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(*Z*)-1,5-Dimethyl-4-[(5-methylthien-2-yl)-methyleneamino]-2-phenyl-1*H*-pyrazol-3(2*H*)-one

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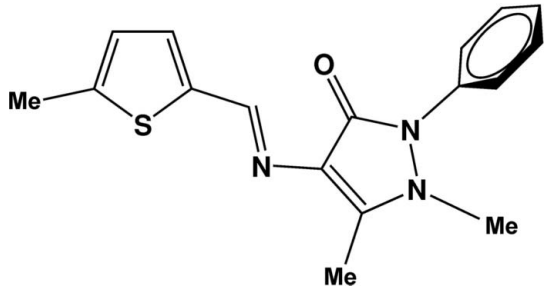
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.003 Å; R factor = 0.050; wR factor = 0.102; data-to-parameter ratio = 15.5.

In the title compound, $C_{17}H_{17}N_3OS$, the thiophene and pyrazolidinone rings are approximately coplanar and are linked by a C=N double bond as a conjugated system. The phenyl ring is not part of the conjugated system, and its mean plane forms a dihedral angle of 53.29 (9)° with the plane of the pyrazolidinone ring. The imine groups in neighbouring molecules form π–π interactions, with the centres of the C=N bonds separated by 3.590 (3) Å.

Related literature

For examples of applications of Schiff bases, see: Alemi & Shaabani (2000); Kim & Shin (1999). A Cu^{II} complex of a comparable Schiff base molecule has been reported (Yan *et al.*, 2006).



Experimental

Crystal data

$C_{17}H_{17}N_3OS$
M_r = 311.40
Triclinic, $P\overline{1}$
a = 7.042 (4) Å
b = 8.664 (5) Å
c = 13.988 (8) Å
α = 106.729 (7)°
β = 95.394 (7)°
γ = 99.568 (8)°
V = 796.8 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.21 mm^{-1}
T = 291 (2) K
0.30 × 0.24 × 0.22 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.94, T_{max} = 0.96
8047 measured reflections
3140 independent reflections
1998 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.102
S = 1.02
3140 reflections
202 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2191).

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Yan, G.-B., Yang, M.-H. & Zheng, Y.-F. (2006). *Acta Cryst.* E**62**, m3481–m3482.

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supplementary materials

Acta Cryst. (2007). E**63**, o3178 [**doi:10.1107/S1600536807027997**]

(*Z*)-1,5-Dimethyl-4-[(5-methylthien-2-yl)methyleneamino]-2-phenyl-1*H*-pyrazol-3(2*H*)-one

L.-G. Wang, Y.-F. Zheng and G.-B. Yan

Comment

Schiff bases have significant importance in chemistry, because they are potentially capable of forming stable complexes with metal ions (Yan *et al.*, 2006). Schiff bases that have solvent-dependent UV-vis spectra (solvatochromicity) can be suitable NLO (non-linear optically active) materials (Alemi & Shaabani, 2000). Some chiral Schiff bases are also applied in the enantioselective oxidation of methyl phenyl sulfide (Kim & Shin, 1999).

In the structure of the title compound (Fig. 1), all bond lengths and angles have normal values. The molecule contains one benzene ring, C1–C6 (denoted A) and two five-membered rings N2/N1/C7—C9 (denoted B) and C13—C16/S1 (denoted C). Rings B and C are nearly coplanar, the dihedral angle between them being 9.23 (13)°. The C12=N3 bond length of 1.268 (3) Å is typical for a C=N double bond; it links rings B and C to form a conjugated system. Ring A is not part of the conjugated system, the dihedral angle between rings A and B being 53.29 (9)°.

There are π-π interactions between neighbouring molecules through the imine functionalities: the *Cg*1—*Cg*1^{i} separation is 3.590 (3) Å, where *Cg* denotes the centroid of atoms C12 and N3 [symmetry code: (i) −*x*, −*y*, −*z*]. Through the π-π interaction, the neighbouring molecules form dimers (Fig. 2), which are connected through intermolecular C—H···O interactions (C14—H14···O^{ii}, symmetry code: (ii) 1 − *x*, −*y*, −*z*) into chains running along the *a* axis (Fig. 2).

