

6a,14a-cis-6,6a,7,14a-Tetrahydrochromeno-
[4',3':3,4]pyrano[3,2-c]coumarinR. Krishna,^{a*} P. G. Aravindan,^a
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Key indicators

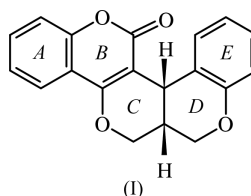
Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.065
wR factor = 0.167
Data-to-parameter ratio = 25.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $\text{C}_{19}\text{H}_{14}\text{O}_4$, crystallizes with two molecules in the asymmetric unit. The dihydropyran rings adopt a half-chair conformation or a conformation intermediate between a sofa and half-chair. The inversion-related type *A* and *B* molecules and *vice versa* are linked by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, forming an infinite chain along the *a* axis. The molecular packing is stabilized by $\text{C}-\text{H}\cdots\text{O}$ interactions.

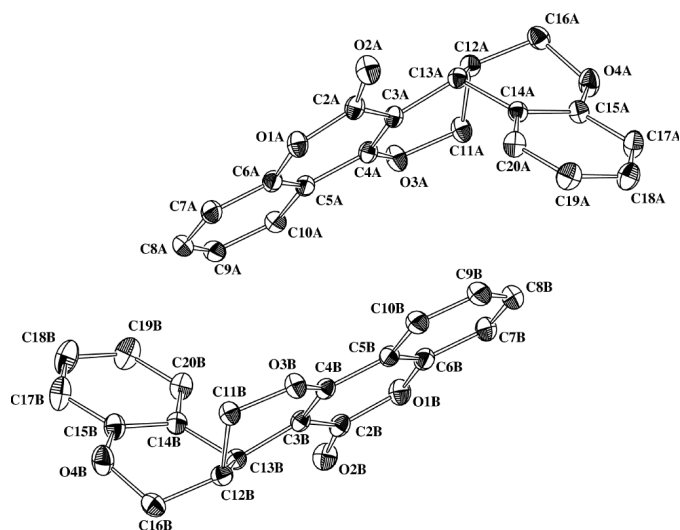
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Comment

Coumarin derivatives can undergo photocycloaddition with themselves (Song *et al.*, 1971). Coumarin dyes are widely used in lasers owing to their tunability (Masilamani *et al.*, 1986; Elnagdi *et al.*, 1997). The coumarin ring system is also present in a number of natural products (Cisowski, 1983, 1984), which are found to possess antimicrobial (Zaha & Hazem, 2002), antioxidant (Wei *et al.*, 1999; Sugioka *et al.*, 1997), anti-coagulation (Cole *et al.*, 1988) and antiplatelet (Roma *et al.*, 2003) activities. 4,7-Disubstituted coumarins give rise to interesting crystal structures in terms of their photochemical reactivity (Gnanaguru *et al.*, 1985). The X-ray crystal structure analysis of the title compound, (I), was carried out as part of our studies of coumarin derivatives.



The title molecule, (I), comprises two dihydropyran rings (*C* and *D*), one (*C*) fused to a coumarin moiety (rings *A* and *B*) and the other (*D*) fused to a benzene ring (*E*) (Fig. 1). There are two crystallographically independent molecules in the asymmetric unit. In both molecules, the $\text{O}1-\text{C}2$ and $\text{O}1-\text{C}6$ bonds are nearly equal in length, but slightly shorter than previously reported values (Krishna *et al.*, 2003). The $\text{C}2=\text{O}2$, $\text{C}2-\text{C}3$, $\text{C}3=\text{C}4$ and $\text{C}5-\text{C}6$ bond lengths and the endocyclic angles of the pyrone ring (*B*) agree well with those reported in related structures (Ruggiero *et al.*, 1989; Chinnakali *et al.*, 1992). The coumarin moiety is planar except for atom *C*2, which is displaced by -0.097 (2) and 0.040 (2) Å in molecules *A* and *B*, respectively. Atom *O*2 is displaced from the coumarin plane by -0.289 (1) and 0.136 (1) Å for molecules *A* and *B*, respectively. The dihedral angles between the aromatic ring (*A*) and the pyrone ring (*B*) are 3.2 (1) and 1.4 (1) $^\circ$ for molecules *A* and *B*, respectively. The dihedral angles between the dihydropyran rings (*C* and *D*) are 66.5 (1) and 64.8 (1) $^\circ$, respectively. In both molecules, the dihydropyran ring *C*


