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

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.064
wR factor = 0.200
Data-to-parameter ratio = 13.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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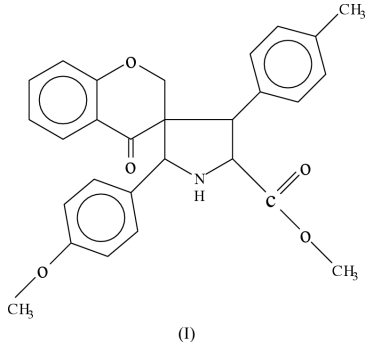
In the title compound, $C_{28}H_{27}NO_5$, the pyran ring in the chroman-4-one moiety adopts a sofa conformation and the pyrrolidine ring adopts an envelope conformation. The chromanone moiety makes a dihedral angle of 79.1 (1)° with the mean plane passing through the pyrrolidine ring. In the crystal structure, the molecules in the crystal lattice are 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, riparichromene, clausenin, calanolide A and inophyllum B (Ellis *et al.*, 1977; Chenera *et al.*, 1993). It has been suggested that they have significant activity against human immunodeficiency virus type I (HIV-1) (Hussain & Amir, 1986).



(I)

The title compound, (I), differs from a closely related compound (Nissa *et al.*, 2001) by having an extra methyl group at the *para* position of the phenyl ring (C22–C27). The total puckering amplitude (Cremer & Pople, 1975) of the pyran ring in the chroman-4-one moiety (Q_T = 0.5093) and the values of the lowest displacement asymmetry parameters (Nardelli, 1983*a*) [Δ_2(C3—C2) = 0.102 (1) and Δ_s(C3) = 0.035 (2)] are indicative of a sofa conformation. Calculation shows that atom C3 is at the apex and deviates by 0.681 (3) Å from the mean plane passing through the other atoms (C1, C2, O2, C9 and C8) of the ring. The puckering parameters of the five-membered pyrrolidine ring are q_2 = 0.4174 and Φ_2 = 29.32, and the value of the lowest displacement asymmetry parameter Δ_s(C18) = 0.042 (2), indicative of an envelope conformation.

The chromanone moiety makes a dihedral angle of 79.1 (1)° with the mean plane passing through the pyrrolidine ring. The

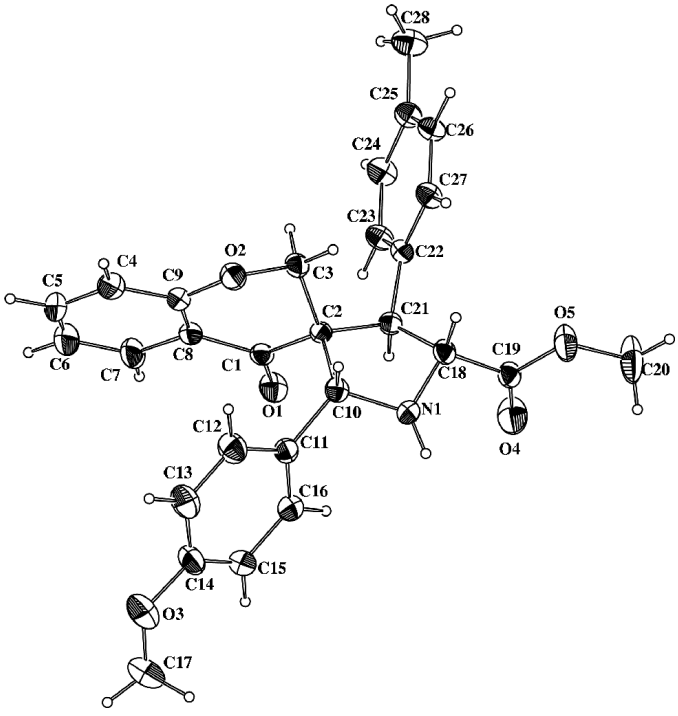


Figure 1
ZORTEP (Zsolnai, 1997) diagram of the structure showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

dihedral angle between the planes of the fused aromatic ring and the methoxyphenyl ring is 46.1 (1)°. The dihedral angle [89.1 (1)°] shows that the fused aromatic ring and the *p*-tolyl ring are perpendicular to each other. The methoxyphenyl group is oriented at an angle of 74.5 (1)° to the pyrrolidine ring. The phenyl rings make a dihedral angle of 66.9 (1)°.

The twisting of the *p*-tolyl ring can be described by the torsion angle C2—C21—C22—C27 of 83.8 (4)°. The torsion angle C17—O3—C14—C13 of −178.8 (5)° shows that the methoxy substituent is in an antiperiplanar conformation. The molecules in the crystal lattice are stabilized by intermolecular C—H···O interactions in addition to van der Waals contacts (Fig. 2). As a result of the additional methyl group, molecules in the crystal lattice pack in a different manner, compared to that of the previously reported related structure (Nissa *et al.*, 2001). Excluding the methyl group C28, superposition of the non-H atoms of the compound with the reported compound (Nissa *et al.*, 2001) [using *BIOSYM INSIGHT*-II (MSI, 1995)] shows that the r.m.s deviation for all the non-H atoms in the entire molecule is 2.2 Å, while the r.m.s deviation for the non-H atoms of the chromanone moiety is 0.3 Å. The r.m.s deviation for the non-H atoms of both compounds comprising the pyrrolidine ring is 0.3 Å.

Experimental

An efficient synthesis of a series of novel spiropyrrolidine derivatives has been achieved *via* the [3+2]-cycloaddition reaction between

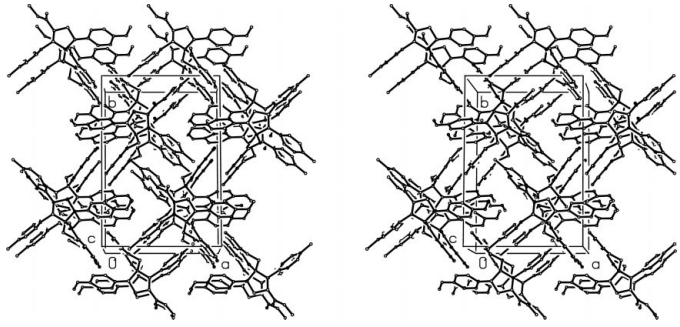


Figure 2
Stereoview of the molecular packing of the title compound, viewed down the *c* axis.

N-metalated azomethine ylides and (*E*)-3-arylidene-4-chromanones (Subramaniyan & Raghunathan, 2001). The following is the general procedure 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 (0.31 g, 68%; m.p.: 425–426 K).

Crystal data

$C_{28}H_{27}NO_5$
M_r = 457.51
Monoclinic, $P2_1/c$
a = 12.4779 (6) Å
b = 18.0879 (19) Å
c = 10.4580 (19) Å
β = 92.782 (9)°
V = 2357.6 (5) Å^3
Z = 4
D_x = 1.289 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 19.7–28.2°
μ = 0.09 mm^{-1}
T = 293 (2) K
Prism, colourless
0.32 × 0.25 × 0.18 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4342 measured reflections
4144 independent reflections
2306 reflections with $I > 2\sigma(I)$
R_{int} = 0.079
θ_{max} = 25.0°
$h = 0 \rightarrow 14$
$k = -21 \rightarrow 0$
$l = -12 \rightarrow 12$
3 standard reflections
every 100 reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.200
S = 1.02
4144 reflections
310 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1092P)^2 + 0.3704P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.005
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···O4^{i}	0.97	2.62	3.591 (4)	175

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

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, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997) and *BIOSYM INSIGHT*-II (MSI, 1995); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1983*b*, 1995).

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