

3,3-Bis(2-methoxyphenyl)-3H-
benzo[*f*]chromeneHua-Ming Huang, Ying Ding, Pei-Li Chen and Ji-Ben
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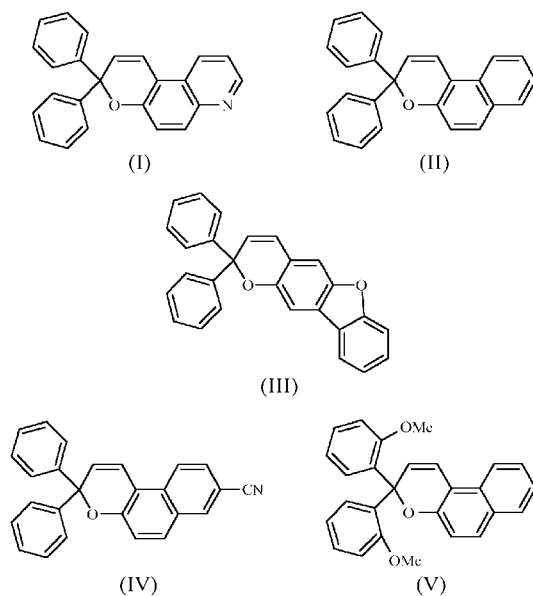
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The substituent methoxy group at the phenyl *ortho* position in the title compound, $C_{27}H_{22}O_3$, has an insignificant effect on the length of the Csp^3-O bond and on the non-planarity of the pyran ring. The cause of the changes in the photochemical properties is discussed.

Comment

2,2-Diphenylchromene derivatives are a special kind of photochromic compound. In contrast to other classes of photochromic compounds, such as spiropyrans and spirooxazines, 2*H*-chromenes do not contain a spiroheterocyclic



fragment. Nevertheless, some chromenes are photoactive and have found commercial applications (Malatesta, 1999). Aldoshin *et al.* (Aldoshin *et al.*, 1995, 1996; Aldoshin, Chuev, Filipenko, Pozzo *et al.*, 1998) have discussed the structures and photochemical properties of 2,2-diphenylchromene derivatives (I), (II), (III) and (IV) (see scheme), and have shown

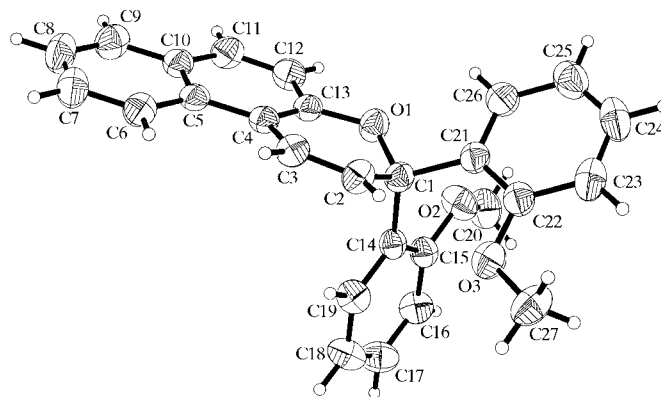


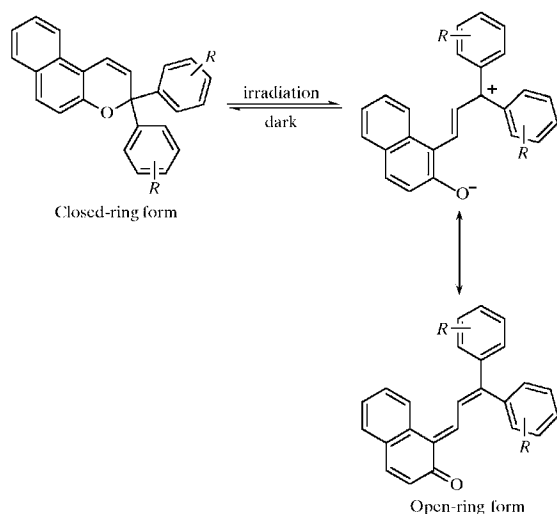
Figure 1

The molecular structure of (V), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

that in these compounds the pyran Csp^3-O1 bond, the rupture of which is responsible for the photochemical properties of the compounds, is elongated as a result of steric interactions. Thus, any factor that affects the Csp^3-O1 bond length and the planarity of the pyran ring will affect the photochemical properties of the compound. Moreover, substituents on the phenyl groups of 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran have a substantial effect on colour intensity and fade rate (Knowles, 1995). Our interest in this subject derives from the fact that derivatives of chromenes are easily synthesized, with potential for commercial application (Kou *et al.*, 2000). In order to understand how the substituents on the phenyl ring influence photochromic properties, we prepared some chromene derivatives with substituted phenyl rings and determined the X-ray structure of the title compound, (V).

