Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

9-Benzoyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione: molecular conformation and supramolecular aggregation in xanthenediones

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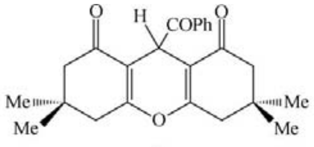
Received 8 September 2008
Accepted 11 September 2008
Online 20 September 2008

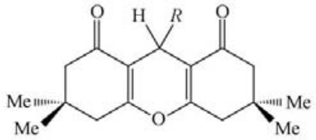
In the title compound, $C_{24}H_{26}O_4$, (I), the central ring of the fused tricyclic ring system adopts a shallow boat conformation, while the two outer rings adopt envelope conformations. The molecules are linked into *C*(9) chains by a single C—H···O hydrogen bond. The significance of this study lies in its comparison of the conformation and supramolecular aggregation of (I) with those of related compounds in the published literature.

Comment

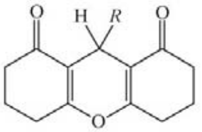
We have recently reported the preparation of new fused heterocyclic compounds containing the pyrimidine fragment, such as pyrimidino[4,5-*b*]quinolines, using multicomponent reactions between 4,4-dimethylcyclohexane-1,3-dione (dimedone), 6-aminopyrimidine derivatives and aryl aldehydes (Quiroga *et al.*, 2006). We have attempted to modify the procedure by replacing the aldehyde component with a glyoxal derivative, and we report here the structure of the title product, (I), synthesized as an intermediate for subsequent reactions with 6-aminopyrimidine derivatives. Compound (I) was formed by a condensation reaction between phenyl glyoxal and dimedone, which was induced by microwave irradiation under solvent-free reaction conditions. Here we not only report the molecular and supramolecular structure of (I), but compare its conformation with those of simple analogues taken from the recent literature or retrieved from the Cambridge Structural Database (CSD, Version 5.29 of January 2008; Allen, 2002).



(I)



(II) R = H
(III) $R = C_6H_4Cl$-4
(IV) $R = C_6H_4Br$-4
(V) $R = C_6H_4NO_2$-2
(VI) $R = C_9H_6NO$



(VII) $R = C_6H_4CH_3$-2 (CUQTAJ)
(VIII) $R = CH_2CH_2CH_2CH_3$ (PAMXOM
(IX) R = 4-pyridyl (XAQNAT)
(X) $R = C_7H_4O_2$ (ESOZIV)

The central ring in the molecule of (I) (Fig. 1) adopts a shallow boat conformation, while the two outer rings adopt envelope conformations. For the atom sequences C1a—C2—C3—C4—C5—C5a and C10a—C10—C9—C8—C7—C6a, respectively, the ring-puckering angles (Cremer & Pople, 1975) are θ = 56.6 (2)° and φ = 127.7 (3)°, and θ = 127.3 (3)° and φ = 312.1 (3)°, with the fold of the envelopes across the lines C2···C4 and C8···C10. For the idealized envelope conformation, the ring-puckering angles are θ = 54.7° (or

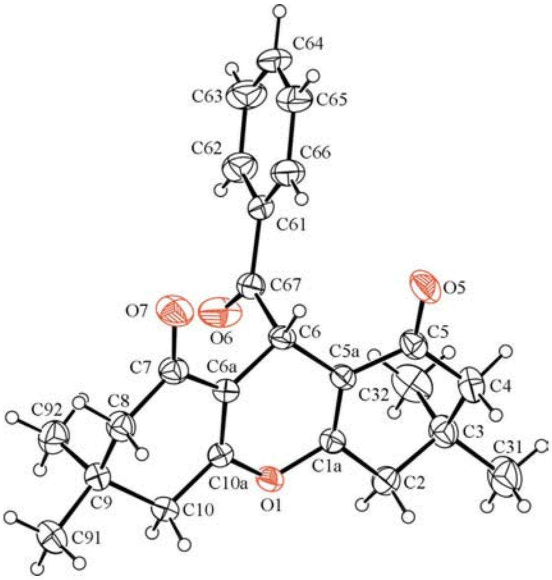


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

doi:10.1107/S0108270108029181

125.3°) and $\varphi = 60k°$, where k represents an integer. The relationship between the puckering angles for the two outer rings indicates that the fused ring system has approximate but noncrystallographic mirror symmetry. However, because of the orientation of the pendent benzoyl group, as indicated by the relevant torsion angles (Table 1), the molecule has no internal symmetry, and hence it is chiral. However, the centrosymmetric space group accommodates equal numbers of the two conformational enantiomers. The C5—O5 and C7—O7 bonds (Table 1) are slightly longer than normal for cyclohexanones (mean value 1.211 Å; upper quartile value 1.216 Å; Allen *et al.*, 1987), while the C67—O6 bond is slightly shorter than typical for benzoyl groups (mean value 1.221 Å; lower quartile value 1.212 Å). Otherwise the bond distances in (I) show no unexpected features.

