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4,4,4′,4′,7,7′-Hexamethyl-2,2′-spirobichroman

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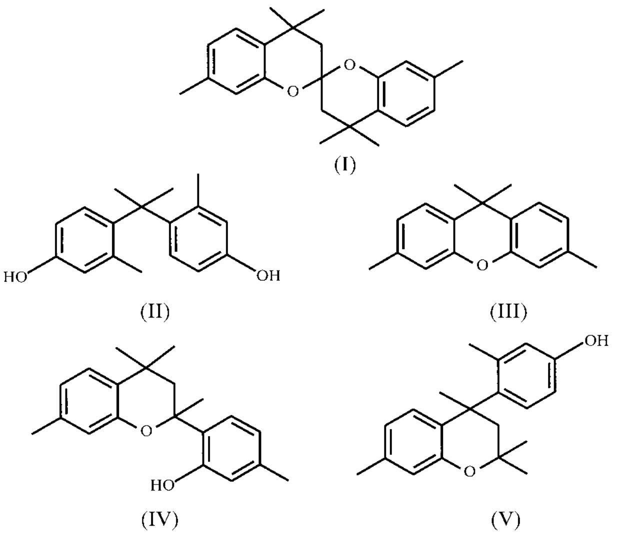
The title compound, $C_{23}H_{28}O_2$, was obtained from the reaction of acetone with *meta*-cresol. The molecular structure consists of two identical subunits which are nearly perpendicular to each other. The oxygen-containing rings are not planar and the molecule is chiral. The crystal structure consists of chains of molecules of the same chirality arranged along the [010] axis.

Comment

4,4,4′,4′,7,7′-Hexamethyl-2,2′-spirobichroman, (I), belongs to the large and structurally diverse family of the condensation products of carbonyl compounds with phenols. In particular, the acid-catalysed reaction between *meta*-cresol and acetone can provide any of the compounds presented in the scheme above. The preponderance of a particular compound in any reaction is dependent on the reaction conditions. Compound (I) was obtained in high yield from (IV) under the influence of boiling hydriodic acid (Baker & Besly, 1939). Another method for its preparation involves the heating (10 h at 423 K) of bisphenol-A with an excess of *meta*-cresol in the presence of methanesulfonic acid (Caruso & Lee, 1997).



(I)
(II)
(III)
(IV)
(V)

The molecule of (I) is chiral, as are all dissymmetric spiranes. In the proton NMR spectrum, the geminal protons at C3 give two doublets with coupling constants of 14 Hz. Analogously, the methyl C atoms on C4 give two separated signals. Another interesting property of (I) is its dimorphism. According to differential scanning calorimetry (DSC) analyses, the crystals melt at 132.9°, solidify and melt again at 138.1°. Such behaviour seems to be a common feature of structurally related spirobichromans (Baker & Besly, 1939).

The molecule of (I) consists of two identical subunits, which are nearly perpendicular to each other (Fig. 1). The dihedral angle between the O1—C2—C3 and O1^{i}—C2—C3^{i} [symmetry code: (i) $\frac{3}{2}-x, \frac{1}{2}-y, z$] planes is 87.2 (1)°. The oxygen-containing ring is not planar, and the C2 and C3 atoms are displaced from the plane defined by the benzene ring by 0.393 (4) and −0.299 (4) Å, respectively. The O1 and C4 atoms are nearly coplanar, with deviations from the ring plane of 0.060 (3) and −0.065 (3) Å, respectively. The analogous half-chair conformation of the pyran ring was observed in (IV) (MacNicol & Mallinson, 1983). The connection of the subunits through the spirane carbon has no significant influence on the geometry of the pyran ring. The bond lengths are the same, within 0.01 Å, as those observed in (IV) (MacNicol & Mallinson, 1983) and (V) (Dianin's compound; Flippen *et al.*, 1970). The non-planar conformation of the pyran ring makes the environment of the H atoms on C3 different. The H31 atom occupies a quasi-axial position with a deviation of 1.26 (2) Å from the mean plane of the pyran ring. The H32 atom lies in the plane and is situated on the same side of the ring as the O1^{i} atom belonging to the second ring. Consequently, the distance between H32 and O1^{i} [2.55 (2) Å] exceeds the sum of the van der Waals radii by 0.05 Å. The difference in the chemical shifts of the methyl groups on C4 is only 0.02 p.p.m. The C41 and C42 atoms are the same distance from the parent aromatic ring, but their displacements from the C3—C4—C10 plane are different [1.207 (5) *versus*

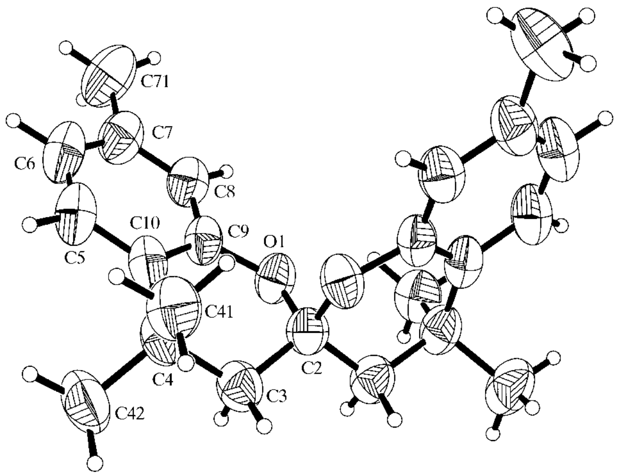


Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level.

