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1,3-Dimethyl-4-phenylsulfanyl-1H-pyrazol-5-ol

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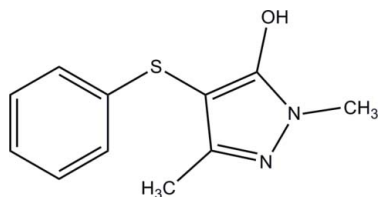
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.039; wR factor = 0.104; data-to-parameter ratio = 21.3.

In the title compound, $\text{C}_{11}\text{H}_{12}\text{N}_2\text{OS}$, the pyrazole ring makes a dihedral angle of $85.40(8)^\circ$ with the phenyl ring. In the crystal, intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds link molecules into a two-dimensional network parallel to the bc plane.

Related literature

For pyrazole derivatives and their microbial activity, see: Ragavan *et al.* (2009, 2010). For related structures, see: Shahani *et al.* (2009, 2010*a,b,c*). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

 $\text{C}_{11}\text{H}_{12}\text{N}_2\text{OS}$ $M_r = 220.30$ Orthorhombic, $Pbca$ $a = 10.9479(2)$ Å $b = 11.3470(3)$ Å $c = 17.7392(4)$ Å $V = 2203.67(9)$ Å³ $Z = 8$ Mo $K\alpha$ radiation $\mu = 0.27$ mm⁻¹ $T = 100$ K $0.33 \times 0.13 \times 0.11$ mm

Data collection

Bruker SMART APEXII CCD
area-detector diffractometer
Absorption correction: multi-scan
(*SADABS*; Bruker, 2009)
 $T_{\min} = 0.917$, $T_{\max} = 0.971$

12209 measured reflections
3027 independent reflections
2406 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.039$ $wR(F^2) = 0.104$ $S = 1.04$

3027 reflections

142 parameters

H atoms treated by a mixture of
independent and constrained
refinement

 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|----------|-------------|-------------|---------------|
| $\text{N1}-\text{H1N1}\cdots\text{O1}^{\text{i}}$ | 0.94 (2) | 1.71 (2) | 2.6446 (16) | 173 (2) |
| $\text{C3}-\text{H3A}\cdots\text{O1}^{\text{ii}}$ | 0.93 | 2.53 | 3.2549 (19) | 135 |

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2676).

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supplementary materials

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1,3-Dimethyl-4-phenylsulfanyl-1*H*-pyrazol-5-ol

T. Shahani, H.-K. Fun, R. V. Ragavan, V. Vijayakumar and S. Sarveswari

Comment

Antibacterial and antifungal activities of the azoles are most widely studied and some of them are in clinical practice as anti-microbial agents. However, the azole-resistant strain had led to the development of new antimicrobial compounds. In particular pyrazole derivatives are extensively studied and used as antimicrobial agents. Pyrazole is an important class of heterocyclic compounds and many pyrazole derivatives are reported to have the broad spectrum of biological properties, such as anti-inflammatory, antifungal, herbicidal, anti-tumour, cytotoxic, molecular modelling, and antiviral activities. Pyrazole derivatives also act as antiangiogenic agents, A3 adenosine receptor antagonists, neuropeptide YY5 receptor antagonists, kinase inhibitor for treatment of type 2 diabetes, hyperlipidemia, obesity, and thrombopiotinmimetics. Recently urea derivatives of pyrazoles have been reported as potent inhibitors of p38 kinase. Since the high electronegativity of halogens (particularly chlorine and fluorine) in the aromatic part of the drug molecules play an important role in enhancing their biological activity, we are interested to have 4-fluoro or 4-chloro substitution in the aryls of 1,5-diaryl pyrazoles. As part of our on-going research aiming the synthesis of new antimicrobial compounds, we have reported the synthesis of novel pyrazole derivatives and their microbial activities (Ragavan *et al.*, 2009, 2010). The structure of the title compound is presented here.

In the title compound, (Fig. 1), the 1*H*-pyrazol ring (C7–C9/N1/N2) [maximum deviation of 0.00117 (14) Å] makes a dihedral angle of 85.40 (8)° with the phenyl ring (C1–C6). The bond lengths (Allen *et al.*, 1987) and angles are within normal ranges and comparable to those closely related structures (Shahani *et al.*, 2009, 2010*a,b,c*).

In the crystal packing (Fig. 2), pairs of intermolecular N1—H1N1···O1 and C3—H3A···O1 hydrogen bonds (Table 1) link the molecules into two-dimensional networks parallel to the *bc* plane.

Experimental

The compound has been synthesized using the method available in the literature (Ragavan *et al.*, 2009) and recrystallized using the ethanol-chloroform 1:1 mixture (yield 60%, *m.p.* 444 K).

Refinement

The H atoms bound to C atoms were positioned geometrically (C—H = 0.93–0.96 Å) with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C})$. The H atoms attached to the N atom was located from the difference map and refined freely, [N—H = 0.94 (2) Å].

Figures

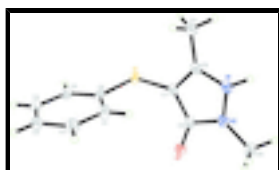


Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom numbering scheme.

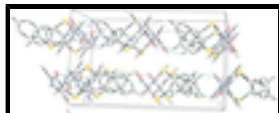


Fig. 2. The crystal structure of the title compound viewed approximately along the *b* axis. Intermolecular interactions are shown in dashed lines. Hydrogen bond not involved in intermolecular interactions are omitted for clarity.

