Two tetramethylxanthenediones

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Abstract

In both title compounds, 1,2,3,4,5,6,7,8-octahydro-3,3,6,6-tetramethylxanthene-1,8-dione, $C_{17}H_{22}O_3$, (I), and 1,2,3,4,5,6,7,8-octahydro-3,3,6,6-tetramethyl-9-(2-nitrophenyl)xanthene-1,8-dione, $C_{23}H_{25}NO_5$, (II), the central ring of the xanthene moiety is planar and the two outer rings are in sofa conformations. Due to π conjugation, there is an electron delocalization stretch. The phenyl ring of the 2-nitrophenyl substituent in (II) is nearly perpendicular [89.52 (7)°] to the xanthene ring system.

Comment

Efonidipine (NZ-105), a potent antihypertensive agent, has been shown to reduce blood pressure gradually in dogs, with long lasting action, and it has afforded excellent results in clinical studies (Sakoda et al., 1993; Bahr et al., 1997). 1,2,3,4,5,6,7,8-Octahydro-3,3,6,6-tetramethyl-9-(2-nitrophenyl)xanthene-1,8-dione (Murugan & Ramakrishnan, 1997), (II), is an analogue of NZ-105, while 1,2,3,4,5,6,7,8-octahydro-3,3,6,6-tetramethylxanthene-1,8-dione, (I), is a similar compound with fewer substituents. The structures of (I) and (II) are described here.

(I)

(II)
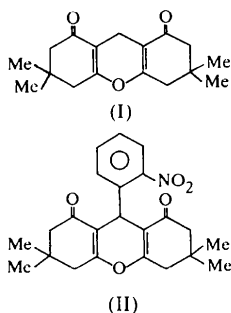
The xanthene moiety is folded along the C9···O10 axis in both (I) and (II), and the mean planes of

the two halves (C1/C2/C3/C4/C4a/C1a/O10/C9 and C5a/C5/C6/C7/C8/C8a/O10/C9) make dihedral angles of 4.61 (3)° in (I) and 3.79 (6)° in (II). The C4=O1 and C5=O2 carbonyl groups have bond lengths of 1.217 (2) and 1.219 (2) Å in (I), and 1.230 (2) and 1.222 (2) Å in (II), in agreement with a previous report by Brito-Arias et al. (1996). The C8a—O10—C1a angles [118.3 (1)° in (I) and 117.8 (2)° in (II)] show the sp^2 hybridized behaviour of O10. In both compounds, the central ring is planar. The sp^2 nature of the O atom causes it to resonate strongly with the ring and the lone pair on the O atom may be involved in electron delocalizations. This conjecture is confirmed by the partial double bonds along O1—C4—C4a—C1a—O10—C8a—C5a—C5—O2.

The dihedral angle between rings A (atoms C1–C4, C1a and C4a) and C (atoms C5–C8, C5a and C8a) is 11.83 (4)° in (I) and 8.31 (7)° in (II). The methyl groups at C2 (C11 and C12) are in axial and equatorial positions [deviations from the six-atom ring are −1.818 (2) and 0.250 (2) Å, respectively, in (I) and −1.858 (4) and
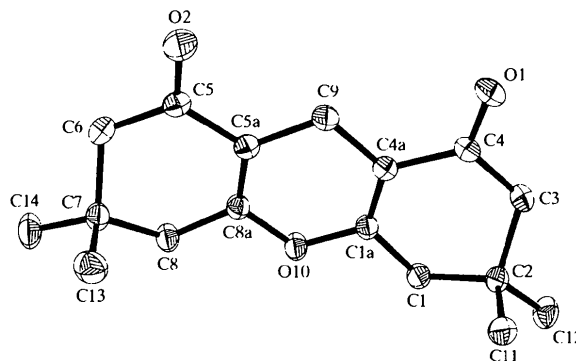

Fig. 1. ORTEPIII (Johnson & Burnett, 1997) diagram of (I) showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

