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Key indicators

Single-crystal X-ray study
 $T = 153$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.039
 wR factor = 0.104
Data-to-parameter ratio = 12.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

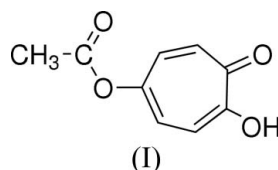
5-(Acetyloxy)tropolone

The title compound (systematic name: 5-acetoxy-2-hydroxy-2,4,6-cycloheptatrien-1-one), $\text{C}_9\text{H}_8\text{O}_4$, contains intra- and intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, resulting in centrosymmetric dimers. The acetoxy group makes an angle of 59.86 (5)° with the seven-membered tropolone ring system. The crystal packing is consolidated by $\pi-\pi$ and $\text{C}-\text{H}\cdots\text{O}$ interactions.

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Comment

Troponoids, being a remarkable class of non-benzenoid π -conjugated systems, have been used as the building blocks of various molecular assemblies, such as liquid crystals (Kubo, 2004; Kubo, Mori *et al.*, 2005) and organogelators (Kubo & Mori, 2005). Recently, the mesomorphic properties of two substituted monocyclic troponoid mesogens, 2,5-dialkanoyloxytropones and 5-alkanoyloxy-2-alkoxytropones, were reported (Mori *et al.*, 2001). The crystal structure of tropolone (Shimanouchi & Sasada, 1973) and its 5-cyano- and 5-nitrotropolone derivatives (Kubo, Yamamoto & Mori, 2001) have been described. We now report the structure of the title compound, (I) (Fig. 1), with the aim of contributing to a deeper understanding of troponoids and their molecular assemblies.



In the molecule of (I), the dihedral angle between the least-squares planes A ($\text{O1}/\text{O2}/\text{C1}-\text{C7}$) and B ($\text{O3}/\text{O4}/\text{C8}/\text{C9}$) is 59.86 (5)°, which is different from the equivalent value of 71.8° in 2-butanoyloxy-5-nitrotropone (Kubo, Tsuruta & Mori, 2001).

Compound (I) forms $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonded dimers about inversion centres, involving the OH group and an intermolecular carbonyl O1^i acceptor (see Table 1 for symmetry code). An intramolecular $\text{O}-\text{H}\cdots\text{O}$ bond to atom O1 occurs simultaneously (Table 1, Fig. 2). The intermolecular $\text{O2}\cdots\text{O1}^i$ distance of 2.716 (2) Å is close to that in tropolone (2.746 Å), where a similar dimerization occurs.

Intermolecular $\pi-\pi$ interactions occur in (I) between the tropolone ring planes, leading to infinite stacks propagating in the [100] direction, with all molecules in a stack aligned in the same way, in a 'head-to-head' arrangement (Fig. 2). The $\text{C1}-\text{C7}^v$ [symmetry code: $(v) x - 1, y, z$] separation is 3.455 (2) Å,

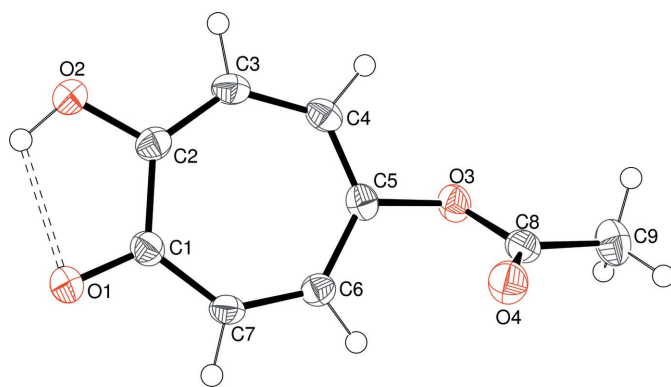


Figure 1

The molecular structure of (I), 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 indicated by dashed lines.

