Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

π-Stacked dimers in 6-methoxy-3,3-dimethyl-3*H*-benzo[*f*]chromene, and centrosymmetric dimers containing C—H···*π*(arene) hydrogen bonds in racemic 3-bromo-2,2,6,6-tetramethyl-3,4-dihydro-2*H*,6*H*-1,5-dioxatriphenylene

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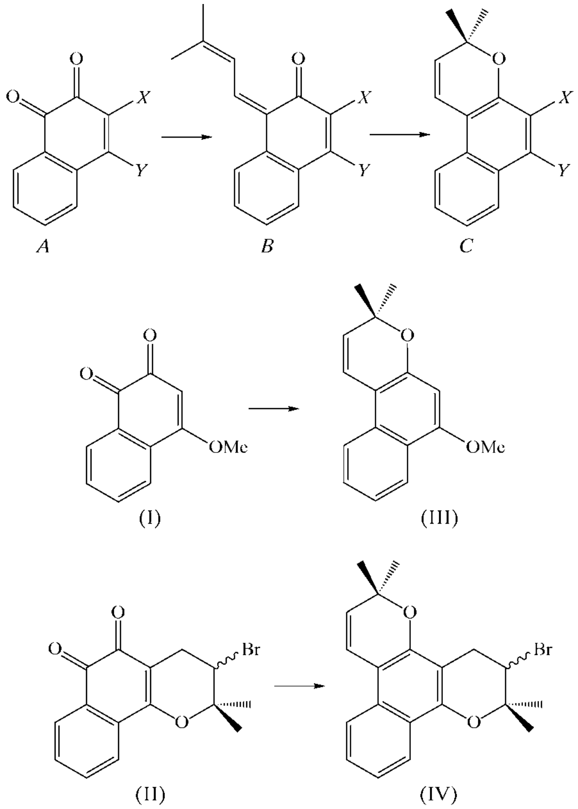
Received 7 August 2007
Accepted 8 August 2007
Online 1 September 2007

The title compounds, namely 6-methoxy-3,3-dimethyl-3*H*-benzo[*f*]chromene, $C_{16}H_{16}O_2$, (III), and racemic 3-bromo-2,2,6,6-tetramethyl-3,4-dihydro-2*H*,6*H*-1,5-dioxatriphenylene, $C_{20}H_{21}BrO_2$, (IV), were both synthesized in one-step regioselective Wittig reactions from substituted 1,2-naphthoquinones. The new ring in both compounds adopts a screw-boat conformation. A single π–π stacking interaction links the molecules of (III) into centrosymmetric dimeric aggregates, and a single C—H···π(arene) hydrogen bond links the molecules of (IV) into centrosymmetric dimers.

Comment

Chromenes are of considerable interest, both because of their biological activity (Hepworth, 1984) and because of their useful applications in modern optics (Zhang *et al.*, 2001; Ahmed *et al.*, 2003). We have developed a one-pot synthesis of chromenes which involves the reaction of a 1,2-naphthoquinone, *A* (see scheme), with the allylic Wittig precursor $[Me_2CH{=}CHCH_2PPh_3]^+Br^-$ in the presence of concentrated aqueous sodium hydroxide solution to give intermediate *B*, which undergoes spontaneous cyclization to the chromene *C*, in a hetero-Diels–Alder reaction. The Wittig reaction is fully regioselective for the 1-position, with no evidence for any reaction at the 2-position. Thus, reaction of 4-methoxy-1,2,naphthoqinone, (I), yields 9-methoxy-2,2-dimethyl-2*H*-benzo[*d*]chromene, (III), while racemic 3-bromo-β-lapachone, (II), yields racemic 3-bromo-2,2,6,6-tetramethyl-3,4-dihydro-2*H*,6*H*-1,5-dioxatriphenylene, (IV). We report here the structures of compounds (III) and (IV) (Figs. 1 and 2), which we compare briefly with that of precursor (II) (De Simone *et al.*, 2002).



