 16.27 (4)°, and that between molecules 2 and 3 is 8.27 (3)°]. They are closely similar to each other and to the molecule of the monoclinic form, but there is one important conformational difference: the OH groups are oriented in the same sense in form (I-M) (anticlockwise in the plane of Fig. 1), but in the opposite sense in all three molecules of form (I-O). Furthermore, the third molecule of form (I-O) has the opposite rotational sense in the common plane to the other two (see, for example, the ring atoms, which are clockwise 1–6 for the third molecule but anticlockwise for molecules 1 and 2).

The packing of form (I-M) was described briefly by Robert *et al.* (2007) and the intermolecular O2—H12···O3 hydrogen bond was recognized. The extended packing (Fig. 3) consists of layers parallel to (102), in which classical hydrogen bonds link the molecules into zigzag chains parallel to $[20\overline{1}]$. Two C—H···O interactions from ring H atoms to the hydroxyl groups (Table 1) provide the crosslinking.

The crystal structure of form (I-O) contains chains of molecules parallel to the *c* axis, generated by O—H···O hydrogen bonds (Fig. 4 and Table 2). The C22—H22···O31 interaction crosslinks the chains to form a layer structure. In contrast with form (I-M), however, neighbouring chains are displaced in the third dimension. Chains are weakly linked to those above and below by C—H···O contacts (not shown in Fig. 4) involving the methyl atoms H18*C* and H28*C*.

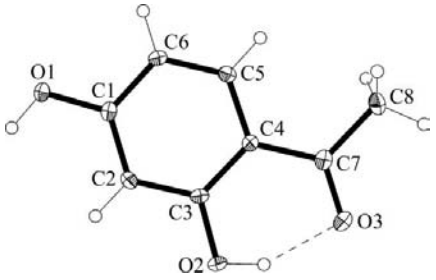


Figure 1
The molecule of the monoclinic polymorph (I-M), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The intramolecular hydrogen bond is shown as a dashed line.

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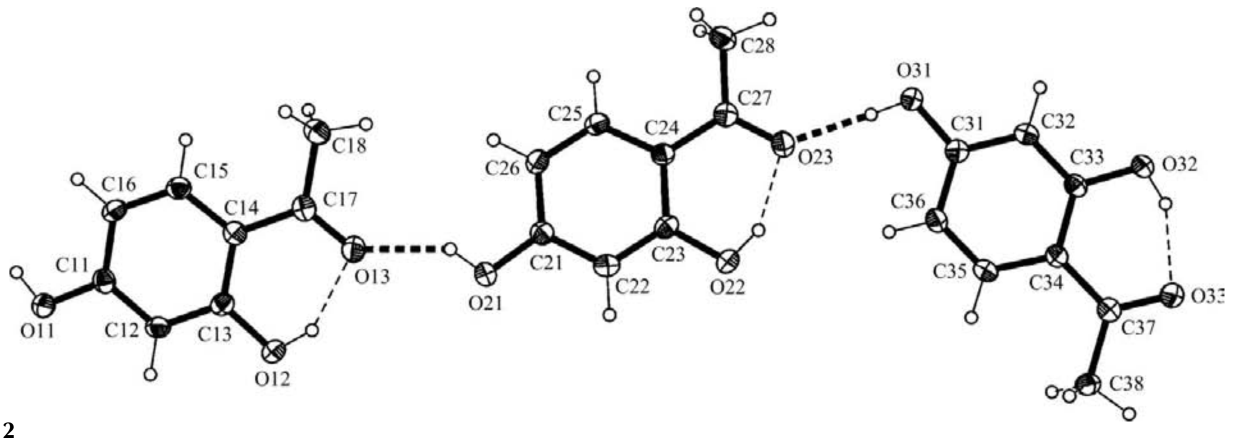

Figure 2
The three independent molecules of the orthorhombic polymorph (I-O), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Intramolecular hydrogen bonds are represented as thin dashed lines and intermolecular hydrogen bonds as thick dashed lines.

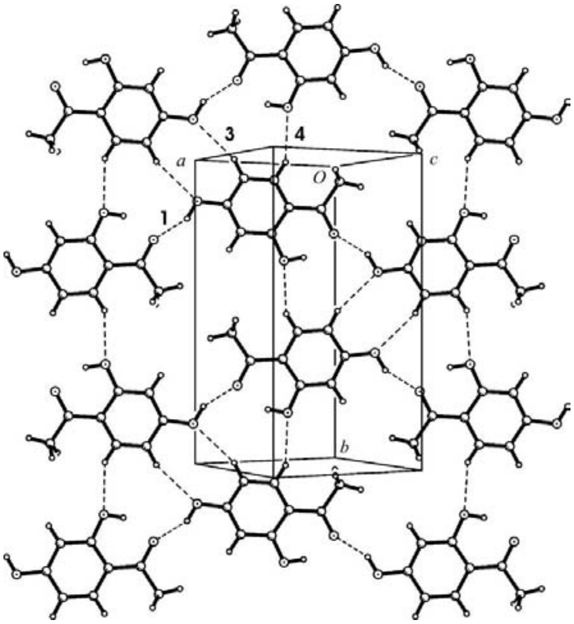

Figure 3
The packing of the monoclinic polymorph (I-M), viewed perpendicular to (102). The hydrogen bonds are numbered according to their order in Table 1 (intramolecular hydrogen bond No. 2 is not shown).