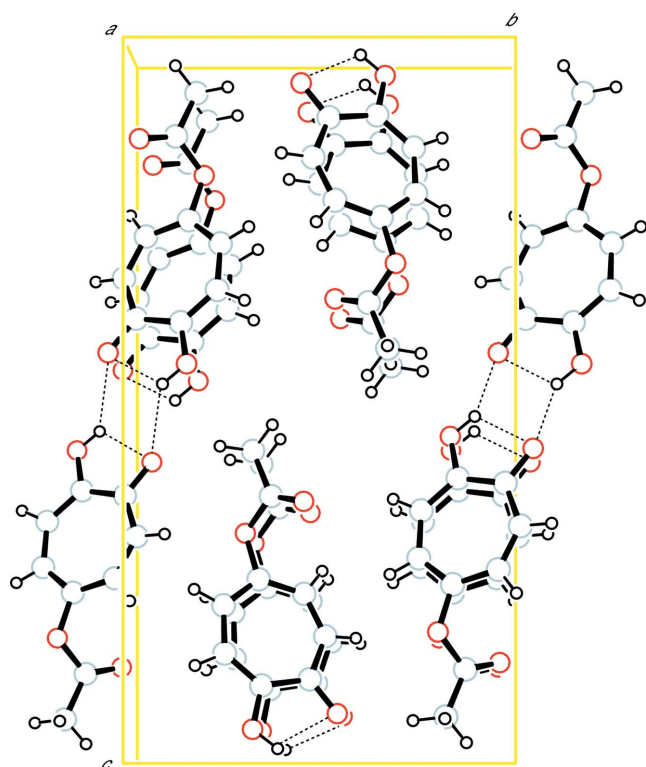


Figure 2

A packing diagram for (I), viewed down the *a* axis, with hydrogen bonds shown as dotted lines.

which is within the range associated with π - π interactions [3.3–3.8 Å]. This value is similar to the equivalent intermolecular separation in tropolone (3.418 Å; Shimanouchi & Sasada, 1973). However, in this latter compound, the stacks of molecules are generated by a 2_1 screw axis and adjacent molecules are aligned in a head-to-tail arrangement.

Various intermolecular C—H...O interactions (Table 1) help to consolidate the crystal packing of (I). Similar interactions have been observed in related materials (Kubo, Matsumoto *et al.*, 2005; Takahashi *et al.*, 2006). The combination of intermolecular O—H...O and C—H...O interactions

and π - π stacking interactions in (I) builds up a three-dimensional network.

Experimental

Compound (I) was prepared by the esterification of 5-hydroxy-tropolone with acetyl chloride (Nagao *et al.*, 1989). Crystals of (I) were grown from a methanol solution by slow evaporation.

Crystal data

C₉H₈O₄
M_r = 180.16
 Monoclinic, *P*2₁/*c*
a = 3.8076 (12) Å
b = 10.987 (3) Å
c = 20.356 (6) Å
 β = 93.576 (17)°
V = 849.9 (4) Å³

Z = 4
D_x = 1.408 Mg m⁻³
 Cu *K*α radiation
 μ = 0.96 mm⁻¹
T = 153.1 K
 Prism, colourless
 0.33 × 0.26 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
T_{min} = 0.656, *T_{max}* = 0.909

7929 measured reflections
 1512 independent reflections
 1407 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.033
 θ_{\max} = 68.1°

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.104$
S = 1.04
 1512 reflections
 124 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.5664P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.38 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.39 \text{ e } \text{Å}^{-3}$
 Extinction correction: SHELXL97
 (Sheldrick 1997)
 Extinction coefficient: 0.0126 (11)

Table 1

Hydrogen-bond geometry (Å, °).

<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...O1	0.90 (2)	2.09 (2)	2.589 (2)	114 (2)
O2—H2...O1 ⁱ	0.90 (2)	1.93 (2)	2.716 (2)	145 (2)
C3—H3...O4 ⁱⁱ	0.95	2.53	3.309 (2)	139
C6—H5...O4 ⁱⁱⁱ	0.95	2.67	3.433 (2)	138
C7—H6...O3 ^{iv}	0.95	2.50	3.438 (2)	171
C9—H7...O1 ⁱⁱ	0.98	2.64	3.586 (2)	163

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

The H atom of the OH group was located in a difference map and its position and *U_{iso}* value were freely refined. All C-bound H atoms were placed in idealized locations (C—H = 0.95–0.98 Å) and refined as riding, with *U_{iso}*(H) = 1.2*U_{eq}*(C) or 1.5*U_{eq}*(methyl C).

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSO, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick 1997); molecular graphics: *ORTEP3* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

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