IUCrData

ISSN 2414-3146

3-(4-Chlorophenyl)-5-[4-(methylsulfanyl)phenyl]-1*H*-pyrazole

Ganesan Suresh and Sarangapani Muniraj*

Department of Chemistry, Ramakrishna Mission Vivekananda College, Chennai 600 004, India. *Correspondence e-mail: muniraj_sl@yahoo.com

Received 25 March 2016
Accepted 22 April 2016

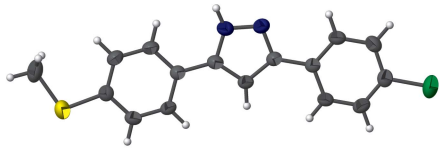
Edited by J. Simpson, University of Otago, New Zealand

Keywords: crystal structure; pyrazole; chalcone; isoniazid; conformations.

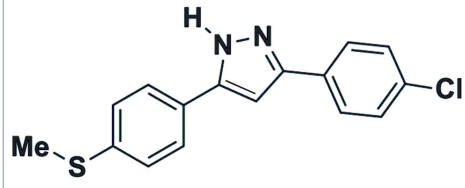
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{16}H_{13}ClN_2S$, the pyrazole ring is almost planar with an r.m.s. deviation of 0.0457 Å which forms dihedral angles of 2.875 (4) and 84.83 (7)° with the chloro-substituted benzene ring and the methylsulfanyl-substituted ring, respectively. In the crystal, N—H···N and C—H···Cl hydrogen bonds contribute to the formation of a three-dimensional network. In addition, several offset π–π stacking interactions are also present.

3D view



Chemical scheme



Structure description

Pyrazoles (Kamatchi *et al.*, 2012) exhibit a variety of pharmacological properties including antibacterial and anti-inflammatory activities (Sullivan *et al.*, 2006; Patel *et al.*, 2010). A pyrazole derivative also shows nucleosidase inhibitory activity against *Staphylococcus aureus* (Siu *et al.* 2008). In view of their importance, we have synthesized the title pyrazole derivative and its crystal structure is reported here.

The molecular structure of the title compound is shown in Fig. 1. The pyrazole ring (N1/N2/C7–C9) is almost planar with an r.m.s deviation of 0.0457 Å. This ring subtends a dihedral angle of 2.875 (4)° with the chloro-substituted benzene ring (C12–C17) while the C1–C6 benzene ring is almost perpendicular to the pyrazole ring with a dihedral angle 84.83 (7)°.

In the crystal, centrosymmetrically related N1—H1···N2 hydrogen bonds (Table 1) form inversion dimers with $R_2^2(6)$ ring motifs. Furthermore, as shown in Fig. 2, molecules are linked in a head-to-tail fashion by π–π stacking interactions with centroid–centroid distances $Cg1\cdots Cg1^{iii}$ = 3.538 (2) and $Cg2\cdots Cg3^{iii}$ = 3.8610 (18) Å [*Cg*1, *Cg*2 and *Cg*3 are the centroids of the N1/N2/C7–C9, C1–C6 and C12–C17 rings, respectively; symmetry code: (iii) $-x+2, -y+1, -z+1$]. In addition to the N1—H1···N1 hydrogen bonds, there are also weak but effective C14—H14···Cl1 hydrogen bonds that also contribute to the formation of a three-dimensional network (Fig. 3).

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14···Cl1^{i}	0.93	2.94	3.771 (3)	149
N1—H1···N2^{ii}	0.89 (1)	2.05 (3)	2.875 (4)	153 (5)
N1—H1···N1^{ii}	0.89 (1)	2.61 (5)	3.170 (5)	122 (4)

Symmetry codes: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+2, -y, -z+1$.

Synthesis and crystallization

A mixture of substituted chalcone (0.01 mol) and isoniazid (0.01 mol) kept in 25 ml round bottom flask then heated for 160°C for 1 h. The reaction mixture was cooled and purified by column chromatography. The purified compound was recrystallized from hexane/ethylacetate (3:6) by the slow evaporation method.