A single C—H$\cdots$O hydrogen bond (Table 2) links molecules of (I), which are related by the *b*-glide plane at $x = \frac{3}{4}$, into *C*(9) (Bernstein *et al.*, 1995) chains running parallel to the [010] direction (Fig. 2). Four chains of this type run through each unit cell but there are no direction-specific interactions between the chains.

The structures of several other tetramethylxanthene-1,8-diones, compounds (II)–(VI) (see scheme), have been reported in recent years and it is of interest to compare briefly both the molecular conformations and the supramolecular aggregation in these compounds with those in (I) as, in many cases, these properties were either not mentioned in the original reports or they were only partly analysed.

In compounds (II) and (V) (Jeyakanthan *et al.*, 1999), so-called sofa conformations were deduced for the two outer rings, apparently by using only the ring-puckering amplitudes; the ring-puckering angles, which are the primary diagnostic of conformation, were not mentioned. For compound (IV) (Bigdeli *et al.*, 2007), the outer rings were reported to be in a *trans* conformation, without any indication of reference points or of ring shape. Compound (III) (Tu *et al.*, 2001) is isomorphous with (IV), although this was not noted in the subsequent report on (IV) (Bigdeli *et al.*, 2007); no analysis of ring conformation was made for (III). The outer rings in (VI) were reported (Selvanayagam *et al.*, 2005) as having half-boat conformations but, as with (II) and (V), no ring-puckering angles were cited, only the puckering amplitudes. Re-analysis of all of these structures, using the published atom coordinates followed by inspection of the ring-puckering angles, shows that, in every case, the outer two rings adopt envelope conformations, folded just as in (I) reported here. In addition to (II)–(VI), several analogues, compounds (VII)–(X) (see scheme), which do not carry the four methyl substituents, have been retrieved from the CSD. Again, the ring-puckering angles show that the outer rings adopt envelope conformations, folded as in (I)–(VI), despite the absence of the methyl groups.

With the exception of (VIII) (CSD refcode PAMXOM), where the molecules lie across a mirror plane in the space group $Cmc2_1$, the senses of the folding in the two outer rings are independent. Thus, the flap atoms of the envelopes could be on the same side of the mean plane describing the rest of the tricyclic system, or on opposite sides. Where they are on the same side they could be directed towards the pendent substituent or away from it, apart from (II), where no such substituent is present. Where the flap atoms are on the same side of the tricyclic system, this has approximate mirror (C_s) symmetry; where the flap atoms are on opposite sides of the tricyclic system, this has approximate twofold rotation (C_2) symmetry.

The overall molecular conformations are most readily assessed *via* the molecular profiles. For (I), the profile (Fig. 3*a*) shows two flap atoms, both on the same face of the tricyclic system as the pendent benzoyl group. Similarly for (II), both

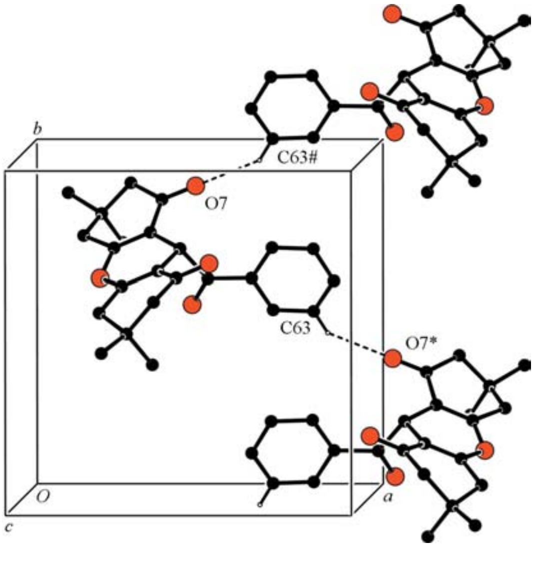


Figure 2
Part of the crystal structure of (I), showing the formation of a *C*(9) chain along [010]. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($\frac{3}{2} - x, -\frac{1}{2} + y, z$) and ($\frac{3}{2} - x, \frac{1}{2} + y, z$), respectively.

