

1,5-Dimethyl-4-[[*(E)*-3-oxo-3-(2-thienyl)-1-(trifluoromethyl)-1-propenyl]amino]-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-oneMing Yu,<sup>a</sup> Jin-Ling Wang<sup>b\*</sup> and Fang-Ming Miao<sup>b</sup><sup>a</sup>Department of Scientific Technology, The Scientific and Technology University of Tianjin, Tianjin 300222, People's Republic of China, and <sup>b</sup>College of Chemical and Life Science, Tianjin Normal University, Tianjin 300074, People's Republic of ChinaCorrespondence e-mail:  
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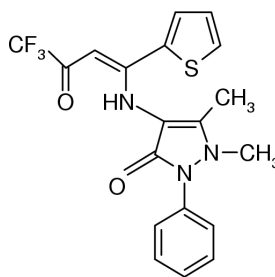
## Key indicators

Single-crystal X-ray study  
*T* = 297 K  
Mean  $\sigma(\text{C}-\text{C})$  = 0.005 Å  
Disorder in main residue  
*R* factor = 0.056  
*wR* factor = 0.172  
Data-to-parameter ratio = 11.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, C<sub>19</sub>H<sub>16</sub>F<sub>3</sub>N<sub>3</sub>O<sub>2</sub>S, the side-chain carbonyl group, the adjacent double bond and the amine N atom are essentially coplanar, with the largest deviation from the mean plane being 0.010 (2) Å. A strong intramolecular N—H···O hydrogen bond [N···O 2.702 (3) Å and N—H···O 139 (3)°] is observed, leading to an enamine tautomer in the solid state.

## Comment

Schiff base ligands derived from 4-aminoantipyrene, such as salicylidene-4-aminoantipyrene, 5-chlorosalicylidene-4-aminoantipyrene, 2,4-dihydroxybenzylidene-4-aminoantipyrene, 2-hydroxy-1-naphthylidene-4-aminoantipyrene and 2-hydroxyacetophenonylidene-4-aminoantipyrene, have been reported by McLendon & Martell (1976) and by Radhakrishnan & Joseph (1976). In order to study the coordination properties of Schiff base compounds, we have synthesized some of these compounds, and we report here the structure of the title compound, (I).

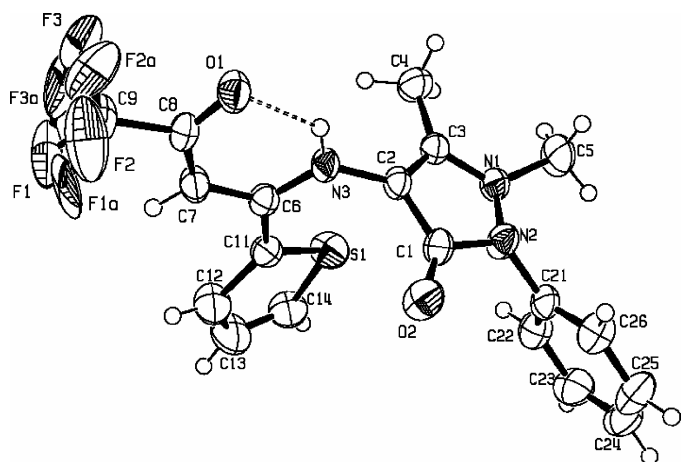


(I)

A view of the molecule of (I) is shown in Fig. 1. Atoms C6, C7, C8 and O1 of the thenoyltrifluoroacetone moiety and atom N3 of 4-aminoantipyrene are essentially coplanar, the largest deviation from the mean plane being 0.010 (2) Å for atom C6; the dihedral angle between this plane and the thienyl plane is 22.48 (3)°. The bond lengths within this part of the molecule [N3—C6 = 1.340 (4) Å, C6—C7 = 1.401 (4) Å, C7—C8 = 1.396 (4) Å and C8—O1 = 1.235 (4) Å] lie between the classical double- and single-bond lengths. These results clearly indicate that there is electron delocalization over this segment.

An intramolecular hydrogen bond is observed (Table 1), which indicates that the molecule exists as the enamine tautomer. This situation is completely different from that of 3-(2,3-dihydro-1,5-dimethyl-3-oxo-2-phenylpyrazol-4-ylimino)-4,4,4-trifluoro-1-(2-thienyl)butane-1,2-dione (Wang *et al.*, 2002), but similar to that of pyrazolinehydrazide (Liu *et al.*, 2001). The displacements of atoms C5 and C21 from the

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**Figure 1**  
View of the title compound, with 50% probability displacement ellipsoids.

pyrazolinone ring are 0.454 (7) and  $-0.479$  (5) Å, respectively, showing that the methyl group bonded to N1 and the phenyl group bonded to N2 are on opposite sides of the ring. Intermolecular contact distances of interest are:  $O2 \cdots S1^i = 3.040$  (4) Å,  $C4-H41 \cdots O1^i = 3.380$  (4) Å [angle of  $135.01$  (4)° at H41],  $C4-H41 \cdots F2^i = 2.930$  (4) Å [angle of  $138.96$  (4)° at H41],  $C5-H53 \cdots F2A^i = 3.418$  (5) Å [angle of  $163.71$  (5)° at H53],  $C4-H42 \cdots O1^{ii} = 3.380$  (4) Å [angle of  $135.01$  (5)° at H42], and  $C4-H43 \cdots F2A^{iii} = 3.366$  (5) Å [angle of  $116.32$  (5)° at H43] [symmetry codes: (i)  $1-x, -y, 1-z$ ; (ii)  $-1+x, y, z$ ; (iii)  $-x, -y, 1-z$ ].