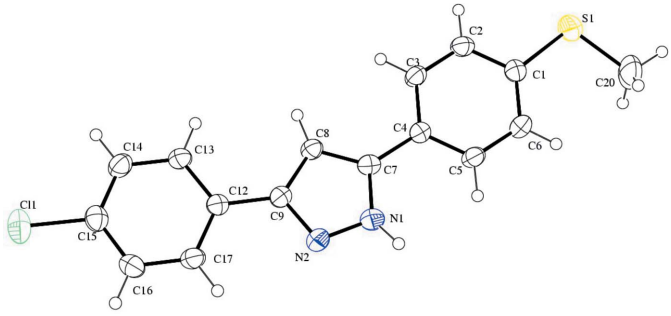


Figure 1
The molecular structure of the title compound, showing 30% probability displacement ellipsoids.

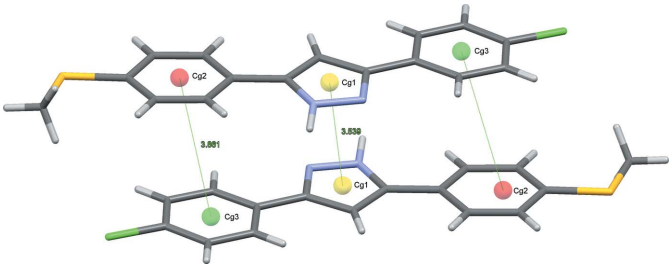


Figure 2
π–π stacking interactions shown as dotted green lines with ring centroids displayed as coloured spheres. For centroid labels and symmetry operations see text.

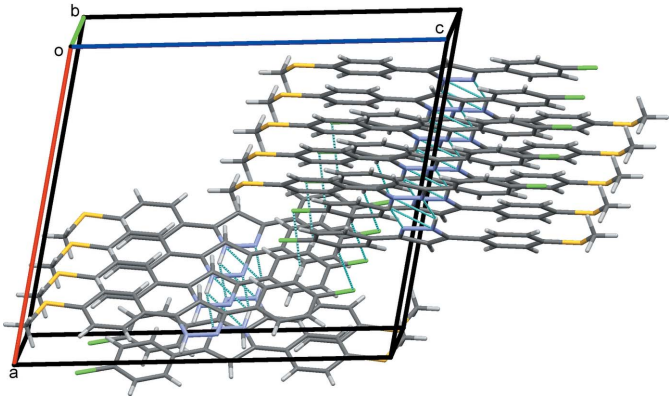


Figure 3
The crystal packing of the title compound, viewed along the *a* axis.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{13}ClN_2S$
M_r	300.79
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, b, c (Å)	15.0422 (12), 5.6323 (5), 17.1019 (15)
β (°)	102.480 (2)
V (Å^3)	1414.7 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.41
Crystal size (mm)	0.25 × 0.25 × 0.15
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.905, 0.941
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20565, 2921, 2210
R_{int}	0.033
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.628
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.058, 0.130, 1.12
No. of reflections	2921
No. of parameters	186
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.40, −0.28

Computer programs: *APEX2*, *SAINT* and *XPREP* (Bruker, 2012), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

The authors are very grateful to staff members of the Department of Chemistry, Ramakrishna Mission Vivekananda College, Mylapore, and Chennai. They also thank the Sophisticated Analytical Instrumentation Facility (SAIF), IIT Madras, for analytical support. GS thanks the CSIR for an SRF grant [No. 08/508 (0001)/2013-EMR-I].

References

Bruker (2012). *APEX2*, *SAINT*, *XPREP* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Kamatchi, P., Jagadeesan, G., Pramesh, M., Perumal, P. T. & Aravindhan, S. (2012). *Acta Cryst.* E**68**, o552.
Patel, C. K., Rami, C. S., Panigrahi, B. & Patel, C. N. (2010). *J. Chem. Pharm. Res.* **2**, 73–78.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Siu, K. K. W., Lee, J. E., Smith, G. D., Horvatin-Mrakovcic, C. & Howell, P. L. (2008). *Acta Cryst.* F**64**, 343–350.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Sullivan, T. J., Truglio, J. J., Boyne, M. E., Novichenok, P., Zhang, X., Stratton, C. F., Li, H., Kaur, T., Amin, A., Johnson, F., Slayden, R. A., Kisker, C. & Tonge, P. J. (2006). *Chem. Biol.* **1**, 43–53.