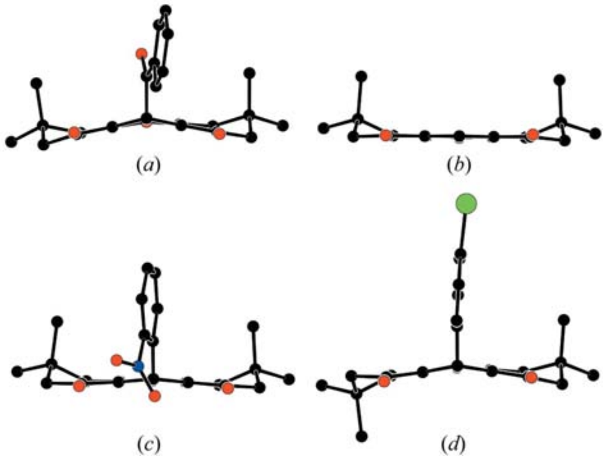
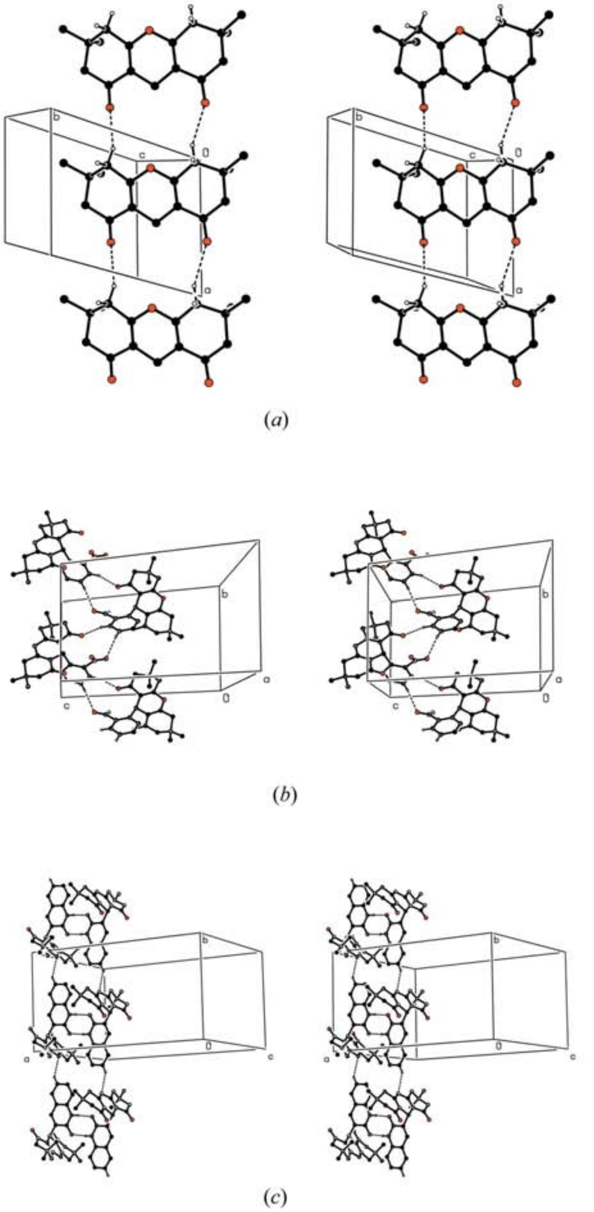


Figure 3
Molecular profiles of selected tetramethylxanthenediones: (*a*) (I), (*b*) (II), (*c*) (V) and (*d*) (IV). For (II), (IV) and (V), the original atom coordinates (Jeyakanthan *et al.*, 1999; Bigdeli *et al.*, 2007) were used. In all cases, H atoms have been omitted for the sake of clarity.

flap atoms are on the same side despite the absence of a pendent aryl substituent (Fig. 3*b*). This type of conformation is also found for (V) (Fig. 3*c*) and (VI), and for (VII)–(IX). On the other hand, the isomorphous pair (III) and (IV) have the flap atoms on opposite faces of the tricyclic system (Fig. 3*d*), as does (X).

