

3-(2,3-Dihydro-1,5-dimethyl-3-oxo-2-phenylpyrazol-4-ylimino)-4,4,4-trifluoro-1-(2-thienyl)butane-1,2-dione

Jin-Ling Wang,^{a*} Ming Yu,^b
Xiu-Mei Su^a and Fang-Ming
Miao^a

^aInstitute of Chemical Crystallography, Tianjin Normal University, Tianjin 300074, People's Republic of China, and ^bThe Tianjin University of Scientific Technology, Tianjin 300122, People's Republic of China

Correspondence e-mail:
wangjinling43@eyou.com

Key indicators

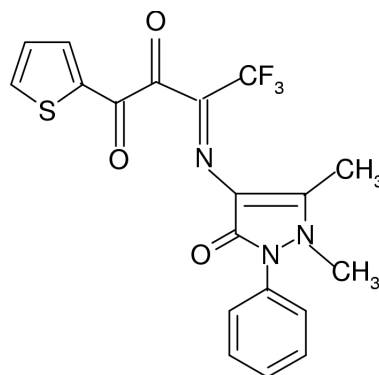
Single-crystal X-ray study
T = 298 K
Mean $\sigma(C-C)$ = 0.004 Å
R factor = 0.042
wR factor = 0.117
Data-to-parameter ratio = 11.4

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

The title compound, $C_{19}H_{14}F_3N_3O_3S$, is built up from pyrazolinone, thiophene, phenyl rings and trifluoropropane-dicarbonyl moieties. Examination of the $-C=N$ and $-C=O$ bond lengths reveals that there is no electron delocalization over the molecule.

Comment

A molecular view of the compound is shown in Fig. 1. The molecule consists of pyrazolinone, thiophene and phenyl rings and a trifluoropropane-dicarbonyl moiety. The C6–N3, C8–O1 and C7–O3 bond lengths are 1.275 (3), 1.223 (3) and 1.203 (3) Å, respectively, corresponding to classical $-C=N$ and $-C=O$ double bonds, whereas the C6–C7 and C7–C8 bond distances are 1.531 (3) and 1.531 (3) Å, respectively, close to normal C–C single bonds. These results clearly indicate that there is no electron delocalization over the whole molecule; although atoms C6, C7, C8, O1 and O3 are roughly coplanar with the thienyl ring, the largest deviation from the mean plane is 0.126 (2) Å for atom C6.



(I)

The displacements of atoms C5 and C21 from the mean plane of the pyrazolinone ring are -0.138 (3) and 0.162 (2) Å, respectively, showing that the methyl group bonded to N1 and the phenyl group are on opposite sides of the ring. The ϕ_{NN} (C21–N2–N1–C5) torsion angle is 16.7 (3)°, showing that the conformation about N2–N1 is *gauche*. Larger torsion angles have been observed in some related compounds, *viz.* 4-[[*(1E)*-(2-hydroxyphenyl)methylidene]amino]-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (Hokelek *et al.*, 2001), 4-(salicylideneamino)-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (Chumakov *et al.*, 2000) and 3,3-dimethyl-1-*N*-(1'-phenyl-2',3'-dimethyl-5'-oxo-3'-pyrazolin-4'-yl)imino-1,2,3,4-tetrahydroisoquinoline (Sokol *et al.*, 1996) with values of 55.7 , 55.6 and 67.2° , respectively. It is worth pointing out that in these

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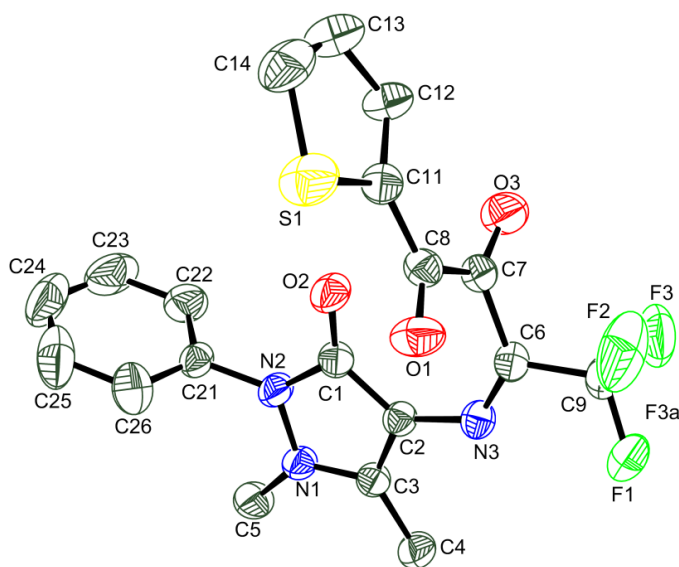


Figure 1
View of the title compound (50% probability displacement ellipsoids).

last three compounds, the dihedral angle between the phenyl and pyrazolinone rings ranges from 41.7 to 43.6°, whereas in the title compound, the phenyl is nearly perpendicular to the pyrazolinone ring, with a dihedral angle of 82.43 (8)°. It is interesting to note that the lone pairs of N3 and O1 might be in the right positions for the molecule to behave as a bidentate ligand.

