organic papers

Spiro[2-carbomethoxy-5-(4-methoxyphenyl)-3-phenyl-pyrrolidine-4,3'-chroman-4'-one]

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In the title compound, $C_{27}H_{25}NO_5$, the pyran ring in the chroman-4-one moiety adopts a sofa conformation and the pyrrolidine ring adopts a twisted or half-chair conformation. The chromanone moiety makes a dihedral angle of 64.3 (1)° with the mean plane passing through the pyrrolidine ring. In the crystal structure, the molecular packing is stabilized by C—H···O intermolecular interactions.

Comment

Highly substituted pyrrolidines have attracted much interest in the past few years, since they constitute the main structural element of many alkaloids and pharmacologically active compounds (Waldmann, 1995). Many 4-chromanone derivatives are used as versatile intermediates in the synthesis of natural products such as hematoxylin, brazillin, ripariochromene, clausenin, calonlide A and inophyllum B (Ellis *et al.*, 1977; Chenera *et al.*, 1993). They have also been suggested to have significant activity against human immunodeficiency virus type I (HIV-1) (Hussain & Amir, 1986).
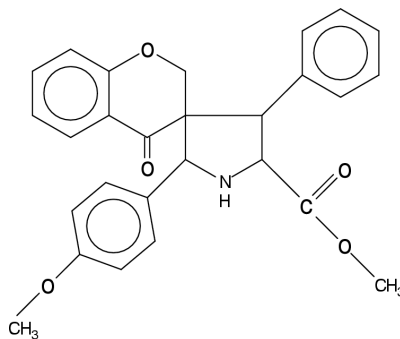

(I)

In order to collect conformational information about spiropyrrolidine derivatives and to find the relationships between their crystal structures and their behaviour, this spiropyrrolidine compound was selected for X-ray crystallographic study. Fig. 1 shows the structure of the title compound, (I), with the atom-labelling scheme. Dimensions of non-bonded interactions are given in Table 1.

The total puckering amplitude (Cremer & Pople, 1975) of the pyran ring in the chroman-4-one moiety, $Q_T = 0.5107$, and the values of the lowest displacement asymmetry parameters (Nardelli, 1983a) [Δ_2(C3—C2) = 0.066 (1) and Δ_s(C3) = 0.077 (1)] are indicative of a distorted half-chair conformation, also called a sofa conformation. Atom C3 is at the apex and deviates by 0.667 (2) Å from the mean plane passing through
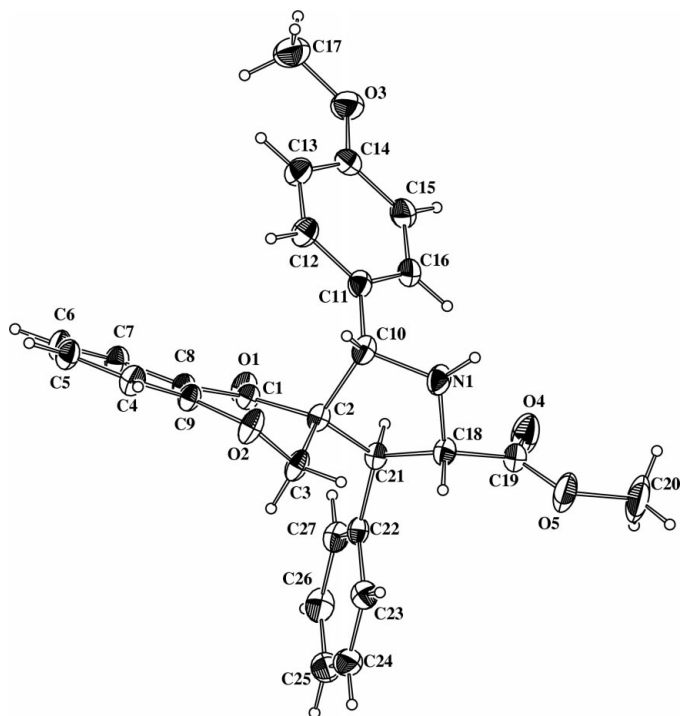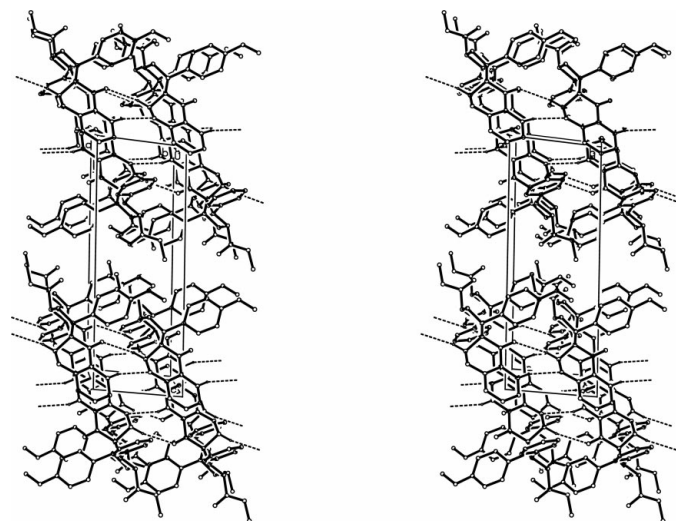
Figure 1
Diagram of the structure of the title compound with 30% probability ellipsoids and the atom-labelling scheme.