Experimental

Under a nitrogen atmosphere, a mixture of 4-amino-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one (2.03 g, 10 mmol), Na_2SO_4 (3.0 g) and 5-methylthiophene-2-carboxaldehyde (1.26 g, 10 mmol) in absolute ethanol (30 ml) was refluxed for 6 h to yield a yellow precipitate. The product was collected by vacuum filtration and washed with ethanol. The crude solid was redissolved in CH_2Cl_2 (100 ml) and washed with water (2 × 10 ml) and brine (10 ml). After drying over Na_2SO_4, the solvent was removed under vacuum, and a yellow solid was isolated in 90% yield (2.80 g). Yellow single crystals suitable for X-ray analysis were grown from CH_2Cl_2 and absolute ethanol (4:1) by slow evaporation of the solvent at room temperature over a period of one week.

Refinement

All H atoms were positioned geometrically and refined using a riding model (including free rotation about the local threefold axes of the methyl groups), with C—H = 0.93–0.96 Å and with U_{iso}(H) = 1.2U_{eq}(C) (1.5U_{eq}(C) for methyl groups).

Figures

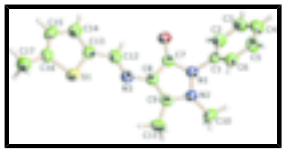

Fig. 1. The molecular structure of the title compound showing 30% probability displacement ellipsoids for non-H atoms.

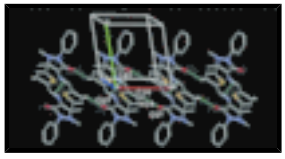

Fig. 2. View of the chains in the title compound, linked by π···π and C—H···O interactions. H atoms except for H14 have been omitted. Symmetry codes: (i) −*x*, −*y*, −*z*; (ii) 1 − *x*, −*y*, −*z*.

(*Z*)-1,5-Dimethyl-4-[(5-methylthien-2-yl)methyleneamino]-2-phenyl- 1*H*-pyrazol-3(2*H*)-one

Crystal data

$C_{17}H_{17}N_3OS$	$Z = 2$
$M_r = 311.40$	$F_{000} = 328$
Triclinic, $P\overline{1}$	$D_x = 1.298$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.042$ (4) Å	Cell parameters from 2812 reflections
$b = 8.664$ (5) Å	$\theta = 2.5$–27.8°
$c = 13.988$ (8) Å	$\mu = 0.21$ mm^{-1}
$\alpha = 106.729$ (7)°	$T = 291$ (2) K
$\beta = 95.394$ (7)°	Block, yellow
$\gamma = 99.568$ (8)°	0.30 × 0.24 × 0.22 mm
$V = 796.8$ (8) Å^3	

Data collection

Bruker SMART APEX CCD diffractometer	3140 independent reflections
Radiation source: sealed tube	1998 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.035$
$T = 291(2)$ K	$\theta_{max} = 26.0^\circ$
φ and ω scans	$\theta_{min} = 1.5^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$h = -8 \rightarrow 8$
$T_{min} = 0.94$, $T_{max} = 0.96$	$k = -10 \rightarrow 10$
8047 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.050$	H-atom parameters constrained
$wR(F^2) = 0.102$	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
3140 reflections	$\Delta\rho_{max} = 0.16$ e Å^{-3}
202 parameters	$\Delta\rho_{min} = -0.17$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Least-squares planes (*x*,*y*,*z* in crystal coordinates) and deviations from them (* indicates atom used to define plane)

2.9350 (0.0057) *x* + 7.0338 (0.0060) *y* − 6.6058 (0.0135) *z* = 1.5325 (0.0040)

* −0.0027 (0.0013) C13 * 0.0001 (0.0015) C14 * 0.0034 (0.0016) C15 * −0.0046 (0.0013) C16 * 0.0036 (0.0010) S1

Rms deviation of fitted atoms = 0.0033

3.0685 (0.0065) *x* + 6.5656 (0.0067) *y* − 8.4118 (0.0119) *z* = 1.5741 (0.0028)

Angle to previous plane (with approximate e.s.d.) = 9.23 (0.13)

* 0.0236 (0.0012) C7 * 0.0020 (0.0012) C8 * −0.0275 (0.0012) C9 * −0.0404 (0.0012) N1 * 0.0424 (0.0012) N2

Rms deviation of fitted atoms = 0.0308

− 5.4111 (0.0052) *x* + 0.4922 (0.0083) *y* + 9.7421 (0.0108) *z* = 1.5837 (0.0060)