Compounds (II) and (IV) each contain a stereogenic centre, at atom C3, but since the precursor, (II), is racemic (De Simone *et al.*, 2002), so also is the product, (IV). Compounds (II) and (IV) both crystallize in centrosymmetric space groups. The reference molecule in the structure of (IV) was selected to have an *S* configuration at C3, just as for compound (II). In each of compounds (III) and (IV), the newly formed ring adopts a screw-boat conformation. In (III), the ring-puckering parameters (Cremer & Pople, 1975) for the atom sequence O1/C2/C3/C4/C4a/C10a are θ = 113.6 (2)° and φ = 215.8 (2)°, while in (IV), the parameters for the atom-sequence O5/C4b/C8a/C8/C7/C6 are θ = 63.2 (4)° and φ = 328.4 (4). For the ideal screw-boat conformer, the values are θ = 67.5 or 112.5°, and $\varphi = (60n + 30)°$, where *n* represents zero or an integer.

The brominated ring in compound (IV) adopts a half-chair conformation, with the Br substituent occupying an equatorial site and with ring-puckering parameters θ = 128.3 (2)° and φ = 262.2 (3) for the atom sequence O1/C2/C3/C4/C4a/C12b. The ideal values are θ = 50.8 or 129.2° and $\varphi = (60n + 30)°$, where *n* represents zero or an integer. This conformation was also found for the heterocyclic ring in compound (I) (De Simone *et al.*, 2002).

In each of compounds (III) and (IV), the carbocyclic portion of the molecule shows the marked bond fixation

DOI: 10.1107/S0108270107039194

typical of naphthalenes (Tables 1 and 2), while the bonds C3—C4 in compound (III) and C7—C8 in compound (IV) are effectively isolated double bonds. The remaining bond distances show no unusual features. The methoxy C atom in compound (III) is almost coplanar with the adjacent carbocyclic ring, as shown by the relevant torsion angles, and the exocyclic O—C—C angles differ by *ca* 10°.

While there are no hydrogen bonds of any kind in the structure of compound (III), pairs of molecules are weakly linked into centrosymmetric dimeric aggregates by means of a single aromatic π–π stacking interaction. The unsubstituted aryl rings of the molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ are strictly parallel, with an interplanar spacing of 3.463 (2) Å; the ring centroid separation is 3.853 (2) Å, corresponding to a ring offset of 1.739 (2) Å. The molecules of compound (IV) are also weakly linked into centrosymmetric dimers, this time by a C—H$\cdots\pi$(arene) hydrogen bond (Table 3), in which atom C4 in the molecule at (x, y, z) acts as hydrogen-bond donor, *via* its equatorial H4*A* atom, to the C4a/C4b/C8a/C8b/C12a/C12b aryl ring in the molecule at $(1 - x, 1 - y, 1 - z)$ (Fig. 3).

By contrast with the dimeric aggregates formed by compounds (III) and (IV), the molecules of compound (II) are linked into chains of edge-fused rings (Fig. 4) by three independent C—H$\cdots$O hydrogen bonds [C3—H3$\cdots$O2$^{\rm ii}$, C9—H9$\cdots$O2$^{\rm iii}$ and C10—H10$\cdots$O3$^{\rm iii}$; symmetry codes: (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x, 1 + y, z$]. This aggregation was not discussed in the original report on this compound, which was concerned

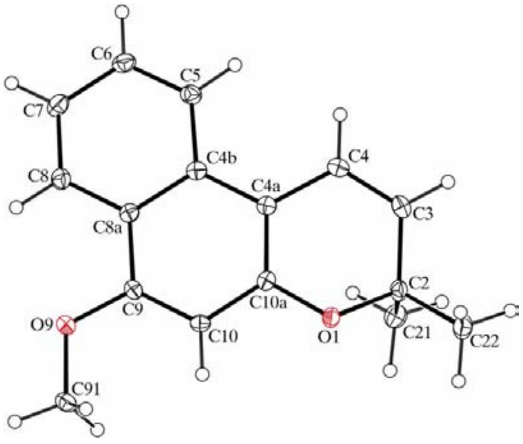


Figure 1
A molecule of compound (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

