

3,3'-[*o*-Phenylenebis(methyleneoxy)]-bis(6-chloroflavone) and 3,3'-propylenedioxybis[6-chloro-2-(2-furyl)-4*H*-1-benzopyran-4-one]

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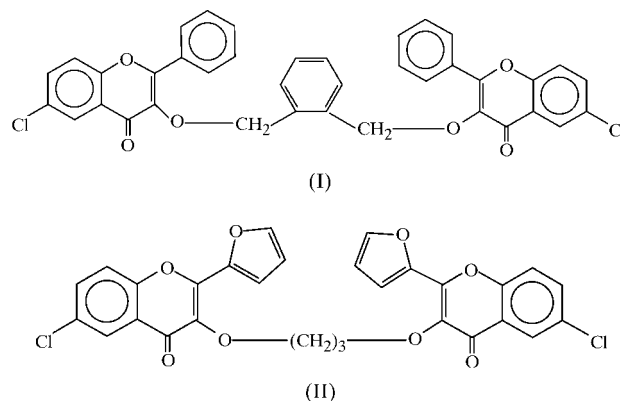
The title compound 3,3'-[*o*-phenylenebis(methyleneoxy)]-bis(6-chloroflavone), C₃₈H₂₄Cl₂O₆, (I), crystallizes in the monoclinic space group *C2/c*, with the molecules lying across twofold rotation axes so that there is half a molecule in the asymmetric unit, while the other title compound, 3,3'-propylenedioxybis[6-chloro-2-(2-furyl)-4*H*-1-benzopyran-4-one], C₂₉H₁₈Cl₂O₈, (II), crystallizes in monoclinic space group *P2₁/n* with one molecule in the asymmetric unit. In both compounds, the benzopyran moiety is nearly planar, with dihedral angles between the two fused rings of 1.43 (8)° in (I), and 2.54 (7) and 3.00 (6)° with respect to the benzopyran moieties in the two halves of (II). The furan rings are twisted by 8.3 (1) and 8.4 (1)° in the two halves of (II). In both compounds, the molecular structure is stabilized by intramolecular C—H···O hydrogen bonds, while the crystal packing is stabilized by C—H···Cl and C—H···O intermolecular hydrogen bonds in (I) and (II), respectively.

Comment

Flavonoids exhibit antidiabetic (Hii & Howell, 1985; Basnet *et al.*, 1993; Ragunathan & Sulochana, 1994) and aldose reductase inhibitory activities (Varma & Kinoshita, 1976; Okuda *et al.*, 1984; Aida *et al.*, 1990). Flavone (2-phenyl-4*H*-1-benzopyran-4-one) derivatives are known to have both a coronary dilatory effect (Itz & Potzsch, 1963) and capillary resistance activity (Gabor, 1981). Chromanone derivatives dilate the heart and are used to treat angina pectoris (Hasegaida, 1967). Against this background and in order to obtain detailed information about the molecular conformations of the title compounds in the solid state, X-ray structure determinations

of (I) and (II) were carried out and the results are presented here.

Figs. 1 and 2 show displacement ellipsoid plots of the molecules of (I) and (II), respectively, with the atom-numbering schemes. The asymmetric unit of the xylene derivative, (I), consists of a half molecule, as the molecules lie across twofold rotation axes, while that of the propylene derivative, (II), comprises one whole molecule. In (I), a phenyl ring is attached to the benzopyran moiety, whereas in (II), it is a furan ring that is attached. Four C and two O atoms form a linear coupling chain between the two flavone moieties in (I), while in (II), the coupling chain consists of three C and two O atoms.