Angle to previous plane (with approximate e.s.d.) = 53.29 (0.09)

* −0.0062 (0.0015) C1 * 0.0107 (0.0015) C2 * −0.0067 (0.0017) C3 * −0.0018 (0.0018) C4 * 0.0064 (0.0017) C5 * −0.0024 (0.0015) C6

Rms deviation of fitted atoms = 0.0064

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2382 (3)	0.5530 (2)	0.26628 (15)	0.0407 (5)
C2	0.3531 (3)	0.5054 (3)	0.33425 (16)	0.0492 (5)

H2	0.3351	0.3956	0.3321	0.059*
C3	0.4955 (3)	0.6234 (3)	0.40559 (18)	0.0573 (6)
H3	0.5758	0.5922	0.4502	0.069*
C4	0.5182 (4)	0.7880 (3)	0.4104 (2)	0.0657 (7)
H4	0.6127	0.8670	0.4587	0.079*
C5	0.4005 (4)	0.8342 (3)	0.34351 (19)	0.0603 (6)
H5	0.4154	0.9446	0.3474	0.072*
C6	0.2586 (3)	0.7164 (3)	0.26973 (17)	0.0489 (5)
H6	0.1799	0.7472	0.2242	0.059*
C7	0.1688 (3)	0.3090 (2)	0.11286 (15)	0.0415 (5)
C8	0.0216 (3)	0.2627 (2)	0.02558 (14)	0.0398 (4)
C9	−0.1188 (3)	0.3556 (2)	0.05033 (15)	0.0415 (4)
C10	−0.1957 (3)	0.5374 (3)	0.21270 (17)	0.0532 (6)
H10A	−0.2793	0.5868	0.1776	0.080*
H10B	−0.1199	0.6201	0.2712	0.080*
H10C	−0.2733	0.4539	0.2332	0.080*
C11	−0.3114 (3)	0.3438 (3)	−0.01048 (18)	0.0558 (6)
H11A	−0.4147	0.3204	0.0266	0.084*
H11B	−0.3280	0.2573	−0.0734	0.084*
H11C	−0.3145	0.4464	−0.0235	0.084*
C12	0.1536 (3)	0.0752 (3)	−0.08877 (16)	0.0481 (5)
H12	0.2465	0.0823	−0.0350	0.058*
C13	0.1674 (3)	−0.0296 (3)	−0.18876 (16)	0.0469 (5)
C14	0.3103 (3)	−0.1160 (3)	−0.21765 (18)	0.0556 (6)
H14	0.4160	−0.1185	−0.1733	0.067*
C15	0.2785 (3)	−0.2008 (3)	−0.32260 (18)	0.0552 (6)
H15	0.3629	−0.2643	−0.3538	0.066*
C16	0.1167 (3)	−0.1822 (3)	−0.37344 (17)	0.0498 (5)
C17	0.0376 (4)	−0.2539 (4)	−0.48488 (19)	0.0726 (7)
H17A	0.1350	−0.3005	−0.5205	0.109*
H17B	0.0040	−0.1686	−0.5102	0.109*
H17C	−0.0762	−0.3381	−0.4946	0.109*
N1	0.1036 (2)	0.4266 (2)	0.18842 (13)	0.0435 (4)
N2	−0.0651 (2)	0.4632 (2)	0.14565 (13)	0.0435 (4)
N3	0.0206 (2)	0.1574 (2)	−0.07154 (13)	0.0444 (4)
O1	0.3281 (2)	0.26705 (19)	0.12588 (11)	0.0546 (4)
S1	−0.00437 (8)	−0.05443 (8)	−0.29243 (4)	0.05310 (18)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0326 (10)	0.0420 (10)	0.0424 (11)	0.0097 (8)	0.0073 (8)	0.0036 (9)
C2	0.0442 (12)	0.0528 (12)	0.0512 (13)	0.0157 (10)	0.0017 (9)	0.0151 (10)
C3	0.0418 (13)	0.0715 (16)	0.0538 (14)	0.0164 (11)	−0.0056 (10)	0.0131 (12)
C4	0.0456 (14)	0.0673 (16)	0.0669 (16)	0.0049 (12)	−0.0048 (12)	0.0018 (13)
C5	0.0579 (15)	0.0437 (12)	0.0670 (16)	0.0014 (11)	0.0073 (12)	0.0036 (11)
C6	0.0489 (13)	0.0492 (12)	0.0477 (12)	0.0147 (10)	0.0074 (9)	0.0112 (10)
C7	0.0326 (10)	0.0420 (10)	0.0482 (12)	0.0076 (8)	0.0073 (8)	0.0110 (9)

