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3′,4′-Bis(4-chlorophenyl)spiro-[chroman-3,5′(4′*H*)-isoxazol]-4-one

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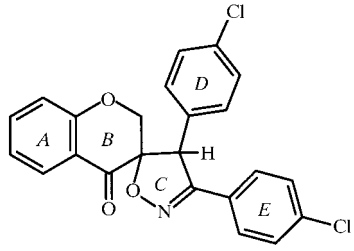
The title compound, $C_{23}H_{15}Cl_2NO_3$, crystallizes with two independent molecules in the asymmetric unit. The chromanone moiety consists of a benzene ring fused with a six-membered heterocyclic ring which adopts a sofa conformation. The five-membered spiroisoxazoline ring is in an envelope conformation. The *p*-chlorophenyl rings bridged by the five-membered ring are nearly perpendicular to each other. The chromanone moiety of one molecule packs into the cavity formed by the *p*-chlorophenyl rings of a second molecule through the formation of C—H···π interactions. The structure is stabilized by weak C—H···O, C—H···Cl and C—H···π interactions.

Comment

Isoxazoline derivatives have been shown to be efficient precursors for many synthetic intermediates including γ-amino alcohols and β-hydroxy ketones (Kozikowski, 1984; Kanemasa & Tsuge, 1990). Spiroisoxazolines display interesting biological properties such as herbicidal, plant-growth regulatory and antitumour activities (Howe & Shelton, 1990; Smietana *et al.*, 1999). Many 4-chromanone derivatives are versatile intermediates for the synthesis of natural products such as brazillin, hematoxylin, ripariochromene, clausenin,



(1)

calonlide A and inophyllum B (Ellis *et al.*, 1997; Chenera *et al.*, 1993). Chromanone heterocycles have also attracted much attention owing to their important pharmacological properties (Ellis *et al.*, 1977). Their high synthetic utility and pharmacological importance have prompted us to synthesize some biologically interesting spiroisoxazoline derivatives.

The asymmetric unit contains two independent molecules of the title compound, (1). In both molecules, the *B* ring adopts a sofa conformation and the *C* ring is in an envelope conformation (see Fig. 1 and Table 1). The chromanone moiety is nearly perpendicular to the five-membered ring, the dihedral angle being 81.9 (1)° in molecule I and 80.0 (1)° in molecule II. The *p*-chlorophenyl rings bridged by the five-membered ring are nearly perpendicular to each other; the relevant dihedral angles are 77.9 (1) and 88.4 (1)° for molecules I and II, respectively. Superposition of the non-H atoms of molecules I and II using *BIOSYM* (Biosym/MSI, 1995) shows that the r.m.s. deviation for the non-H atoms comprising the chroma-

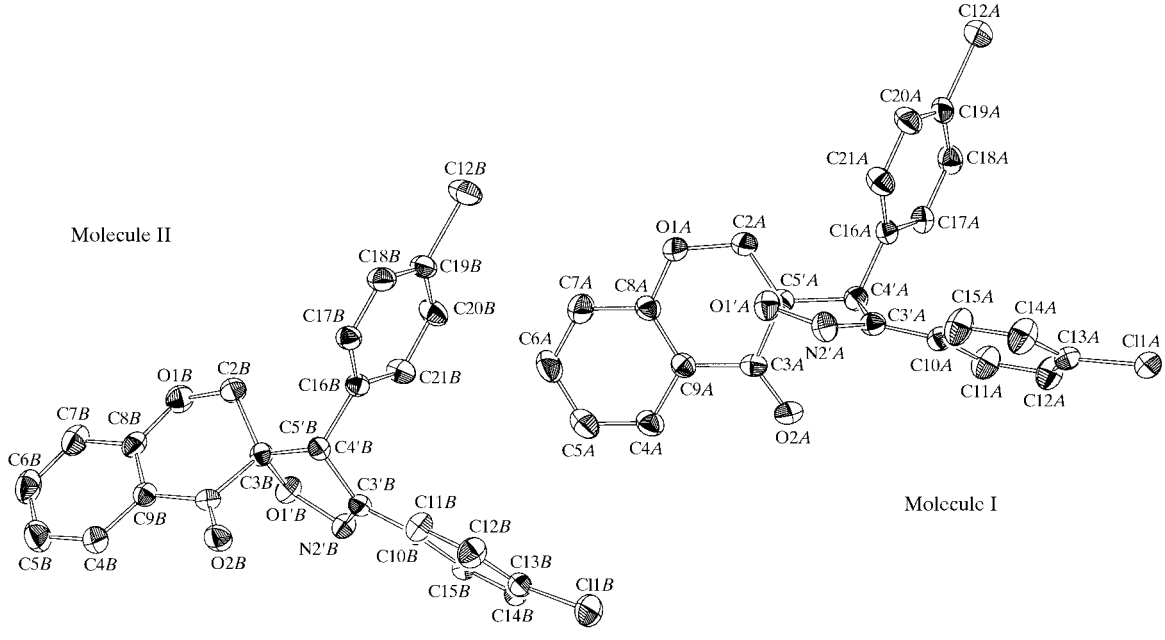


Figure 1
The molecular structure of (I) showing displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