Finally, we compare very briefly the hydrogen-bonded aggregation in (I)–(VI) with the simple $C(9)$ chains found in (I). The report on (II) and (V) (Jeyakanthan *et al.*, 1999) makes no mention of any intermolecular interactions. In fact, two independent C—H$\cdots$O hydrogen bonds, both with a ketonic O atom as the acceptor, link the molecules of (II) into a $C(6)C(6)[R_2^2(14)]$ chain of rings (Fig. 4*a*). In (V), there are again two C—H$\cdots$O hydrogen bonds, one each with ketonic and nitro O atoms as the acceptors, and these link the molecules into a $C(6)C(8)[R_2^2(12)]$ chain of rings (Fig. 4*b*). Again, for (IV), the original report (Bigdeli *et al.*, 2007) makes no mention of intermolecular interactions, but in fact a single C—H$\cdots$O hydrogen bond links the molecules into a simple $C(7)$ chain. A similar chain can be expected in the isomorphous compound (III) (Tu *et al.*, 2001), but no H-atom coordinates are available for this structure. Two hydrogen bonds were reported for (VI) (Selvanayagam *et al.*, 2005) and the authors mention $R_2^2(8)$ dimers further linked by a C—H$\cdots$O hydrogen bond, but without further specification of the structural consequences. In fact, the molecules are linked into a chain of alternating edge-fused $R_2^2(8)$ and $R_4^4(28)$ rings (Fig. 4*c*).


(*a*)

(*b*)

(*c*)

Figure 4
Stereoviews of parts of the crystal structures of selected tetramethylxanthenediones, showing the formation of chains of rings: (*a*) (II), (*b*) (V) and (*c*) (VI). The original atom coordinates (Jeyakanthan *et al.*, 1999; Selvanayagam *et al.*, 2005) were used. In all cases, H atoms not involved in the motifs shown have been omitted for the sake of clarity.

Experimental

A mixture of 4,4-dimethylcyclohexane-1,3-dione (dimedone, 2.0 mmol) and phenyl glyoxal hydrate (1.0 mmol) was placed in an open Pyrex glass flask and irradiated in a domestic microwave oven for 6 min at 600 W. The product mixture was extracted with ethanol and, after removal of the solvent, the product, (I), was recrystallized from ethanol to give crystals suitable for single-crystal X-ray diffraction (yield 45%, m.p. 478–479 K). MS (EI 70 eV) *m*/*z*: 379 (2), 378 (M^+, 1), 373 (100), 217 (23), 131 (13), 77 (19).

Crystal data

$C_{24}H_{26}O_4$
M_r = 378.45
Orthorhombic, *Pbca*
a = 11.6394 (15) Å
b = 11.5736 (15) Å
c = 30.782 (4) Å
V = 4146.6 (9) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 293 (2) K
0.80 × 0.20 × 0.18 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min}$ = 0.964, $T_{\max}$ = 0.986
17519 measured reflections
4239 independent reflections
2266 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.060

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.144
S = 1.01
4239 reflections
253 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.13 e Å^{-3}
$\Delta\rho_{\min}$ = −0.17 e Å^{-3}

The space group *Pbca* was uniquely assigned from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H = 0.93 (aromatic), 0.96 (CH_3), 0.97 (CH_2) or 0.98 Å (aliphatic CH), and with $U_{\rm iso}(H) = kU_{\rm eq}(C)$, where k = 1.5 for the methyl groups and 1.2 for all other H atoms.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL*

Table 1
Selected geometric parameters (Å, °).

C5—O5	1.228 (2)	C7—O7	1.220 (2)
C67—O6	1.211 (2)		
C5a—C6—C67—C61	−108.35 (19)	C6—C67—C61—C62	170.66 (17)
C6a—C6—C67—C61	133.84 (18)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C63—H63···O7^{i}	0.93	2.40	3.204 (3)	145

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

(McArdle, 2003) and *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

JC and JMT thank the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support. JMT also thanks the Universidad de Jaén for a scholarship grant supporting a short stay at the EPSRC X-ray Crystallographic Service, University of Southampton, UK, where the X-ray data were collected. JQ and SC thank COLCIENCIAS, UNIVALLE (Universidad del Valle, Colombia) and UDENAR (Universidad de Nariño, Colombia) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3167). Services for accessing these data are described at the back of the journal.

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