C8	0.0337 (11)	0.0444 (10)	0.0391 (11)	0.0071 (8)	0.0058 (8)	0.0099 (9)
C9	0.0334 (10)	0.0479 (11)	0.0419 (11)	0.0053 (8)	0.0055 (8)	0.0136 (9)
C10	0.0388 (12)	0.0599 (13)	0.0589 (14)	0.0180 (10)	0.0129 (10)	0.0091 (11)
C11	0.0330 (12)	0.0783 (16)	0.0549 (14)	0.0099 (11)	0.0027 (9)	0.0208 (12)
C12	0.0434 (12)	0.0503 (12)	0.0460 (12)	0.0079 (10)	0.0044 (9)	0.0096 (10)
C13	0.0408 (11)	0.0466 (12)	0.0515 (13)	0.0115 (9)	0.0074 (9)	0.0105 (10)
C14	0.0510 (14)	0.0553 (13)	0.0582 (14)	0.0202 (11)	0.0026 (11)	0.0106 (11)
C15	0.0509 (14)	0.0566 (13)	0.0597 (14)	0.0245 (11)	0.0178 (11)	0.0100 (11)
C16	0.0474 (13)	0.0499 (12)	0.0475 (12)	0.0124 (10)	0.0074 (10)	0.0063 (10)
C17	0.0628 (16)	0.0858 (19)	0.0563 (15)	0.0200 (14)	0.0022 (12)	0.0013 (14)
N1	0.0323 (9)	0.0471 (9)	0.0450 (10)	0.0104 (7)	−0.0008 (7)	0.0054 (8)
N2	0.0301 (9)	0.0522 (10)	0.0459 (10)	0.0153 (7)	0.0045 (7)	0.0079 (8)
N3	0.0399 (10)	0.0456 (9)	0.0438 (10)	0.0065 (8)	0.0094 (7)	0.0081 (8)
O1	0.0381 (8)	0.0607 (9)	0.0583 (10)	0.0194 (7)	0.0027 (7)	0.0042 (8)
S1	0.0431 (3)	0.0625 (4)	0.0508 (3)	0.0231 (3)	0.0049 (2)	0.0068 (3)

Geometric parameters (Å, °)

C1—C6	1.385 (3)	C10—H10B	0.960
C1—C2	1.386 (3)	C10—H10C	0.960
C1—N1	1.435 (3)	C11—H11A	0.960
C2—C3	1.389 (3)	C11—H11B	0.960
C2—H2	0.930	C11—H11C	0.960
C3—C4	1.389 (4)	C12—N3	1.268 (3)
C3—H3	0.930	C12—C13	1.454 (3)
C4—C5	1.379 (4)	C12—H12	0.930
C4—H4	0.930	C13—C14	1.375 (3)
C5—C6	1.402 (3)	C13—S1	1.737 (2)
C5—H5	0.930	C14—C15	1.417 (3)
C6—H6	0.930	C14—H14	0.930
C7—O1	1.249 (2)	C15—C16	1.344 (3)
C7—N1	1.411 (3)	C15—H15	0.930
C7—C8	1.438 (3)	C16—C17	1.513 (3)
C8—C9	1.384 (3)	C16—S1	1.735 (2)
C8—N3	1.400 (3)	C17—H17A	0.960
C9—N2	1.365 (3)	C17—H17B	0.960
C9—C11	1.503 (3)	C17—H17C	0.960
C10—N2	1.466 (3)	N1—N2	1.404 (2)
C10—H10A	0.960		
C6—C1—C2	121.4 (2)	C9—C11—H11B	109.5
C6—C1—N1	120.60 (19)	H11A—C11—H11B	109.5
C2—C1—N1	117.92 (18)	C9—C11—H11C	109.5
C1—C2—C3	119.3 (2)	H11A—C11—H11C	109.5
C1—C2—H2	120.3	H11B—C11—H11C	109.5
C3—C2—H2	120.3	N3—C12—C13	123.0 (2)
C4—C3—C2	120.2 (2)	N3—C12—H12	118.5
C4—C3—H3	119.9	C13—C12—H12	118.5
C2—C3—H3	119.9	C14—C13—C12	128.2 (2)
C5—C4—C3	119.9 (2)	C14—C13—S1	110.38 (17)