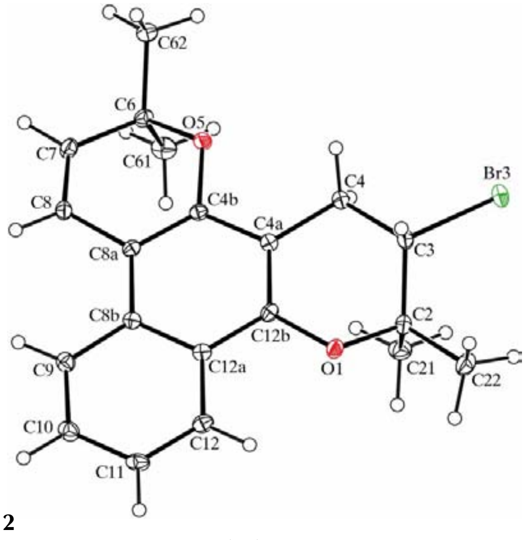


Figure 2
The *S* enantiomer of compound (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

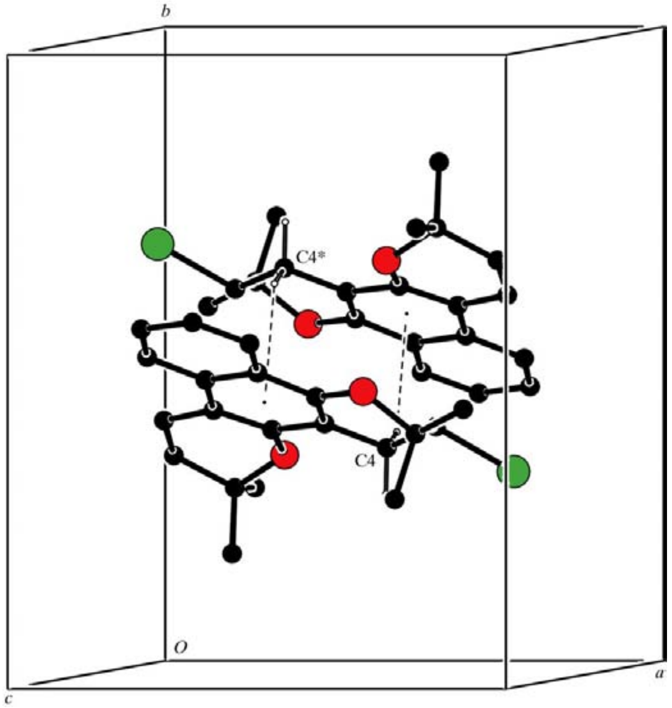


Figure 3
Part of the crystal structure of compound (IV), showing the formation of a centrosymmetric dimer built from C—H$\cdots\pi$(arene) hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

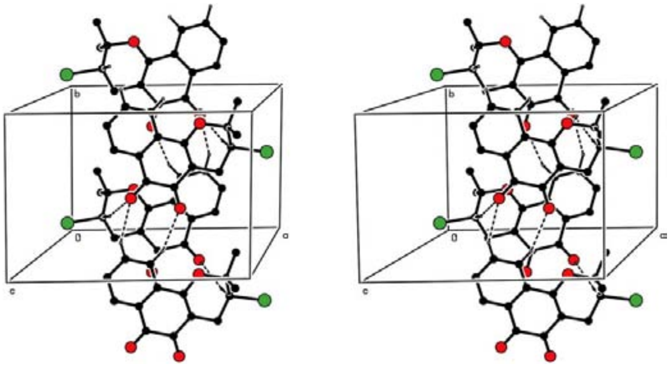


Figure 4
A stereoview of part of the crystal structure of compound (II), showing the formation of a chain of edge-fused rings along [010] generated by three independent C—H$\cdots$O hydrogen bonds. The original atomic coordinates (De Simone *et al.*, 2002) have been used. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

with proof of structure and conformation (De Simone *et al.*, 2002).