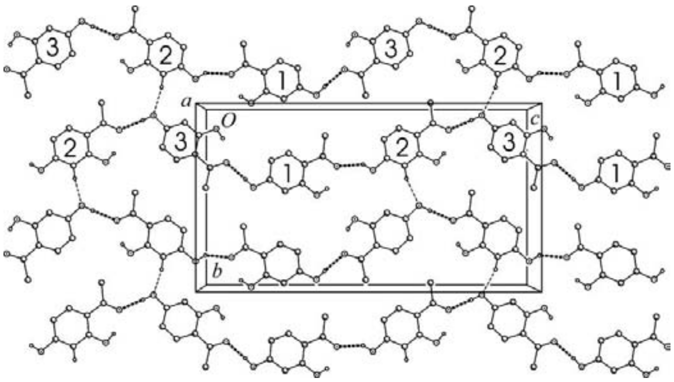

Figure 4
The packing of the orthorhombic polymorph, viewed parallel to the *a* axis. The three independent molecules are numbered 1–3, and the reference molecules at (*x*, *y*, *z*) are those so marked within the unit cell. Intramolecular hydrogen bonds are not shown.

It is tempting to regard the almost exactly planar layer structure of form (I-M) as the energy minimum for the packing of (I), whereas the offset layer structure of form (I-O) could be regarded as a kinetic stopping-off point on the way to form (I-M). This is consistent with the slightly higher density of form (I-M), *viz.* 1.430 *versus* 1.424 Mg m^{-3} for form (I-O). However, more detailed theoretical and physical studies would be necessary to prove this supposition.

Experimental

From an unsuccessful reaction intended to produce a coronand, flash chromatography using a dichloromethane–methanol mixture (99:1 *v*/*v*) as eluant gave a series of fractions which were combined and then allowed to evaporate at ambient temperature. After 48 h, crystals of 4-acetylresorcinol (one of the starting materials) were obtained which were suitable for single-crystal X-ray diffraction analysis.

Polymorph (I-M)

Crystal data

$C_8H_8O_3$
M_r = 152.14
Monoclinic, $P2_1/c$
a = 7.1194 (3) Å
b = 13.6690 (6) Å
c = 7.2695 (4) Å
β = 92.859 (6)°

V = 706.55 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 K
0.40 × 0.40 × 0.25 mm

Data collection

Oxford Diffraction Xcalibur S diffractometer
12428 measured reflections
2149 independent reflections

1508 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.042

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.105
S = 0.95
2149 reflections
109 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.43 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.25 e Å^{-3}

Polymorph (I-O)

Crystal data

$C_8H_8O_3$
M_r = 152.14
Orthorhombic, $P2_12_12_1$
a = 6.7640 (3) Å
b = 13.1193 (6) Å
c = 23.9936 (9) Å
V = 2129.17 (16) Å^3
Z = 12
Cu $K\alpha$ radiation
μ = 0.92 mm^{-1}
T = 103 K
0.25 × 0.08 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur Nova O diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)
$T_{\min}$ = 0.780, $T_{\max}$ = 0.964
20232 measured reflections
2327 independent reflections
2185 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.083
S = 1.04
2327 reflections
325 parameters
276 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for form (I-M).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H11···O3$^{\rm i}$	0.908 (19)	1.807 (18)	2.6466 (10)	152.7 (17)
O2—H12···O3	0.896 (18)	1.743 (18)	2.5610 (11)	150.5 (16)
C6—H6···O1$^{\rm ii}$	0.95	2.56	3.4759 (13)	161
C5—H5···O2$^{\rm iii}$	0.95	2.46	3.3127 (13)	149

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

Hydroxyl H atoms were located in difference maps and refined freely. Methyl H atoms were located in difference maps, idealized to C—H = 0.98 Å and H—C—H = 109.5°, and refined as rigid groups that were allowed to rotate but not to tilt, with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C). Other H atoms were treated as riding atoms in calculated positions, with C—H = 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). For the orthorhombic form, which crystallizes in a Sohncke space group, the Flack x parameter (Flack, 1983) was 0.48 (10), indicating either insignificant anomalous dispersion or an inversion twin with approximately equal components. Friedel opposite reflections were therefore merged, so that the Flack parameter was indeterminate. To counteract the necessarily rather poor data/parameter ratio (although the data are 99.3% complete to 2θ = 135°), the displacement parameters were restrained using the *SHELXL97* (Sheldrick, 2008) commands SIMU and DELU, applied to neighbouring atoms and corresponding, respectively, to approximately equal U^{ij} components and to a rigid bond restraint.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008) [Version 1.171.32.24 for (I-M); Version 1.171.32.15 for (I-O)]; cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008) [Version 1.171.32.24 for (I-M); Version 1.171.32.15 for (I-O)]; data reduction: *CrysAlis RED* [Version 1.171.32.24 for (I-M); Version 1.171.32.15 for (I-O)]; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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

D—H···A	D—H	H···A	D···A	D—H···A
O11—H111···O33$^{\rm i}$	0.85 (2)	1.86 (2)	2.7101 (16)	175 (2)
O12—H112···O13	0.88 (3)	1.79 (3)	2.5682 (16)	147 (2)
O21—H121···O13	0.84 (3)	1.93 (3)	2.6650 (16)	145 (2)
O22—H122···O23	0.86 (3)	1.76 (3)	2.5519 (16)	152 (2)
O31—H131···O23	0.85 (3)	1.84 (3)	2.6875 (15)	174 (2)
O32—H132···O33	0.85 (3)	1.79 (3)	2.5691 (15)	153 (2)
C28—H28C···O12$^{\rm ii}$	0.98	2.68	3.537 (2)	147
C18—H18C···O31$^{\rm iii}$	0.98	2.42	3.254 (2)	143
C22—H22···O31$^{\rm iv}$	0.95	2.57	3.421 (2)	149

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3292). Services for accessing these data are described at the back of the journal.

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