Figure 2
Stereoview of the molecular packing (viewed down the *b* axis).

$C-H \cdots O$ interactions in addition to van der Waals contacts (Fig. 2).

Experimental

An efficient synthesis of a series of novel spiropyrrolidine derivatives has been achieved *via* the [3+2]-cycloaddition reaction between *N*-metalated azomethine ylides and *E*-3-arylidene-4-chromanones (Subramanian & Raghunathan, 2001). The following procedure is general for the cycloaddition reaction between 3-arylidene-4-chromanones and imines in the presence of silver acetate as catalyst. To a solution of benzylideneglycine ester (1 mmol) in dry acetonitrile (10 ml), triethylamine (1 mmol), benzylidenechromanone (1 mmol) and then AgOAc (0.15 equivalents) were added. After completion of the reaction as determined by TLC, the reaction mixture was filtered through a celite pad, washed with a saturated aqueous solution of NH_4Cl, and then extracted with CH_2Cl_2 (2 × 20 ml). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and the solvent evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (100–200 mesh) with petroleum ether–ethyl acetate (4:1) to afford the cycloadduct, which was crystallized from EtOH (0.35 g, 78%; m.p.: 416–418 K).

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the other atoms (C1, C2, O2, C9 and C8) of the ring. Many reported structures have this type of conformation for the pyran ring (Ajees *et al.*, 2001; Sriram, Srinivasan & Santhosh, 1997; Sriram, Srinivasan, Santhosh & Balasubramanian, 1997; Chantrapromma *et al.*, 1997). The normal conformation of pyran rings is half-chair (Alex *et al.*, 1993).

The puckering parameters of the five-membered pyrrolidine ring ($q_2 = 0.4495$ and $\Phi_2 = -92.72$) and the values of the lowest displacement asymmetry parameters [$\Delta_2(N1) = 0.014$ (1)] are indicative of a twisted or half-chair conformation with a local pseudo-twofold axis running through N1 in the ring. The chromanone moiety makes a dihedral angle of 64.3 (1)° with the mean plane passing through the pyrrolidine ring. The dihedral angle between the planes of the fused aromatic ring and the methoxy phenyl ring is 41.4 (1)°. The fused aromatic ring and the phenyl ring bridged by the bond C21—C22 are nearly perpendicular to each other; the relevant dihedral angle is 78.5 (1)°. The methoxyphenyl group is oriented at an angle of 83.9 (1)° to the pyrrolidine ring. The phenyl ring and the methoxyphenyl ring make a dihedral angle of 70.3 (1)°.

The twisting of the phenyl ring can be described by the torsion angles C2—C10—C11—C12 = 88.5 (2)° and C2—C21—C22—C27 = 102.2 (2)°. As can be seen from the torsion angle of C13—C14—O3—C17 [−0.2 (3)°], the methoxy substituent is in a synperiplanar conformation. The molecules in the crystal lattice are stabilized by intermolecular

Crystal data

$C_{27}H_{25}NO_5$	$Z = 2$
$M_r = 443.48$	$D_x = 1.305$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.709$ (5) Å	Cell parameters from 25
$b = 9.958$ (5) Å	reflections
$c = 17.743$ (5) Å	$\theta = 19.7–28.2°$
$\alpha = 95.757$ (5)°	$\mu = 0.09$ mm^{-1}
$\beta = 94.587$ (5)°	$T = 293$ (2) K
$\gamma = 105.600$ (5)°	Prism, colourless
$V = 1128.9$ (11) Å^3	0.3 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius CAD-4	$h = -7 \to 7$
diffractometer	$k = -11 \to 11$
Non-profiled $\omega/2\theta$ scans	$l = 0 \to 21$
4080 measured reflections	3 standard reflections
3942 independent reflections	every 100 reflections
2907 reflections with $I > 2\sigma(I)$	frequency: 120 min
$R_{int} = 0.012$	intensity decay: <1%
$\theta_{max} = 25.0°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$+ 0.2895P]$
$wR(F^2) = 0.128$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
3942 reflections	$\Delta\rho_{max} = 0.38$ e Å^{-3}
298 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
H-atom parameters constrained	

Table 1
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3B···O1[i]	0.97	2.48	3.432 (3)	167
C7—H7···O2[ii]	0.93	2.34	3.201 (3)	153

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

All H atoms were fixed geometrically and refined isotropically using a riding model.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997) and *PLUTON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1983*b*, 1995).

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