Figure 1

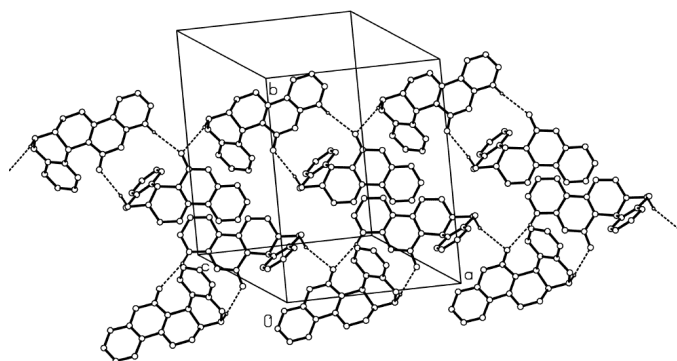
The molecular structure of the title compound, showing 35% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

adopts a conformation intermediate between a sofa and a half-chair, with asymmetry parameters (Nardelli, 1983) of $\Delta C_5(C4A) = 0.059$ (1) and $\Delta C_2(C4A-C3A) = 0.063$ (1) for molecule *A*, and $\Delta C_5(C4B) = 0.065$ (1) and $\Delta C_2(C4B-C3B) = 0.061$ (1) for molecule *B*. Dihydropyran ring *D* has a half-chair conformation in molecule *A* [$\Delta C_2(C15A-C14A) = 0.015$ (1)] and is intermediate between a sofa and a half-chair in molecule *B* [$\Delta C_5(C15B) = 0.059$ (1) and $\Delta C_2(C15B-C14B) = 0.027$ (1)].

Carbonyl atom O2 of the symmetry related molecule *A* at $(1-x, y-\frac{1}{2}, \frac{1}{2}-z)$ and $(2-x, y-\frac{1}{2}, \frac{1}{2}-z)$ acts as a bifurcated acceptor from the H atoms on C7 and C16 of molecule *B* and carbonyl atom O2 of the symmetry-related molecule *B* at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$ has an intermolecular interaction with C16 of molecule *A* of the donor atom. The molecular packing is stabilized by C—H...O interactions (Table 2).

Experimental

To a refluxing solution of 3-(2-allyloxybenzylidene)chroman-2,4-dione (0.31 g, 1 mmol) in nitromethane (20 ml) was added lithium per-


Figure 2

The crystal packing in the title compound. Only the H atoms involved in hydrogen bonding (dotted lines) have been included.

chlorolate (0.11 g, 1 mmol). After 12 h, work-up and flash-column chromatography, the cycloadduct was obtained in 38% yield. The crystals were grown from a combination of methanol/chloroform by slow evaporation.

Crystal data

$C_{19}H_{14}O_4$
 $M_r = 306.30$
 Monoclinic, $P2_1/c$
 $a = 12.2252$ (1) Å
 $b = 16.3351$ (3) Å
 $c = 15.3425$ (3) Å
 $\beta = 109.207$ (1)°
 $V = 2893.35$ (8) Å³
 $Z = 8$

$D_x = 1.406$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 9616 reflections
 $\theta = 2.8$ – 33.2 °
 $\mu = 0.10$ mm⁻¹
 $T = 293$ (2) K
 Block, colourless
 0.44 × 0.40 × 0.22 mm

Data collection

Siemens SMART 1K CCD area-detector diffractometer
 ω scans
 Absorption correction: none
 25479 measured reflections
 10531 independent reflections