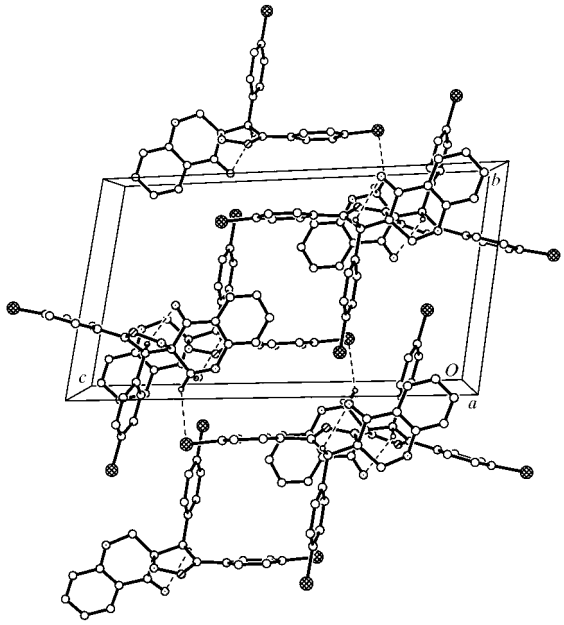


Figure 2
The molecular packing viewed approximately along the *a* axis. Dashed lines indicate intramolecular C—H···O and intermolecular C—H···Cl interactions. Atoms are identified as follows: Cl are cross-hatched, O are dotted, N are shaded, C are large open circles and H are small open circles.

none and isoxazoline rings is 0.0429 Å, while that for all the non-H atoms in the entire molecule is 0.908 Å. The packing of the molecules viewed down the *a* axis is shown in Fig. 2 (Spek, 1990). The packing is such that molecule I and the inverted image of II (*II*, say) are related by an approximate centre of symmetry at (0.0232,0.2343,−0.2488), the r.m.s. deviation between the atoms of I and the corresponding atoms of *II* after inversion through this centre being 1.7 Å. The chromanone moiety of molecule I packs into the cavity formed by the *p*-chlorophenyl rings of molecule II through the formation of C—H···π interactions between the two molecules (see Table 2). In order to optimize the packing, the chromanone moiety of molecule I appears to distort slightly and this, in turn, leads to an intramolecular C—H···O interaction in molecule I which is not present in molecule II. Each of the *p*-chlorophenyl rings of molecule I also enters into a C—H···π interaction with the phenyl rings of the chromanone moiety of symmetry-related molecules. The geometry of these C—H···π interactions is comparable with the literature values (Gallagher *et al.*, 2000; Kooijman *et al.*, 2000; Hashizume *et al.*, 2000; Bryan, 2000). The packing of the molecules in the crystal structure is thus stabilized by weak C—H···O, C—H···Cl and C—H···π interactions (Fig. 2).

Experimental

To a solution of 3-arylidene-4-chromanone (0.810 g, 3 mmol) and *N*-benzhydroxyiminoyl chloride (0.567 g, 3 mmol) in dry chloroform (10 ml), triethylamine (0.334 g, 3.3 mmol) was added. The reaction mixture was stirred at room temperature until the disappearance of the starting materials, as monitored by thin-layer chromatography, was observed. After the reaction was complete, the solution was filtered to remove triethylamine hydrochloride, and the solvent was removed *in vacuo*. The resulting crude product was purified by column chromatography (hexane/ethyl acetate, 9:1) (yield 81%, m.p. 415–417 K). Elemental analysis, found: C 65.09, H 3.45, N 3.20%; calculated for $C_{23}H_{15}Cl_2NO_3$: C 65.30, H 3.57, N 3.30%. Crystals of (1) were grown by slow evaporation from a methanol/chloroform solution.

Crystal data

$C_{23}H_{15}Cl_2NO_3$
M_r = 424.26
Triclinic, $P\overline{1}$
a = 9.764 (3) Å
b = 11.006 (2) Å
c = 19.780 (3) Å
α = 97.56 (2)°
β = 102.29 (2)°
γ = 101.73 (2)°
V = 1999.4 (8) Å^3
Z = 4
D_x = 1.409 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 14–25°
μ = 3.129 mm^{-1}
T = 293 (2) K
Rectangular prism, colourless
0.35 × 0.10 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.830, T_{max} = 0.997
7848 measured reflections
7458 independent reflections
3326 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 69.85°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 13$
$l = -24 \rightarrow 23$
3 standard reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.139
S = 1.006
7458 reflections
524 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 0.478P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00118 (14)

Table 1
Cremer & Pople (1975) conformational parameters for the rings in the two molecules.

Ring	Molecule	q_2 (Å)	q_3 (Å)	Q_T (Å)	φ_2 (°)	Conformation
B	I	0.335 (4)	0.271 (4)	0.431 (4)	−39.7 (6)	sofa
B	II	0.312 (4)	−0.252 (4)	0.401 (4)	141.0 (7)	sofa
C	I	0.183 (4)			140.8 (11)	envelope
C	II	0.237 (4)			−41.5 (8)	envelope

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

*Cg*1, *Cg*2 and *Cg*3 are the centroids of rings C4*B*–C9*B*, C10*B*–C15*B* and C16*B*–C21*B*, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4′*A*—H4′*A*···O2*A*	0.98	2.40	2.780 (5)	103
C2*B*—H2*B*2···Cl1*A*^{i}	0.97	2.76	3.600 (4)	145
C5*A*—H5*A*···*Cg*2	0.93	2.99	3.683 (5)	160
C6*A*—H6*A*···*Cg*3	0.93	2.83	3.671 (5)	151
C17*A*—H17*A*···*Cg*^{ii}	0.93	2.63	3.515 (5)	159
C15*A*—H15*A*···*Cg*^{iii}	0.93	2.74	3.578 (5)	151

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

All H atoms were placed in calculated positions, refined using a riding model and given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic parameter of their parent atoms. The C—H distances used depend on the type of C atom, *i.e.* 0.93, 0.97 and 0.98 Å for aromatic, methylene and methine H atoms, respectively.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *SDP* Software (Frenz, 1978); data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1995); software used to prepare material for publication: *PARST*97 (Nardelli, 1995) and *PLATON* (Spek, 2000).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1437). Services for accessing these data are described at the back of the journal.

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