In compound (I), the C8—O2 bond length (Table 1) agrees with the value of 1.385 (3) Å reported by Bruno *et al.* (2001). In compound (II), the C8—O2 and C24—O7 bond lengths (Table 3) agree with the literature values [*viz.* 1.364 (2) Å in Shuib *et al.* (1999) and 1.352 (3) Å in Thinagar *et al.* (2000)]. The C3—C8—C7 angle in (I) agrees with a value reported in the literature [122.1 (3)° in Özbey *et al.* (1999)], while the C7—C8—C3 and C19—C24—C23 angles in (II) are comparable with a reported value [121.4 (4)° in Letcher *et al.* (1992)].

The pyran rings are planar in both compounds and contrast with the normal half-chair conformation, as reported in Alex *et al.* (1993). The hetero atoms, *viz.* atom O2 in the ring and the oxo substituent O1 at position 4, cause slight variations in the geometric parameters within the ring. The values of the bond angles within the heterocyclic ring are in the range 113.3 (2)–122.6 (2)° in (I) and in the ranges 114.5 (2)–122.8 (2) and 114.4 (2)–123.0 (2)° in the two halves of (II). Similar variations in the geometric parameters of the pyran ring of the benzopyran system have been reported previously (Rybarczyk-Pirek *et al.*, 2002).

In (I), the torsion angle C1—C9—C10—C11 shows a +synclinal (+*sc*) orientation of the phenyl ring with respect to the 4*H*-chromen-4-one moiety (O1/O2/C1—C9), while in (II), the torsion angles C1—C9—C10—C13 and C17—C25—C26—C29 indicate +synperiplanar (+*sp*) orientations of the two furan rings with respect to the 4*H*-chromen-4-one moieties (O1/O2/C1—C9 and O6/O7/C17—C25, respectively). Also, the torsion angle O3—C16—C17—C18 in (I) is +anticlinal (+*ac*), while O4—C14—C15—C16 and O5—C16—C15—C14 in (II) are +synclinal.

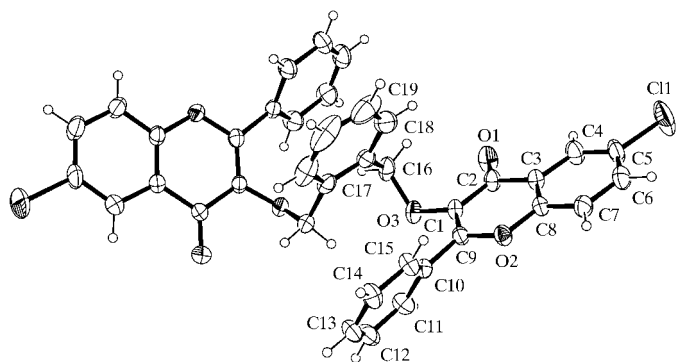


Figure 1
ORTEP (Johnson, 1976) plot of the molecular structure of (I), showing 35% probability displacement ellipsoids and the atom-numbering scheme.

The benzopyran systems of (I) and (II) are not strictly planar and the dihedral angle formed by the benzene and pyran planes is $1.43 (8)^\circ$ in (I), and $2.54 (7)$ and $3.00 (6)^\circ$ in the two halves of (II). The dihedral angle between the best planes of the 4*H*-chromen-4-one moiety (O1/O2/C1–C9) and the phenyl ring is $53.5 (1)^\circ$ in (I). In (II), the furan rings are not quite coplanar with the furylbenzopyran moieties O2/O3/C1–C13 and O7/O8/C17–C29, the dihedral angles being $6.88 (6)$ and $6.77 (6)^\circ$, respectively. The dihedral angles formed by the O3/C10–C13 and O8/C26–C29 furan rings with the O1/O2/C1–C9 and O6/O7/C17–C25 4*H*-chromen-4-one moieties are $9.22 (6)$ and $9.41 (6)^\circ$, respectively. The oxo and oxy atoms lie practically in the benzopyran planes in (I) and the two halves of (II).