full crystallographic data

IUCrData (2016). **1**, x160679 [doi:10.1107/S2414314616006799]

3-(4-Chlorophenyl)-5-[4-(methylsulfanyl)phenyl]-1*H*-pyrazole

Ganesan Suresh and Sarangapani Muniraj

3-(4-Chlorophenyl)-5-[4-(methylsulfanyl)phenyl]-1*H*-pyrazole

Crystal data

$C_{16}H_{13}ClN_2S$
M_r = 300.79
Monoclinic, $P2_1/n$
a = 15.0422 (12) Å
b = 5.6323 (5) Å
c = 17.1019 (15) Å
β = 102.480 (2)°
V = 1414.7 (2) Å^3
Z = 4
$F(000)$ = 624
D_x = 1.412 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8419 reflections
θ = 2.8–30.1°
μ = 0.41 mm^{-1}
T = 296 K
Block, pale-yellow
0.25 × 0.25 × 0.15 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2012)
T_{min} = 0.905, T_{max} = 0.941
20565 measured reflections
2921 independent reflections
2210 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 26.5°, θ_{min} = 2.0°
h = −18→18
k = −7→7
l = −21→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.130
S = 1.12
2921 reflections
186 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0259P)^2 + 2.3699P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Special details

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

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.86308 (19)	0.4265 (5)	0.14839 (17)	0.0358 (7)
C2	0.8308 (2)	0.6014 (6)	0.19216 (18)	0.0391 (7)
H2	0.8035	0.7364	0.1662	0.047*
C3	0.83852 (19)	0.5781 (5)	0.27367 (18)	0.0367 (7)
H3	0.8165	0.6974	0.3019	0.044*
C4	0.87890 (18)	0.3781 (5)	0.31398 (16)	0.0311 (6)
C5	0.9089 (2)	0.2024 (5)	0.26987 (18)	0.0389 (7)
H5	0.9345	0.0652	0.2956	0.047*
C6	0.9017 (2)	0.2257 (6)	0.18792 (18)	0.0417 (7)
H6	0.9230	0.1054	0.1595	0.050*
C7	0.88814 (18)	0.3566 (5)	0.40110 (17)	0.0332 (6)
C8	0.85749 (19)	0.5015 (5)	0.45494 (17)	0.0352 (6)
H8	0.8232	0.6395	0.4433	0.042*
C9	0.88822 (18)	0.3997 (5)	0.53004 (17)	0.0327 (6)
C12	0.87854 (18)	0.4797 (5)	0.60968 (16)	0.0321 (6)
C13	0.8377 (2)	0.6961 (5)	0.61894 (18)	0.0388 (7)
H13	0.8159	0.7904	0.5743	0.047*
C14	0.8292 (2)	0.7730 (6)	0.69368 (19)	0.0438 (8)
H14	0.8008	0.9170	0.6990	0.053*
C15	0.8623 (2)	0.6378 (6)	0.75962 (18)	0.0404 (7)
C16	0.9032 (2)	0.4230 (6)	0.75310 (19)	0.0450 (8)
H16	0.9255	0.3313	0.7983	0.054*
C17	0.9107 (2)	0.3454 (6)	0.67792 (18)	0.0417 (7)
H17	0.9379	0.1995	0.6731	0.050*
C20	0.8972 (3)	0.2228 (8)	0.0090 (2)	0.0764 (13)
H20A	0.9598	0.2052	0.0360	0.115*
H20B	0.8934	0.2383	−0.0475	0.115*
H20C	0.8634	0.0857	0.0190	0.115*
N1	0.93368 (18)	0.1756 (5)	0.44264 (16)	0.0426 (6)
N2	0.93436 (17)	0.2002 (5)	0.52172 (15)	0.0422 (6)
S1	0.85099 (7)	0.48113 (18)	0.04526 (5)	0.0577 (3)
Cl1	0.85408 (7)	0.74040 (19)	0.85373 (5)	0.0638 (3)
H1	0.974 (3)	0.066 (8)	0.437 (3)	0.17 (3)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0343 (15)	0.0373 (17)	0.0360 (16)	−0.0041 (13)	0.0079 (12)	−0.0013 (13)
C2	0.0395 (17)	0.0340 (16)	0.0435 (17)	0.0051 (14)	0.0081 (13)	0.0062 (14)
C3	0.0380 (16)	0.0308 (15)	0.0421 (17)	0.0060 (13)	0.0104 (13)	−0.0015 (13)