Experimental

0.01 mol of 4-aminoantipyrine (4-ATP), 0.01 mol of thenoyltri-fluoroacetone (TTA) and 5 ml of acetic acid were mixed in heated anhydrous ethanol solution. After keeping the temperature at 333 K and stirring 30 min, 0.05 mol of Mn (CH₃COO)₂·4H₂O and 10 ml of N(CH₂CH₃)₃ were added and refluxed for 4 h at 373 K; this yielded yellow crude products. These were filtered off and washed with cooled anhydrous ethanol several times and dried in a vacuum desiccator over CaCl₂. Bright-yellow single crystals suitable for X-ray analysis were obtained by slowly cooling a warmed DMSO solution. Elemental analysis for C₁₉H₁₄F₃N₃O₃S, calculated: C 54.16, H 3.35, N 9.96%; found: C 54.06, H 3.34, N 9.91%.

Crystal data

C ₁₉ H ₁₄ F ₃ N ₃ O ₃ S	$D_x = 1.478 \text{ Mg m}^{-3}$
$M_r = 421.39$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2901 reflections
$a = 10.964 (3) \text{ \AA}$	$\theta = 1.7\text{--}25.1^\circ$
$b = 12.570 (3) \text{ \AA}$	$\mu = 0.23 \text{ mm}^{-1}$
$c = 13.840 (4) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\beta = 96.822 (5)^\circ$	Prism, yellow
$V = 1893.9 (9) \text{ \AA}^3$	$0.35 \times 0.30 \times 0.28 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART 1000 CCD diffractometer	$R_{\text{int}} = 0.025$
ω scans	$\theta_{\text{max}} = 25.0^\circ$
7715 measured reflections	$h = -13 \rightarrow 12$
3338 independent reflections	$k = -10 \rightarrow 14$
2467 reflections with $I > 2\sigma(I)$	$l = -13 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.117$
 $S = 1.02$
 3338 reflections
 293 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.7204P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

S1—C14	1.686 (3)	O3—C7	1.203 (2)
S1—C11	1.719 (2)	C1—C2	1.432 (3)
N1—C3	1.335 (3)	C2—C3	1.388 (3)
N1—N2	1.397 (2)	C3—C4	1.485 (3)
N1—C5	1.450 (3)	C7—C8	1.531 (3)
N2—C1	1.385 (3)	C7—C6	1.531 (3)
N2—C21	1.431 (3)	C8—C11	1.451 (3)
N3—C6	1.275 (3)	C6—C9	1.508 (3)
N3—C2	1.379 (3)	C11—C12	1.387 (3)
O1—C8	1.223 (3)	C12—C13	1.410 (3)
O2—C1	1.241 (2)	C13—C14	1.338 (4)
C14—S1—C11	91.81 (13)	C2—C3—C4	128.89 (19)
C3—N1—N2	109.00 (15)	O3—C7—C8	124.52 (19)
C3—N1—C5	129.76 (18)	O3—C7—C6	119.90 (19)
N2—N1—C5	120.48 (17)	C8—C7—C6	114.85 (17)
C1—N2—N1	109.16 (16)	O1—C8—C11	123.13 (19)
C1—N2—C21	127.14 (17)	O1—C8—C7	116.34 (19)
N1—N2—C21	122.72 (16)	C11—C8—C7	120.44 (18)
C6—N3—C2	126.21 (18)	N3—C6—C9	115.49 (19)
O2—C1—N2	123.70 (19)	N3—C6—C7	131.52 (18)
O2—C1—C2	131.45 (19)	C9—C6—C7	112.81 (17)
N2—C1—C2	104.85 (17)	C12—C11—C8	131.2 (2)
N3—C2—C3	121.99 (18)	C12—C11—S1	110.93 (16)
N3—C2—C1	129.66 (18)	C8—C11—S1	117.85 (16)
C3—C2—C1	108.35 (17)	C11—C12—C13	111.0 (2)
N1—C3—C2	108.57 (18)	C14—C13—C12	113.7 (2)
N1—C3—C4	122.52 (18)	C13—C14—S1	112.6 (2)
C3—N1—N2—C1	−2.9 (2)	C3—N1—N2—C21	−172.29 (18)
C5—N1—N2—C1	−173.88 (19)	C5—N1—N2—C21	16.7 (3)

Some rather high residual electron density close to the CF₃ moiety, and staggered with respect to the F atoms, appeared on a difference Fourier map. A disordered distribution of the F atoms was then considered using the available tools available in *SHELXL97* (SAME, SADI and FLAT). Introduction of this disorder slightly improved the refinement, leading to much lower residual electron density and to better R and $wR2$ values.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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