6116 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.031$
 $\theta_{max} = 33.2$ °
 $h = -18 \rightarrow 9$
 $k = -24 \rightarrow 24$
 $l = -23 \rightarrow 23$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.167$
 $S = 1.07$
 10531 reflections
 415 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 8.287P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.28$ e Å⁻³
 $\Delta\rho_{min} = -0.22$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1A—C6A	1.375 (2)	O1B—C6B	1.374 (2)
O1A—C2A	1.377 (2)	O1B—C2B	1.382 (2)
O2A—C2A	1.214 (2)	O2B—C2B	1.211 (2)
O3A—C4A	1.344 (2)	O3B—C4B	1.344 (2)
O3A—C11A	1.441 (2)	O3B—C11B	1.443 (2)
O4A—C15A	1.371 (2)	O4B—C15B	1.370 (2)
O4A—C16A	1.435 (2)	O4B—C16B	1.430 (2)
C2A—C3A	1.443 (2)	C2B—C3B	1.444 (2)
C3A—C4A	1.357 (2)	C3B—C4B	1.360 (2)
C3A—C13A	1.512 (2)	C3B—C13B	1.511 (2)
C4A—C5A	1.445 (2)	C4B—C5B	1.448 (2)
C5A—C6A	1.392 (2)	C5B—C6B	1.390 (2)
C11A—C12A	1.516 (2)	C11B—C12B	1.513 (2)
C12A—C16A	1.508 (2)	C12B—C16B	1.510 (2)
C12A—C13A	1.534 (2)	C12B—C13B	1.532 (2)
C13A—C14A	1.529 (2)	C13B—C14B	1.530 (2)
C6A—O1A—C2A	121.3 (1)	O4A—C15A—C14A	123.8 (1)
C4A—O3A—C11A	117.1 (1)	C6B—O1B—C2B	121.5 (1)
C15A—O4A—C16A	116.5 (1)	C4B—O3B—C11B	116.7 (1)
O2A—C2A—O1A	116.2 (1)	C15B—O4B—C16B	116.9 (1)
O2A—C2A—C3A	125.3 (2)	O1B—C2B—C3B	118.6 (1)
O1A—C2A—C3A	118.6 (1)	C4B—C3B—C2B	119.3 (2)
C4A—C3A—C2A	119.1 (1)	C4B—C3B—C13B	122.0 (1)
C4A—C3A—C13A	121.8 (1)	O3B—C4B—C3B	124.5 (1)
O3A—C4A—C3A	124.7 (1)	C3B—C4B—C5B	121.7 (1)
C3A—C4A—C5A	121.6 (1)	C6B—C5B—C4B	117.1 (2)
C6A—C5A—C4A	117.1 (2)	O1B—C6B—C5B	121.7 (2)
O1A—C6A—C5A	121.5 (1)	O3B—C11B—C12B	112.5 (1)
O3A—C11A—C12A	112.8 (1)	O4B—C15B—C14B	123.6 (2)
C16A—C12A—C13A	110.5 (1)	O4B—C16B—C12B	112.1 (1)
C13A—C3A—C4A—C5A	−176.2 (1)	C13B—C3B—C4B—C5B	175.7 (1)
C10A—C5A—C6A—O1A	−177.5 (2)	C10B—C5B—C6B—O1B	179.1 (2)
C20A—C14A—C15A—O4A	179.2 (2)	C20B—C14B—C15B—O4B	−179.0 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C20B-H20B \cdots O2B$	0.93	2.55	3.262 (2)	134
$C7B-H7B \cdots O2A^i$	0.93	2.46	3.357 (2)	163
$C16A-H16B \cdots O2B^{ii}$	0.97	2.38	3.265 (2)	152
$C16B-H16C \cdots O2A^{iii}$	0.97	2.50	3.336 (2)	145

Symmetry codes: (i) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$.

H atoms were positioned geometrically, with C–H distances in the range 0.93–0.98 Å. They were allowed to ride on their parent atoms with the isotropic displacement parameter $U_{iso}(H)$ set at $1.2U_{eq}$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997) and *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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