C4	0.0261 (13)	0.0312 (15)	0.0358 (15)	−0.0011 (12)	0.0065 (11)	−0.0002 (12)
C5	0.0428 (17)	0.0288 (15)	0.0441 (17)	0.0051 (13)	0.0077 (13)	0.0006 (13)
C6	0.0477 (18)	0.0334 (16)	0.0453 (18)	0.0039 (14)	0.0130 (14)	−0.0058 (14)
C7	0.0279 (14)	0.0312 (15)	0.0400 (16)	−0.0002 (12)	0.0062 (12)	0.0033 (13)
C8	0.0346 (15)	0.0316 (15)	0.0392 (15)	0.0053 (13)	0.0079 (12)	0.0020 (13)
C9	0.0298 (14)	0.0305 (15)	0.0388 (16)	−0.0009 (12)	0.0094 (12)	−0.0005 (12)
C12	0.0280 (14)	0.0321 (15)	0.0371 (15)	−0.0008 (12)	0.0090 (12)	0.0023 (12)
C13	0.0415 (17)	0.0351 (16)	0.0405 (16)	0.0090 (14)	0.0101 (13)	0.0057 (13)
C14	0.0461 (18)	0.0363 (17)	0.0514 (19)	0.0069 (15)	0.0162 (15)	−0.0022 (15)
C15	0.0390 (17)	0.0445 (18)	0.0396 (16)	−0.0067 (15)	0.0130 (13)	−0.0031 (14)
C16	0.0510 (19)	0.0459 (19)	0.0379 (17)	0.0032 (16)	0.0092 (14)	0.0088 (14)
C17	0.0460 (18)	0.0335 (17)	0.0472 (18)	0.0081 (14)	0.0138 (14)	0.0062 (14)
C20	0.099 (3)	0.087 (3)	0.045 (2)	0.019 (3)	0.021 (2)	−0.013 (2)
N1	0.0458 (16)	0.0394 (15)	0.0428 (15)	0.0111 (13)	0.0097 (12)	0.0059 (12)
N2	0.0468 (15)	0.0370 (14)	0.0452 (15)	0.0090 (12)	0.0154 (12)	0.0016 (12)
S1	0.0807 (7)	0.0554 (6)	0.0372 (5)	0.0033 (5)	0.0128 (4)	0.0001 (4)
Cl1	0.0752 (6)	0.0743 (7)	0.0446 (5)	−0.0040 (5)	0.0188 (4)	−0.0161 (5)

Geometric parameters (Å, º)

C1—C6	1.380 (4)	C12—C17	1.387 (4)
C1—C2	1.387 (4)	C12—C13	1.389 (4)
C1—S1	1.761 (3)	C13—C14	1.382 (4)
C2—C3	1.380 (4)	C13—H13	0.9300
C2—H2	0.9300	C14—C15	1.363 (4)
C3—C4	1.390 (4)	C14—H14	0.9300
C3—H3	0.9300	C15—C16	1.372 (5)
C4—C5	1.378 (4)	C15—Cl1	1.740 (3)
C4—C7	1.471 (4)	C16—C17	1.385 (4)
C5—C6	1.388 (4)	C16—H16	0.9300
C5—H5	0.9300	C17—H17	0.9300
C6—H6	0.9300	C20—S1	1.781 (4)
C7—N1	1.343 (4)	C20—H20A	0.9600
C7—C8	1.382 (4)	C20—H20B	0.9600
C8—C9	1.391 (4)	C20—H20C	0.9600
C8—H8	0.9300	N1—N2	1.357 (4)
C9—N2	1.344 (4)	N1—H1	0.891 (10)
C9—C12	1.471 (4)		
C6—C1—C2	118.5 (3)	C17—C12—C9	121.7 (3)
C6—C1—S1	125.1 (2)	C13—C12—C9	120.6 (3)
C2—C1—S1	116.4 (2)	C14—C13—C12	120.8 (3)
C3—C2—C1	121.0 (3)	C14—C13—H13	119.6
C3—C2—H2	119.5	C12—C13—H13	119.6
C1—C2—H2	119.5	C15—C14—C13	120.0 (3)
C2—C3—C4	120.7 (3)	C15—C14—H14	120.0
C2—C3—H3	119.6	C13—C14—H14	120.0
C4—C3—H3	119.6	C14—C15—C16	121.1 (3)