Fig. 2. ORTEPIII (Johnson & Burnett, 1997) diagram of (II) showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.
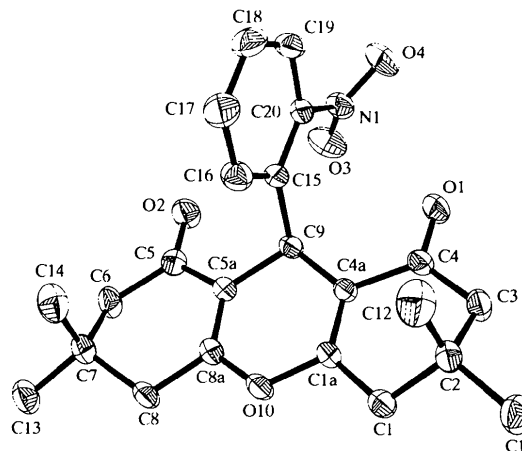
0.149 (3) Å, respectively, in (II)], and those at C7 (C13 and C14) are also in axial and equatorial positions [deviations from the six-atom ring are -1.821 (2) and 0.252 (2) Å, respectively, in (I) and -1.857 (3) and 0.153 (3) Å, respectively, in (II)]. Similar deviations of the two methyl groups are reported by Sivaraman et al. (1996). In both compounds, the axial methyl groups at C2 and C7 are nearly parallel to each other.

The sofa conformations of the two outer rings, A and C, are confirmed by the puckering amplitudes (Cremer & Pople, 1975): $Q_T = 0.462$ (2) and 0.443 (1) Å for rings A and C, respectively, in (I) and 0.496 (3) and 0.475 (3) Å for rings A and C, respectively, in (II). In ring A, atom C2 deviates from the mean plane of the ring by -0.294 (2) Å in (I) and by -0.331 (3) Å in (II), while in ring C, atom C7 deviates from the mean plane of the ring by -0.292 (1) Å in (I) and by -0.331 (3) Å in (II). The mean of the ring bond lengths involving the C9 atom is 1.497 (3) Å in (I) and 1.510 (3) Å in (II) [1.507 (7) Å in xanthene-9-carboxylic acid (Blackburn et al., 1996)], while the mean of the ring bond lengths involving O10 is 1.380 (3) Å in (I) and 1.377 (3) Å in (II) [1.377 (6) Å in xanthene-9-carboxylic acid (Blackburn et al., 1996)]. The C4a—C9—C5a central ring angle is 110.51 (1)° in (I) and 109.6 (2)° in (II) [111.5 (3)° in xanthene-9-carboxylic acid (Blackburn et al., 1996)] and the C1a—O10—C8a central ring angle is 118.3 (1)° in (I) and 117.8 (2)° in (II) [118.5 (3)° in xanthene-9-carboxylic acid (Blackburn et al., 1996)].

The planar phenyl ring of the 2-nitrophenyl substituent in compound (II) is almost perpendicular to the central ring, with the dihedral angle between their least-squares planes being 89.52 (7)° and the mean Csp^2—Csp^2 bond length within this ring being 1.382 (8) Å. These values are comparable to the values found in the literature (Miao et al., 1996; Brito-Arias et al., 1996). The O3—N1—O4 plane is tilted out of the plane of the phenyl ring by an angle of 31.4 (2)°.

Experimental

Compound (I) was synthesized by the condensation of dimedone (5,5-dimethylcyclohexane-1,3-dione) with formaldehyde followed by refluxing in acetic anhydride. Compound (II) was synthesized by the condensation of dimedone with o-nitrobenzaldehyde to give 2,2'-(o-nitrobenzylidene)bis(dimedone), followed by refluxing with acetic anhydride. After concentration, the crystallized materials were filtered and dried to isolate the products. Both compounds were recrystallized from ethanol by slow evaporation (Murugan & Ramakrishnan, 1997).

Compound (I)

Crystal data

$C_{17}H_{22}O_3$
$M_r = 274.35$
Triclinic
$P\bar{1}$
$a = 7.1458$ (8) Å
$b = 9.7690$ (12) Å
$c = 11.886$ (2) Å
$\alpha = 110.784$ (10)°
$\beta = 96.074$ (11)°
$\gamma = 101.302$ (10)°
$V = 746.6$ (2) Å^3
$Z = 2$
$D_x = 1.220$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 27 reflections
$\theta = 9.07$–$24.84°$
$\mu = 0.082$ mm^{-1}
$T = 293$ (2) K
Rectangular block
$0.64 \times 0.28 \times 0.24$ mm
Colourless

Data collection

Siemens P4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4130 measured reflections
3333 independent reflections
2301 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$

$\theta_{max} = 27.5°$
$h = -1 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.139$
$S = 0.994$
3331 reflections
186 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0772P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: SHELXTL (Siemens, 1996)
Extinction coefficient: 0.011 (5)
Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (I)*

