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8a,13b-*cis*-8,8,13-Trimethyl-11-phenyl-8,8a,9,13b-tetrahydropyrazolo[3″,4″-*b*′]-thiapyrano[5′,4′:3,4]pyrano[5,6-*c*]coumarin

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In the title compound, $C_{25}H_{22}N_2O_3S$, the dihydropyran ring adopts a half-chair conformation and the dihydrothiapyran ring adopts a sofa conformation.

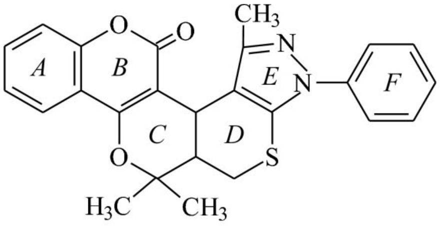
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.084
wR factor = 0.194
Data-to-parameter ratio = 15.6

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

Comment

Coumarin derivatives show antimicrobial (Zaha & Hazem, 2002) and vasorelaxant (Campos-Toimil *et al.*, 2002) activities and serve as antiplatelet agents (Roma *et al.*, 2003). These derivatives occurring in plants have different biological activities (Cisowski, 1983, 1984) and are used as dual inhibitors of acetylcholinesterase and monoamine oxidase (Bruhlmann *et al.*, 2001). Recent results have shown that these derivatives act as potent and anti-HIV agents (Yu *et al.*, 2003; Shikishima *et al.*, 2001). In view of the above biological importance, the title compound, (I), was chosen for crystallographic study to determine its structure and conformation.



(I)

The title molecule (Fig. 1) consists of two benzene rings (*A* and *F*), one pyran ring (*B*), one dihydropyran ring (*C*), one dihydrothiapyran ring (*D*) and one pyrazole ring (*E*).

The geometry of the coumarin ring system is comparable to that observed in other coumarin derivatives (Chinnakali *et al.*, 1998, 1999; Krishna *et al.*, 2003). The bond distances agree well with the mean literature values (Allen *et al.*, 1987). The sum of the angles at N23 of the pyrazole ring (*E*), 358.7° is in accordance with sp^2-hybridization. In the coumarin moiety (*A* and *B*), the pyran ring (*B*) is planar within 0.052 (3) Å and the dihedral angle between the weighted least-squares planes through the benzene and pyran ring is 2.0 (1)°. The pyrazole ring (*E*) is planar, with a maximum deviation of −0.018 (3) Å for atom C21. The pyrazole ring (*E*) and the phenyl ring (*F*) subtend an angle of 51.2 (1)°. The dihydropyran ring (*C*) adopts a half-chair conformation, with the lowest asymmetry parameter of ΔC_2(C9—C8) = 0.045 (1) (Nardelli, 1983). The dihydrothiapyran ring adopts a sofa conformation, with asymmetry parameters ΔC_s(C13) = 0.021 (1) and ΔC_2(C20—C13) = 0.087 (1) (Nardelli, 1983).

Experimental

To a solution of 3-methyl-5-(2-methylpropenylsulfanyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (1 mmol) in ethanol was added an alcohol solution of 4-hydroxycoumarin (1 mmol) and ethylenediamine (1 drop)/diacetic acid (2 drops) (catalyst) at room temperature. The solution was refluxed for 3–4 h. The completion of the reaction was evidenced by thin-layer chromatography. The solvent was removed *in vacuo* and subjected to column chromatography using petroleum ether and ethyl acetate (8:2) as eluant. Good quality crystals were obtained from a mixture of ethyl acetate and hexane (1:1) by slow evaporation.

Crystal data

$C_{25}H_{22}N_2O_3S$
$M_r = 430.51$
Monoclinic, $P2_1/n$
$a = 10.1017\ (11)$ Å
$b = 10.2760\ (12)$ Å
$c = 20.187\ (2)$ Å
$\beta = 95.278\ (2)^\circ$
$V = 2086.7\ (4)$ Å^3
$Z = 4$

$D_x = 1.370$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2365 reflections
$\theta = 2.4–21.7^\circ$
$\mu = 0.19$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
0.24 × 0.20 × 0.16 mm

Data collection

Bruker SMART APEX diffractometer
ω scans
Absorption correction: none
12360 measured reflections
4420 independent reflections

3260 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 28.0^\circ$
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -21 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.084$
$wR(F^2) = 0.194$
$S = 1.16$
4420 reflections
283 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0803P)^2 + 0.9689P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C19	1.737 (3)	C14—O15	1.475 (4)
S1—C20	1.801 (4)	C19—N23	1.352 (4)
C5—O6	1.368 (4)	N22—N23	1.368 (3)
O6—C7	1.392 (4)	N23—C25	1.421 (4)
C9—C10	1.465 (4)		
C13—C20—S1	117.0 (2)	C19—N23—C25	127.3 (3)
C19—N23—N22	110.8 (2)	N22—N23—C25	120.6 (3)
C19—C18—C21—C24	−173.0 (3)	C19—N23—C25—C26	−57.4 (4)
C24—C21—N22—N23	174.4 (3)		

The H atoms were positioned geometrically and were treated as riding on their parent C atoms, with aromatic C—H distances of 0.93 Å, methyl C—H distances of 0.96 Å, ethylene C—H distances of 0.97 Å and methylene C—H distances of 0.98 Å, and with $U_{\rm iso} = 1.5U_{\rm eq}$(C) for methyl H and $1.2U_{\rm eq}$(C) for other H atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

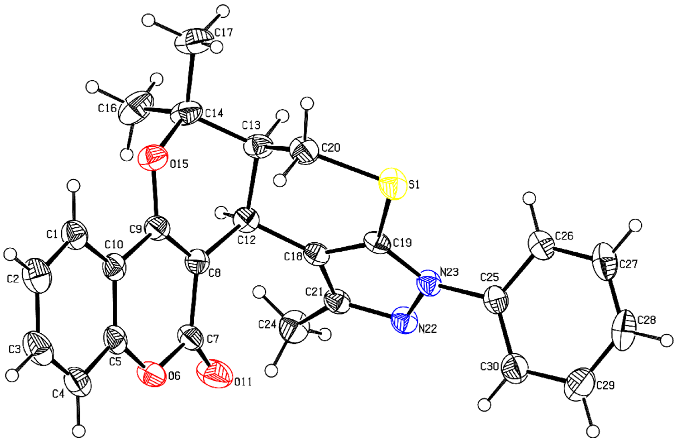


Figure 1
The molecular structure and atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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