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6,7-Dihydro-6-methyl-3-(methylsulfanyl)-1-(*p*-tolyl)pyrano[4,3-*c*]pyrazol-4(1*H*)-one

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.110
Data-to-parameter ratio = 16.4

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

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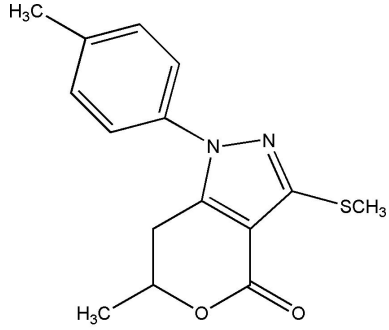
The title compound, $C_{15}H_{16}N_2O_2S$, which is a potentially new bioactive molecule containing pyrazole and pyrone ring systems, was synthesized by the reaction of 1-*p*-tolylhydrazine and 3-[bis(methylthio)methylene]dihydro-6-methyl-3*H*-pyran-2,4-dione in ethanol.

Comment

In recent years, there have a number of reports on the biological activity of pyranone derivatives, including inhibition of HIV proteinase (Ellsworch & Lunney, 1995; Thaisrivongs & Yang, 1994), tobacco virucidal activity, plant growth regulation activity, and fungicidal and herbicidal activity (Li *et al.*, 2004). Activity against *Biomphalaria glabrata* egg masses has also been reported (de Souza *et al.*, 2004). Pyrazole compounds also exhibit biological activity, including insecticidal, fungicidal, herbicidal (Li *et al.*, 1997; Wang *et al.*, 2000) and phytohormone activity (Liu *et al.*, 1999). In view of these facts, and as a continuation of our interest in the chemistry of heterocycles, we attempted to synthesize a series of pyranopyrazole derivatives, including the title compound, (I), by the reaction of 1-*p*-tolylhydrazine and 3-[bis(methylthio)methylene]dihydro-6-methyl-3*H*-pyran-2,4-dione in ethanol.



(I)

The molecular structure of (I) is shown in Fig. 1. The present crystal structure determination reveals that the *p*-tolyl is substituted on N1 rather than N2. The *p*-tolyl ring is twisted about the N1—C9 bond with respect to the pyrazole ring, with a value of 46.7 (3)° for the C4—N1—C9—C10 torsion angle. The S—CH_3 bond is also rotated out of the plane of the pyrazole ring, with the torsion angle C8—S1—C7—N2 = −9.5 (2)°.

Experimental

The title compound was synthesized by addition of anhydrous potassium carbonate (0.138 g, 1 mmol) and 1-*p*-tolylhydrazine dihy-

drochloride (0.195 g, 1 mmol) to an absolute ethanol solution (30 ml) containing 3-[bis(methylthio)methylene]dihydro-6-methyl-3*H*-pyran-2,4-dione (0.232 g, 1 mmol). The mixture was stirred for 3 h at room temperature. The product was obtained by silica-gel column chromatography, using a 1:5 mixture of ethyl acetate and petroleum ether as eluant. Colourless single crystals of (I) suitable for X-ray diffraction analysis were obtained by diffusion of *n*-hexane into a solution of the crude product in dichloromethane. Spectroscopic analysis: ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 7.27–7.38 (*m*, 4H), 4.60–4.67 (*m*, 1H), 2.96 (*d*, 2H, J = 6.9 Hz), 2.62 (*s*, 3H), 2.42 (*s*, 3H), 1.53 (*d*, 3H, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$, δ, p.p.m.): 161.95, 150.74, 145.74, 138.26, 135.64, 130.00, 122.63, 107.89, 74.96, 30.00, 21.05, 20.65, 13.46. Analysis calculated for $C_{15}H_{16}N_2O_2S$: C 62.48, H 5.59, N 9.71%; found: C 62.27, H 5.57, N 10.00%.

Crystal data

$C_{15}H_{16}N_2O_2S$	D_x = 1.290 Mg m^{-3}
M_r = 288.36	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2931 reflections
a = 10.662 (2) Å	θ = 2.2–26.1°
b = 18.315 (4) Å	μ = 0.22 mm^{-1}
c = 7.6831 (15) Å	T = 293 (2) K
β = 98.377 (3)°	Prism, colourless
V = 1484.3 (5) Å^3	0.26 × 0.24 × 0.14 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector diffractometer	3015 independent reflections
φ and ω scans	2130 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	R_{int} = 0.029
T_{min} = 0.736, T_{max} = 0.970	θ_{max} = 26.3°
8492 measured reflections	$h = -11 \rightarrow 13$
	$k = -20 \rightarrow 22$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 0.0755P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.038	$(\Delta/\sigma)_{max}$ = 0.005
$wR(F^2)$ = 0.110	$\Delta\rho_{max}$ = 0.21 e Å^{-3}
S = 0.98	$\Delta\rho_{min}$ = −0.19 e Å^{-3}
3015 reflections	
184 parameters	
H-atom parameters constrained	

All H atoms were placed in calculated positions, with C—H = 0.93, 0.96, 0.97 or 0.98 Å, and included in the refinement using a riding model, with U_{iso}(H) = 1.2U_{eq}(C) [1.5U_{eq}(C) for methyl H atoms].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

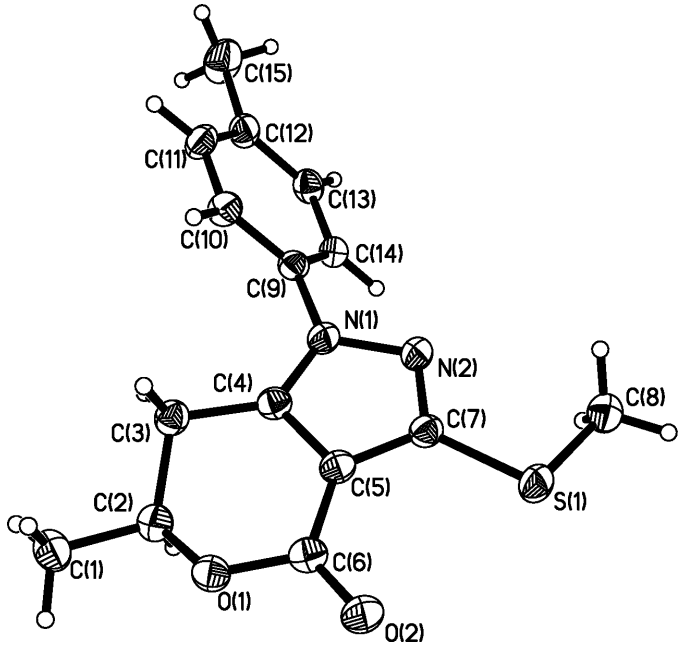


Figure 1
A view of compound (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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