In addition to van der Waals interactions, an intermolecular C–H...Cl hydrogen bond stabilizes the crystal packing of (I). The H18...Cl1 (2.88 Å) contact is significantly shorter than the sum of the van der Waals radii (2.95 Å; Bondi, 1964; Taylor & Kennard, 1982). The molecular packing is stabilized by one intramolecular C–H...O hydrogen bond. In (II), the molecular structure is stabilized by two intramolecular C–H...O hydrogen bonds, while the crystal packing is stabilized by two intermolecular C–H...O hydrogen bonds. Details of the

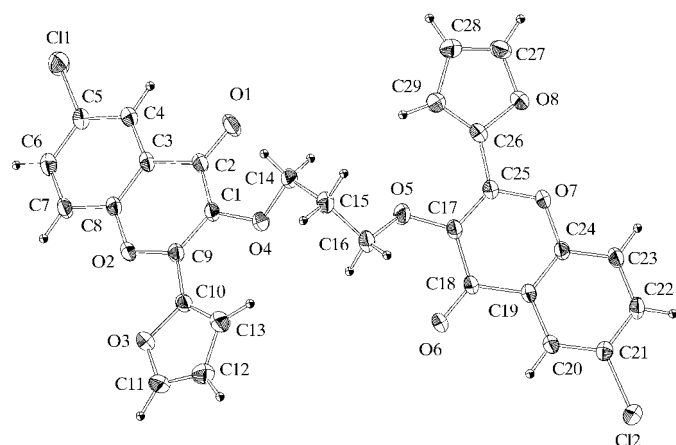


Figure 2
ZORTEP (Zsolnai, 1997) plot of the molecular structure of (II), showing 35% probability displacement ellipsoids and the atom-numbering scheme.

hydrogen bonding for (I) and (II) are given in Tables 2 and 4, respectively.

Experimental

A suspension of 6-chloro-2-(2-furyl)-3-hydroxy-4-oxo-4*H*-1-benzopyran (1 g, 0.0038 mol), a 1, ω -dibromoalkane (0.0019 mol) [*viz.* 1,2-bis(bromomethyl)benzene for (I) and 1,3-dibromopropane for (II)], tetra-*n*-butylammonium iodide (1 g) and freshly ignited K₂CO₃ (1 g) were refluxed in dry acetone (30 ml) for 4 h. The colour of the reaction mixture changed from yellow to colourless. The reaction mixture, after filtration and distillation of the acetone, was poured into cold water, giving a monochromenone/bischromenone mixture, which was then crystallized from acetone to give the pure bischromenone title compounds.

Compound (I)

Crystal data

C ₃₈ H ₂₄ Cl ₂ O ₆	$D_x = 1.382 \text{ Mg m}^{-3}$
$M_r = 647.47$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 25 reflections
$a = 13.2360 (10) \text{ \AA}$	$\theta = 1.2\text{--}28^\circ$
$b = 10.799 (4) \text{ \AA}$	$\mu = 0.26 \text{ mm}^{-1}$
$c = 21.775 (4) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 91.393 (3)^\circ$	Block, colourless
$V = 3111.5 (13) \text{ \AA}^3$	$0.47 \times 0.43 \times 0.40 \text{ mm}$
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{\text{max}} = 30.4^\circ$
Non-profiled $\omega/2\theta$ scans	$h = 0 \rightarrow 18$
4781 measured reflections	$k = 0 \rightarrow 15$
4612 independent reflections	$l = -31 \rightarrow 31$
1928 reflections with $I > 2\sigma(I)$	3 standard reflections every 100 reflections
$R_{\text{int}} = 0.024$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1073P)^2 + 1.2599P]$
$R[F^2 > 2\sigma(F^2)] = 0.054$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.230$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
4612 reflections	$\Delta\rho_{\text{min}} = -0.45 \text{ e \AA}^{-3}$
208 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