C5—C4—H4	120.0	C12—C13—S1	121.38 (16)
C3—C4—H4	120.0	C13—C14—C15	112.4 (2)
C4—C5—C6	120.7 (2)	C13—C14—H14	123.8
C4—C5—H5	119.6	C15—C14—H14	123.8
C6—C5—H5	119.6	C16—C15—C14	114.6 (2)
C1—C6—C5	118.4 (2)	C16—C15—H15	122.7
C1—C6—H6	120.8	C14—C15—H15	122.7
C5—C6—H6	120.8	C15—C16—C17	129.1 (2)
O1—C7—N1	122.89 (19)	C15—C16—S1	110.47 (17)
O1—C7—C8	131.38 (19)	C17—C16—S1	120.48 (18)
N1—C7—C8	105.67 (17)	C16—C17—H17A	109.5
C9—C8—N3	123.41 (18)	C16—C17—H17B	109.5
C9—C8—C7	107.40 (17)	H17A—C17—H17B	109.5
N3—C8—C7	128.90 (18)	C16—C17—H17C	109.5
N2—C9—C8	110.14 (17)	H17A—C17—H17C	109.5
N2—C9—C11	121.05 (18)	H17B—C17—H17C	109.5
C8—C9—C11	128.74 (19)	N2—N1—C7	108.63 (16)
N2—C10—H10A	109.5	N2—N1—C1	119.75 (16)
N2—C10—H10B	109.5	C7—N1—C1	121.40 (17)
H10A—C10—H10B	109.5	C9—N2—N1	107.56 (15)
N2—C10—H10C	109.5	C9—N2—C10	126.39 (17)
H10A—C10—H10C	109.5	N1—N2—C10	118.71 (17)
H10B—C10—H10C	109.5	C12—N3—C8	120.05 (18)
C9—C11—H11A	109.5	C16—S1—C13	92.15 (11)

Fig. 1

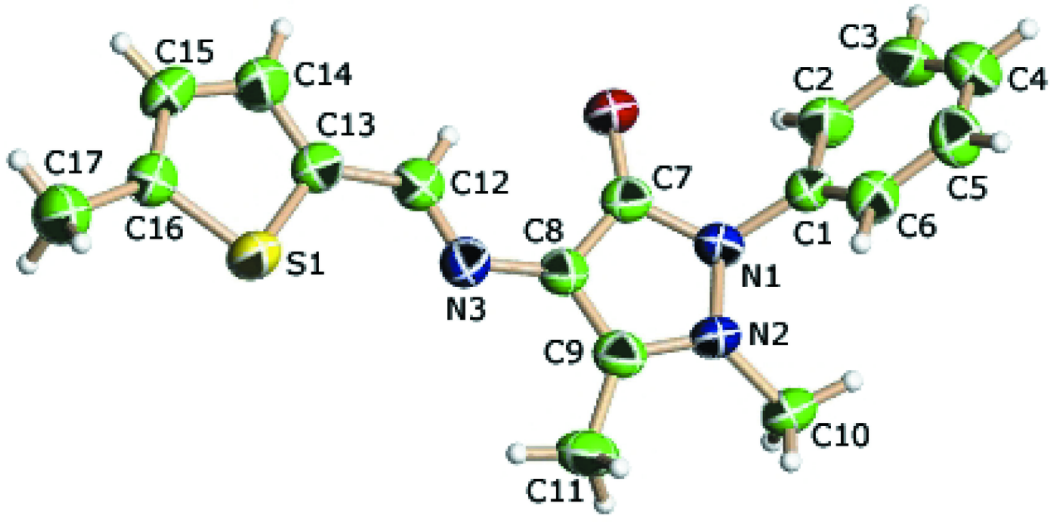
C15
C14
C13
C17
C16
S1
C12
N3
C8
C7
C3
C2
C4
C5
C6
C1
N1
N2
C9
C10
C11

Fig. 2