C5—C4—C3	118.0 (3)	C14—C15—Cl1	119.5 (3)
C5—C4—C7	121.6 (3)	C16—C15—Cl1	119.4 (2)
C3—C4—C7	120.3 (3)	C15—C16—C17	118.8 (3)
C4—C5—C6	121.4 (3)	C15—C16—H16	120.6
C4—C5—H5	119.3	C17—C16—H16	120.6
C6—C5—H5	119.3	C16—C17—C12	121.7 (3)
C1—C6—C5	120.3 (3)	C16—C17—H17	119.2
C1—C6—H6	119.8	C12—C17—H17	119.2
C5—C6—H6	119.8	S1—C20—H20A	109.5
N1—C7—C8	107.5 (3)	S1—C20—H20B	109.5
N1—C7—C4	121.6 (3)	H20A—C20—H20B	109.5
C8—C7—C4	130.8 (3)	S1—C20—H20C	109.5
C7—C8—C9	106.2 (3)	H20A—C20—H20C	109.5
C7—C8—H8	126.9	H20B—C20—H20C	109.5
C9—C8—H8	126.9	C7—N1—N2	110.0 (3)
N2—C9—C8	108.8 (3)	C7—N1—H1	139 (4)
N2—C9—C12	120.7 (3)	N2—N1—H1	109 (4)
C8—C9—C12	130.4 (3)	C9—N2—N1	107.3 (2)
C17—C12—C13	117.7 (3)	C1—S1—C20	104.04 (17)
C6—C1—C2—C3	1.2 (4)	N2—C9—C12—C13	174.4 (3)
S1—C1—C2—C3	−178.8 (2)	C8—C9—C12—C13	−4.2 (5)
C1—C2—C3—C4	−0.1 (5)	C17—C12—C13—C14	−0.4 (4)
C2—C3—C4—C5	−1.5 (4)	C9—C12—C13—C14	−179.4 (3)
C2—C3—C4—C7	179.0 (3)	C12—C13—C14—C15	1.1 (5)
C3—C4—C5—C6	1.8 (4)	C13—C14—C15—C16	−1.0 (5)
C7—C4—C5—C6	−178.7 (3)	C13—C14—C15—Cl1	178.2 (2)
C2—C1—C6—C5	−0.9 (4)	C14—C15—C16—C17	0.3 (5)
S1—C1—C6—C5	179.1 (2)	Cl1—C15—C16—C17	−178.9 (2)
C4—C5—C6—C1	−0.7 (5)	C15—C16—C17—C12	0.4 (5)
C5—C4—C7—N1	6.3 (4)	C13—C12—C17—C16	−0.4 (4)
C3—C4—C7—N1	−174.2 (3)	C9—C12—C17—C16	178.7 (3)
C5—C4—C7—C8	−174.9 (3)	C8—C7—N1—N2	−0.7 (3)
C3—C4—C7—C8	4.6 (5)	C4—C7—N1—N2	178.4 (2)
N1—C7—C8—C9	0.9 (3)	C8—C9—N2—N1	0.4 (3)
C4—C7—C8—C9	−178.0 (3)	C12—C9—N2—N1	−178.5 (2)
C7—C8—C9—N2	−0.8 (3)	C7—N1—N2—C9	0.2 (3)
C7—C8—C9—C12	178.0 (3)	C6—C1—S1—C20	0.9 (3)
N2—C9—C12—C17	−4.6 (4)	C2—C1—S1—C20	−179.1 (3)
C8—C9—C12—C17	176.8 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···Cl1^{i}	0.93	2.94	3.771 (3)	149

N1—H1···N2^{ii}	0.89 (1)	2.05 (3)	2.875 (4)	153 (5)
N1—H1···N1^{ii}	0.89 (1)	2.61 (5)	3.170 (5)	122 (4)

Symmetry codes: (i) $-x+3/2, y+1/2, -z+3/2$; (ii) $-x+2, -y, -z+1$.