O2–C8	1.383 (3)	C2–C3	1.468 (4)
C1–C9	1.345 (4)	C3–C8	1.371 (4)
C1–C2	1.454 (4)		
C9–O2–C8	119.0 (2)	C3–C8–C7	122.4 (3)
C9–C1–C2	122.6 (2)	C3–C8–O2	121.7 (2)
C1–C2–C3	113.3 (2)	C1–C9–O2	122.1 (2)
C8–C3–C2	121.2 (2)		
C1–C9–C10–C11	54.1 (4)	O3–C16–C17–C18	106.2 (3)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$) for (I).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
C16–H16 <i>B</i> ...O1	0.97	2.50	3.091 (4)	119
C18–H18...Cl1 ⁱ	0.93	2.88	3.676 (5)	144

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

Compound (II)

Crystal data

$C_{29}H_{18}Cl_2O_8$
 $M_r = 565.33$
 Monoclinic, $P2_1/n$
 $a = 15.0485$ (2) Å
 $b = 7.6144$ (1) Å
 $c = 20.7890$ (2) Å
 $\beta = 100.784$ (1)°
 $V = 2340.04$ (5) Å³
 $Z = 4$
 $D_x = 1.605$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 10 418 reflections
 $\theta = 1.5$ – 28.6 °
 $\mu = 0.34$ mm⁻¹
 $T = 293$ (2) K
 Prism, colourless
 $0.44 \times 0.18 \times 0.16$ mm

Data collection

Siemens SMART CCD area-detector
 ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.867$, $T_{\max} = 0.948$
 15 953 measured reflections

5813 independent reflections
 3529 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.088$
 $\theta_{\text{max}} = 28.6$ °
 $h = -19 \rightarrow 20$
 $k = -5 \rightarrow 10$
 $l = -27 \rightarrow 27$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.153$
 $S = 0.92$
 5813 reflections

352 parameters
 H-atom parameters constrained
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.56$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.46$ e Å⁻³

Table 3

Selected geometric parameters (Å, °) for (II).

O2—C8	1.360 (3)	C3—C8	1.381 (2)
O7—C24	1.357 (2)	C17—C25	1.355 (3)
C1—C9	1.355 (2)	C17—C18	1.446 (3)
C1—C2	1.437 (3)	C18—C19	1.460 (3)
C2—C3	1.464 (3)	C19—C24	1.378 (2)
C9—O2—C8	119.5 (2)	O2—C9—C1	122.8 (2)
C25—O7—C24	119.4 (2)	C25—C17—C18	120.7 (2)
C9—C1—C2	121.2 (2)	C17—C18—C19	114.4 (2)
C1—C2—C3	114.5 (2)	C24—C19—C18	120.3 (2)
C8—C3—C2	120.3 (2)	O7—C24—C19	121.7 (2)
O2—C8—C3	121.6 (2)	C19—C24—C23	122.0 (2)
C7—C8—C3	121.8 (2)	O7—C25—C17	123.0 (2)
C1—C9—C10—C13	11.2 (4)	C14—C15—C16—O5	61.4 (2)
O4—C14—C15—C16	59.9 (2)	C17—C25—C26—C29	10.5 (4)

Table 4

Hydrogen-bonding geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C13—H13 ⁱ ···O4	0.93	2.49	2.896 (3)	107
C29—H29 ⁱ ···O5	0.93	2.48	2.898 (3)	107
C6—H6 ⁱ ···O6 ⁱ	0.93	2.41	3.299 (3)	160
C22—H22 ⁱ ···O1 ⁱⁱ	0.93	2.44	3.161 (3)	134

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

In both compounds, all the H atoms were fixed geometrically and allowed to ride on the attached non-H atoms, with C—H distances of 0.93 and 0.97 Å, and $U_{\text{iso}} = 1.2U_{\text{eq}}(C)$ for non-methyl H atoms.

For compound (I), data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); molecular graphics: *ORTEPII* (Johnson, 1976). For compound (II), data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; molecular graphics: *ZORTEP* (Zsolnai, 1997). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1583). Services for accessing these data are described at the back of the journal.

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