Fig. 1 shows that the pyran ring in (V) is non-planar, with folding along the $O1 \cdots C2$ and $O1 \cdots C3$ axes, in a similar manner to that reported for (II). The dihedral angle between the $O1/C1/C2$ and $O1/C2/C3$ planes is $20.0 (1)^\circ$, and between the $O1/C2/C3$ and $O1/C3/C4$ planes is $9.6 (2)^\circ$, while the corresponding values in (II) are $22.9 (2)$ and $10.0 (2)^\circ$, respectively (Aldoshin, Chuev, Filipenko, Lokshin *et al.*, 1998; Aldoshin, Chuev, Filipenko, Pozzo *et al.*, 1998). The $C1-O1$ bond [$1.462 (2)$ Å; Table 1] is longer than a typical $C-O$ bond in a six-membered heterocycle ($1.41-1.43$ Å; Birukov & Unkovskij, 1976), but is indistinguishable from those in (I)–(IV) [$1.441 (2)$ – $1.468 (2)$ Å]. Therefore, chromenes (V) and (II) have similar pyran ring structures. The mutual arrangement of the phenyl rings in the molecules of (V) and (II) is similar; the dihedral angles between these fragments are $93.3 (2)$ and $96.6 (2)^\circ$, respectively. However, the arrangement of the phenyl rings with respect to the pyran ring differs. In a Newman projection along $C1-C_{Ph}$, atom $O1$ of the pyran ring in (V) is almost eclipsed with both phenyl rings [$O1-C1-C21-C26 = 1.7 (2)^\circ$ and $C2-C1-C14-C15 = 179.68 (16)^\circ$]. In (II), atom $O1$ is eclipsed with only one of the phenyl rings. The corresponding torsion angles along the $C1-C_{Ph}$ bond are $14.2 (2)$ and $3.2 (2)^\circ$. The latter conformation is partly stabilized by $C27-H27A$ forming a $C-H \cdots \pi$ interaction with an

adjacent phenyl ring, with $H \cdots Cg = 2.85 \text{ \AA}$ and $C-H \cdots Cg = 152^\circ$ [where Cg is the centroid of the C21–C26 ring at $(1-x, -y, 1-z)$]. Thus, the conformations of the phenyl groups do not essentially affect the structure of the pyran fragment and C_{spiro} centre. It might be expected that (V) and (II) have similar photochromic properties. However, the photochemical properties are different. Compared with (II), compound (V) has a dramatically enhanced optical density and slower rate of fade (van Gemert & Bergomi, 1991). Apparently, the electron-donating substituent methoxy group in the phenyl ring stabilizes the pyramidal carbocation at atom C1, which is formed upon elongation and rupture of the C1–O1 bond at the first stage of photoconversion. The steric effects of these groups hinder reversion to the closed-ring form (see scheme below), increasing the lifetime of the open-ring form of (V) and thus decreasing its fade rate.



Experimental

The title compound was synthesized by the reaction of 7,8-benzocoumarin and phenylmagnesium bromide as described by Cottam & Livingstone (1964).

Table 1

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

O1–C13	1.373 (2)	C2–C3	1.327 (3)
O1–C1	1.462 (2)	C3–C4	1.451 (2)
C1–C2	1.503 (3)	C4–C13	1.367 (3)
C13–O1–C1	119.98 (14)	C2–C1–C14	112.48 (16)
O1–C1–C2	109.61 (14)	C3–C2–C1	122.54 (17)
O1–C1–C21	105.50 (15)	C2–C3–C4	120.74 (19)
C2–C1–C21	109.34 (15)	C13–C4–C3	116.66 (17)
O1–C1–C14	107.23 (14)	C4–C13–O1	122.86 (16)
C13–O1–C1–C2	–31.4 (2)	C1–C2–C3–C4	–3.6 (3)
C13–O1–C1–C21	–149.03 (15)	C1–O1–C13–C4	19.7 (3)
C13–O1–C1–C14	90.97 (18)	O1–C1–C14–C19	–119.59 (18)
O1–C1–C2–C3	23.9 (3)	O1–C1–C14–C15	59.1 (2)
C21–C1–C2–C3	139.08 (19)	O1–C1–C21–C26	1.7 (2)
C14–C1–C2–C3	–95.3 (2)		

Crystal data

$C_{27}H_{22}O_3$
 $M_r = 394.45$
 Monoclinic, $P2_1/c$
 $a = 9.609 (3) \text{ \AA}$
 $b = 15.799 (4) \text{ \AA}$
 $c = 13.426 (4) \text{ \AA}$
 $\beta = 98.189 (5)^\circ$
 $V = 2017.5 (10) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.299 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 877 reflections
 $\theta = 2.8\text{--}25.0^\circ$
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Needle, colourless
 $0.22 \times 0.20 \times 0.18 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 9496 measured reflections
 4105 independent reflections
 2445 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$
 $\theta_{\text{max}} = 26.4^\circ$
 $h = -9 \rightarrow 12$
 $k = -15 \rightarrow 19$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.121$
 $S = 1.00$
 4105 reflections
 273 parameters
 H atoms parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 0.1508P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1244). Services for accessing these data are described at the back of the journal.

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