1.275 (5) Å] because the C41 methyl group is directed outwards while the second methyl group approaches another chroman subunit. The molecule is rigid, hence it can be concluded that the different chemical shifts of C41 and C42 result from non-valence intramolecular interactions.

The crystals of (I) are racemic, *i.e.* they are built from both enantiomers, as in (IV) and (V). In the crystal structure of the latter, six molecules form the structural unit which consists of three pairs of enantiomers. The molecules of the same chirality are placed on one side of the O—H···O ring (Goldup & Smith, 1970). In clathrates of (IV), the enantiomers are arranged in pairs connected by hydrogen bonds with the guest molecules (Gall *et al.*, 1985).

At the present stage of our investigations, we cannot formulate any convincing explanation for the nature and driving force of the transformation of (I) into its high-temperature polymorph.

Experimental

A mixture of acetone (14.7 ml, 0.2 mol), *meta*-cresol (324 g, 3 mol) and methanesulfonic acid (1 ml) was left for 120 h at room temperature and then heated for 9 h to 413–423 K. The unreacted *meta*-cresol was distilled off in a vacuum. The residue was dissolved in benzene and extracted with water until neutral. The solvent was evaporated and a brown residue containing (I), (III) and (IV) was chromatographed using hexane as the eluent. 4,4,4′,4′,7,7′-Hexamethyl-2,2′-spirobichroman (5.04 g, 23%) was isolated from the last fractions as a white powder. Crystals suitable for X-ray diffraction studies were obtained by crystallization from methanol. MS, *m*/*z* (integration): 336 (4), 321 (35), 281 (13), 265 (21), 174 (14), 173 (100), 149 (71), 121 (11), 105 (12); ^{1}H NMR (DMSO-d_6): 7.23 (*d*, ^{3}J = 7.3 Hz, 2H) and 6.71 (*d*, ^{3}J = 7.3 Hz, 2H) (aromatic protons at C5, C5^{i}, C6 and C6^{i}), 6.36 (*s*, 2H, H8 and H8^{i}), 2.11 (*s*, 6H, Ar-methyl groups), 2.07 (*d*, 1H) and 1.92 (*d*, ^{2}J = 13.9 Hz, 1H) (methylene CH$_2$ protons of the pyran ring), 1.51 (*s*, 6H) and 1.26 (*s*, 6H) (methyl protons of the isopropenyl bridge); ^{13}C NMR (CDCl$_3$): 150.3 (C9, C9^{i}); 136.8 (C10, C10^{i}); 128.5 (C7, C7^{i}), 126.1, 122.4 and 118.1 (remaining aromatic C atoms); 97.7 (spirane carbon, C2); 46.8 (methylene groups, C3 and C3^{i}); 32.5 and 32.3 (methyl groups on C4 and C4^{i}); 30.6 (C4, C4^{i}); 20.8 (methyl groups at C7 and C7^{i}).

Crystal data

$C_{23}H_{28}O_2$
M_r = 336.45
Orthorhombic, *Pccn*
a = 16.613 (3) Å
b = 10.557 (2) Å
c = 11.259 (2) Å
V = 1974.6 (6) Å^3
Z = 4
D_x = 1.132 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 21 reflections
θ = 10–20°
μ = 0.070 mm^{-1}
T = 293 (2) K
Plate, colourless
0.7 × 0.4 × 0.3 mm

Data collection

Kuma KM-4 diffractometer
ω–θ scans
9984 measured reflections
1592 independent reflections
1175 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.021
$\theta_{\max}$ = 25.06°
$h = -18 \rightarrow 13$
$k = 0 \rightarrow 12$
$l = -13 \rightarrow 10$
2 standard reflections every 50 reflections intensity decay: 1.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.131
S = 1.156
1592 reflections
170 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 0.4667P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.162 e Å^{-3}
$\Delta\rho_{\min}$ = −0.118 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C9	1.378 (2)	C3—C4	1.533 (3)
O1—C2	1.423 (2)	C4—C10	1.512 (3)
C2—C3	1.508 (2)	C9—C10	1.387 (3)
C9—O1—C2	117.7 (1)	C2—C3—C4	115.5 (2)
O1—C2—O1^{i}	108.6 (2)	O1—C9—C8	114.7 (2)
O1—C2—C3	110.7 (1)	O1—C9—C10	123.3 (2)
O1^{i}—C2—C3	106.8 (1)	C8—C9—C10	122.1 (2)
C3—C2—C3^{i}	113.3 (2)	C9—C10—C4	122.3 (2)

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

H-atom positions were refined by the full-matrix least-squares method. The C—H distances were in the range 0.97 (2)–1.02 (3)Å for H atoms attached to phenyl rings and in the range 0.91 (5)–1.09 (3)Å range for methyl H atoms.

Data collection: *Kuma Diffraction Software* (Kuma, 1998); cell refinement: *Kuma Diffraction Software*; data reduction: *Kuma Diffraction Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1069). Services for accessing these data are described at the back of the journal.

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