Experimental

The 1,2-naphthoquinone precursor, (II) (see scheme), was prepared from commercially available lapachol according to the method of Hooker (1892). This product has been shown to be a racemic mixture of enantiomers (De Simone *et al.*, 2002). For the synthesis of compounds (III) and (IV), a mixture of the appropriate 1,2-naphthoquinone (0.02 mol), the Wittig precursor $[Me_2CH{=}CH\text{-}CH_2PPh_3]^+Br^-$ (0.04 mol), $CHCl_3$ (15 ml) and aqueous NaOH (15 ml of a solution 50% by mass) was stirred vigorously for 48 h at ambient temperature. The organic phase was then separated, washed with water (3 × 10 ml) and dried over magnesium sulfate, and the solvent removed under reduced pressure. The crude products, (III) and (IV), were purified by chromatography on silica using a hexane–dichloromethane (1:1 *v*/*v*) mixture as eluent. Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in ethanol.

Compound (III)

Crystal data

$C_{16}H_{16}O_2$
$M_r = 240.29$
Orthorhombic, *Pbca*
$a = 6.3357$ (9) Å
$b = 15.5230$ (2) Å
$c = 25.3654$ (6) Å
$V = 2494.7$ (4) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.08$ mm^{-1}
$T = 120$ (2) K
0.74 × 0.40 × 0.14 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.957$, $T_{\max} = 0.989$
18107 measured reflections
2848 independent reflections
2033 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.108$
$S = 1.05$
2848 reflections
166 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}

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

C3—C4	1.3282 (16)	C8—C8a	1.4104 (16)
C4a—C4b	1.4339 (16)	C8a—C9	1.4269 (16)
C4b—C5	1.4174 (16)	C9—C10	1.3692 (16)
C5—C6	1.3637 (17)	C10—C10a	1.4075 (15)
C6—C7	1.4035 (18)	C10a—C4a	1.3802 (15)
C7—C8	1.3710 (17)	C4b—C8a	1.4234 (16)
O9—C9—C8a	114.27 (10)	O9—C9—C10	124.33 (10)
C8a—C9—O9—C91	178.09 (10)	C10—C9—O9—C91	−0.82 (17)

Compound (IV)

Crystal data

$C_{20}H_{21}BrO_2$
$M_r = 373.28$
Monoclinic, $P2_1/c$
$a = 10.7350$ (2) Å
$b = 13.7043$ (3) Å
$c = 12.0692$ (2) Å
$\beta = 106.3430$ (10)°
$V = 1703.83$ (6) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.42$ mm^{-1}
$T = 120$ (2) K
0.44 × 0.40 × 0.18 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.378$, $T_{\max} = 0.647$
27068 measured reflections
3910 independent reflections
3289 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.088$
$S = 1.18$
3910 reflections
212 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.49$ e Å^{-3}

Table 2
Selected bond lengths (Å) for (IV).

C7—C8	1.334 (3)	C10—C11	1.403 (3)
C4a—C4b	1.416 (3)	C11—C12	1.369 (3)
C4b—C8a	1.375 (3)	C12—C12a	1.419 (3)
C8a—C8b	1.436 (3)	C12a—C12b	1.420 (3)
C8b—C9	1.419 (3)	C12b—C4a	1.372 (3)
C9—C10	1.373 (3)	C8b—C12a	1.427 (3)

Table 3
Hydrogen-bond geometry (Å, °) for (IV).

Cg is the centroid of the C4a/C4b/C8a/C8b/C12a/C12b ring.

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4*A*···*Cg*$^{\rm i}$	0.99	2.95	3.765 (2)	140

Symmetry code: (i) $-x+1, -y+1, -z+1$.

For compounds (III) and (IV), the space groups *Pbca* and $P2_1/c$, respectively, were 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 = 0.95 (aromatic and alkenic), 0.98 (CH_3), 0.99 (CH_2) and 1.00 Å (aliphatic CH), and with $U_{\rm iso}({\rm H}) = kU_{\rm eq}({\rm C})$, where $k = 1.5$ for the methyl groups and 1.2 for all other H atoms.

For both compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC National Crystallography Service, University of Southampton, UK; the authors thank the staff of the Service for all their help and advice. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3118). Services for accessing these data are described at the back of the journal.

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