The torsion angle  $C21-N2-N1-C5$  is  $51.2$  (4)°, close to the values of  $55.6$  (3) and  $55.7$  (3)° for the compounds 4-(salicylideneamino)-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (Chumakov *et al.*, 2000) and 4-[[*(1E)*-(2-hydroxyphenyl)methylidene]amino]-1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazol-3-one (Hökelek *et al.*, 2001). By contrast, conjugation leads to a small torsion angle of  $7.75$ ° in 4-(antipyridin-4-yliminomethyl)benzoic acid (Zhang *et al.*, 2002).

The mean plane through the side-chain carbonyl group, the adjacent double bond and the amino N atom is nearly perpendicular to the pyrazolinone ring, with a dihedral angle of  $84.10$  (6)°, close to the value of  $82.43$  (8)° reported by Wang *et al.* (2002). However, the dihedral angle between the pyrazolinone ring and the phenyl ring is  $115.26$  (5)°, quite different from the value of  $41.7$  (5)° in 4-(salicylideneamino)-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (Chumakov *et al.*, 2000). These results indicate that the compounds may have quite different coordination properties as ligands to metal ions.

## Experimental

Ethanol solutions of 0.1 mol of 4-aminoantipyridine and 0.1 mol of thenoyltrifluoroacetone were refluxed together for 4 h over a steam bath. The excess solvent was removed by evaporation and the concentrated solution was cooled in an ice bath, with stirring. The title compound separated out as a cream-colored powder, which was collected and dried in air (m.p. 434 K). It was recrystallized from

ethanol and dried in a vacuum over  $CaCl_2$ . The product is stable in air, and soluble in acetone and ethanol. Elemental analysis for  $C_{19}H_{16}F_3N_3O_2S$ , calculated: C 56.01, H 10.31, N 3.96%; found: C 55.87, H 10.16, N 3.94%. Bright-yellow single crystals suitable for X-ray analysis were obtained by slow cooling of a warmed solution in dimethyl sulfoxide.

## Crystal data

$C_{19}H_{16}F_3N_3O_2S$   
 $M_r = 407.42$   
Triclinic,  $P\bar{1}$   
 $a = 5.8063$  (10) Å  
 $b = 10.9254$  (17) Å  
 $c = 15.288$  (2) Å  
 $\alpha = 74.790$  (3)°  
 $\beta = 97.463$  (3)°  
 $\gamma = 94.731$  (4)°  
 $V = 926.7$  (2) Å<sup>3</sup>

$Z = 2$   
 $D_x = 1.460$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 3101 reflections  
 $\theta = 1.5$ – $25.1$ °  
 $\mu = 0.22$  mm<sup>-1</sup>  
 $T = 297$  (2) K  
Prism, yellow  
 $0.35 \times 0.30 \times 0.25$  mm

## Data collection

Bruker SMART 1000 CCD diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (SADABS; Bruker, 1999)  
 $T_{min} = 0.926$ ,  $T_{max} = 0.946$   
3860 measured reflections

3245 independent reflections  
2229 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.018$   
 $\theta_{max} = 25.0$ °  
 $h = -5 \rightarrow 6$   
 $k = -12 \rightarrow 8$   
 $l = -18 \rightarrow 17$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.057$   
 $wR(F^2) = 0.173$   
 $S = 1.04$   
3245 reflections  
286 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0983P)^2 + 0.1991P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.002$   
 $\Delta\rho_{max} = 0.33$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.45$  e Å<sup>-3</sup>  
Extinction correction: SHELXL97  
Extinction coefficient: 0.011 (4)

**Table 1**

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N3-H3 \cdots O1$	0.81 (4)	2.04 (4)	2.702 (3)	139 (3)

Some rather high residual electron densities close to the  $CF_3$  group and staggered with respect to the F atoms appeared in a difference Fourier map. A disordered distribution of the F atoms was refined with geometrical restraints; this led to much lower residual electron density and to lower  $R$  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: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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## References

- Bruker (1999). SADABS, SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.  
Chumakov, Yu. M., Antosyak, B. Ya., Mazus, M. D., Tsapkov, V. I. & Samus, N. N. (2000). *Zh. Strukt. Khim.* **41**, 1095–1997.  
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

- Hökelek, T., Isiklan, M. & Kilic, Z. (2001). *Acta Cryst.* **C57**, 117–119.
- Liu, L., Jia, D.-Z., Qiao, Y.-M. & Yu, K.-B. (2001). *Acta Chim. Sin.* **59**, 1495–1501.
- McLendon, G. & Martell, A. E. (1976). *Coord. Chem. Rev.* **19**, 1–39.
- Radhakrishnan, T. & Joseph, P. T. (1976). *J. Inorg. Nucl. Chem.* **38**, 2217–2219.
- Sheldrick, G. M. (1997). *SHELX97*. University of Göttingen, Germany.
- Wang, J.-L., Yu, M. & Miao, F.-M. (2002). *Acta Cryst.* **E58**, o385–o387.
- Zhang, Y., L Y., Tao, H. & Zhu, L. (2002). *Acta Cryst.* **E58**, o24–o26.