O1—C4	1.217 (2)	C4a—C9	1.497 (2)
O2—C5	1.219 (2)	C5—C5a	1.467 (2)
C1a—C4a	1.338 (2)	C5a—C8a	1.340 (2)
C1a—O10	1.3802 (15)	C5a—C9	1.497 (2)
C4—C4a	1.467 (2)	C8a—O10	1.3786 (15)
C4a—C1a—O10	122.81 (11)	C14—C7—C13	109.28 (12)
C4a—C1a—C1	126.18 (12)	C4a—C9—C5a	110.51 (11)
C12—C2—C11	109.40 (13)	C8a—O10—C1a	118.27 (10)

Compound (II)

Crystal data

$C_{23}H_{25}NO_5$
$M_r = 395.44$
Monoclinic
$C2/c$
$a = 26.581$ (2) Å
$b = 10.094$ (1) Å
$c = 19.624$ (2) Å
$\beta = 128.75$ (1)°
$V = 4106.3$ (7) Å^3
$Z = 8$
$D_x = 1.279$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 39 reflections
$\theta = 5.36$–$11.02°$
$\mu = 0.090$ mm^{-1}
$T = 293$ (2) K
Rectangular block
$0.42 \times 0.32 \times 0.28$ mm
Yellow

Data collection

Siemens *P*4 diffractometer	$\theta_{max} = 27.5°$
$\theta/2\theta$ scans	$h = -1 \rightarrow 34$
Absorption correction: none	$k = -1 \rightarrow 13$
5589 measured reflections	$l = -25 \rightarrow 20$
4711 independent reflections	3 standard reflections
1670 reflections with	every 97 reflections
$I > 2\sigma(I)$	intensity decay: $<3\%$
$R_{int} = 0.044$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$\Delta\rho_{max} = 0.13$ e Å^{-3}
$wR(F^2) = 0.107$	$\Delta\rho_{min} = -0.15$ e Å^{-3}
$S = 0.740$	Extinction correction: none
4711 reflections	Scattering factors from
262 parameters	*International Tables for*
H atoms constrained	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 2. *Selected geometric parameters (Å, °) for (II)*

N1—O3	1.218 (2)	C4—C4a	1.465 (3)
N1—O4	1.226 (2)	C4a—C9	1.505 (3)
N1—C20	1.475 (3)	C5—C5a	1.472 (3)
O1—C4	1.230 (2)	C5a—C8a	1.329 (3)
O2—C5	1.222 (2)	C5a—C9	1.514 (3)
C1a—C4a	1.337 (3)	C8a—O10	1.372 (3)
C1a—O10	1.382 (2)		
O3—N1—O4	122.5 (3)	C8a—O10—C1a	117.8 (2)
O3—N1—C20	120.3 (2)	C19—C20—N1	115.2 (2)
O4—N1—C20	117.1 (2)	C15—C20—N1	122.2 (2)
C4a—C9—C5a	109.6 (2)		

For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXTL* (Siemens, 1996); program(s) used to refine structures: *SHELXTL*; molecular graphics: *ORTEP*III (Johnson & Burnett, 1997); software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1174). Services for accessing these data are described at the back of the journal.

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Bis[4-(2-methoxycarbonyl-5-thienyl)]phenyl ether†

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Abstract

The title compound, $C_{24}H_{18}O_5S_2$, possesses crystallographic C_2 symmetry. The thienyl ring adopts a planar conformation. The methoxycarbonyl group is twisted 9.7 (1)° out of plane of its parent thienyl ring.

Comment

The synthesis of non-natural cavity-shaped molecules has invaded the field of molecular recognition in recent years (Haldar *et al.*, 1997). The focus on heterocyclic compounds has generated novel receptors which are capable of binding suitable guests through hydrogen bonding, π-stacking forces and van der Waals interactions. This has further enriched the field of supramolecular chemistry. In connection with our studies towards the synthesis of novel cavity-shaped receptors for the selective recognition of long-chain dicarboxylic acids, we have synthesized some bis-thiophene-5-carboxamide derivatives (Gupta *et al.*, 1999) where the diphenyl ether moiety has been used as a spacer between the two thiophene units.

The title compound, (I), is the precursor of our designed artificial receptor. In this cavity-shaped molecule,

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† Alternative name: dimethyl 5,5′-(oxydi-*p*-phenylene)bis(thiophene-2-carboxylate).