1,3-Dimethyl-4-phenylsulfanyl-1*H*-pyrazol-5-ol

Crystal data

| | |
|---------------------------------|---|
| $C_{11}H_{12}N_2OS$ | $F(000) = 928$ |
| $M_r = 220.30$ | $D_x = 1.328 \text{ Mg m}^{-3}$ |
| Orthorhombic, <i>Pbca</i> | Mo <i>K</i> α radiation, $\lambda = 0.71073 \text{ \AA}$ |
| Hall symbol: -P 2ac 2ab | Cell parameters from 2873 reflections |
| $a = 10.9479 (2) \text{ \AA}$ | $\theta = 2.8\text{--}29.1^\circ$ |
| $b = 11.3470 (3) \text{ \AA}$ | $\mu = 0.27 \text{ mm}^{-1}$ |
| $c = 17.7392 (4) \text{ \AA}$ | $T = 100 \text{ K}$ |
| $V = 2203.67 (9) \text{ \AA}^3$ | Block, colourless |
| $Z = 8$ | $0.33 \times 0.13 \times 0.11 \text{ mm}$ |

Data collection

| | |
|---|--|
| Bruker SMART APEXII CCD area-detector diffractometer | 3027 independent reflections |
| Radiation source: fine-focus sealed tube graphite | 2406 reflections with $I > 2\sigma(I)$ |
| φ and ω scans | $R_{\text{int}} = 0.041$ |
| Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2009) | $\theta_{\text{max}} = 29.4^\circ$, $\theta_{\text{min}} = 2.3^\circ$ |
| $T_{\text{min}} = 0.917$, $T_{\text{max}} = 0.971$ | $h = -11 \rightarrow 15$ |
| 12209 measured reflections | $k = -15 \rightarrow 15$ |
| | $l = -16 \rightarrow 24$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.039$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.104$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.04$ | $w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.8061P]$ |
| 3027 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 142 parameters | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 0 restraints | $\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$ |
| | $\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$ |

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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.

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|---------------|----------------------------------|
| S1 | 0.09449 (3) | 0.31932 (3) | 0.09298 (2) | 0.01802 (11) |
| O1 | 0.32686 (10) | 0.34450 (8) | -0.02532 (6) | 0.0207 (2) |
| N1 | 0.20240 (12) | 0.61926 (10) | 0.00845 (8) | 0.0202 (3) |
| N2 | 0.28173 (12) | 0.54374 (10) | -0.02791 (7) | 0.0192 (3) |
| C1 | 0.28747 (15) | 0.36136 (13) | 0.19278 (9) | 0.0225 (3) |
| H1A | 0.3057 | 0.4285 | 0.1649 | 0.027* |
| C2 | 0.35663 (15) | 0.33304 (13) | 0.25590 (9) | 0.0254 (3) |
| H2A | 0.4211 | 0.3816 | 0.2700 | 0.031* |
| C3 | 0.33066 (15) | 0.23327 (14) | 0.29808 (9) | 0.0236 (3) |
| H3A | 0.3766 | 0.2154 | 0.3407 | 0.028* |
| C4 | 0.23531 (15) | 0.16043 (13) | 0.27606 (9) | 0.0243 (3) |
| H4A | 0.2180 | 0.0929 | 0.3037 | 0.029* |
| C5 | 0.16551 (14) | 0.18758 (13) | 0.21304 (9) | 0.0212 (3) |
| H5A | 0.1019 | 0.1382 | 0.1986 | 0.025* |
| C6 | 0.19092 (13) | 0.28904 (12) | 0.17148 (8) | 0.0173 (3) |
| C7 | 0.16428 (13) | 0.43840 (11) | 0.04922 (8) | 0.0166 (3) |
| C8 | 0.26321 (13) | 0.43076 (11) | -0.00304 (8) | 0.0164 (3) |
| C9 | 0.13144 (14) | 0.55679 (12) | 0.05474 (8) | 0.0178 (3) |
| C10 | 0.38173 (15) | 0.58669 (13) | -0.07387 (10) | 0.0239 (3) |
| H10A | 0.4171 | 0.5222 | -0.1013 | 0.036* |
| H10B | 0.4427 | 0.6217 | -0.0420 | 0.036* |
| H10C | 0.3517 | 0.6446 | -0.1087 | 0.036* |
| C11 | 0.03683 (15) | 0.61354 (14) | 0.10271 (9) | 0.0248 (3) |
| H11A | 0.0198 | 0.6912 | 0.0839 | 0.037* |
| H11B | 0.0661 | 0.6189 | 0.1536 | 0.037* |
| H11C | -0.0365 | 0.5672 | 0.1016 | 0.037* |
| H1N1 | 0.1983 (19) | 0.700 (2) | -0.0036 (13) | 0.047 (6)* |

supplementary materials

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|------------|---------------|---------------|--------------|
| S1 | 0.01876 (19) | 0.01847 (18) | 0.0168 (2) | -0.00372 (13) | -0.00109 (13) | 0.00267 (13) |
| O1 | 0.0267 (6) | 0.0139 (4) | 0.0215 (6) | 0.0008 (4) | 0.0046 (4) | 0.0000 (4) |
| N1 | 0.0264 (7) | 0.0129 (5) | 0.0212 (7) | 0.0017 (5) | -0.0005 (5) | -0.0006 (5) |
| N2 | 0.0240 (6) | 0.0131 (5) | 0.0206 (7) | -0.0002 (5) | 0.0034 (5) | 0.0007 (5) |
| C1 | 0.0273 (8) | 0.0198 (7) | 0.0204 (8) | -0.0046 (6) | -0.0027 (6) | 0.0034 (6) |
| C2 | 0.0285 (8) | 0.0257 (7) | 0.0221 (9) | -0.0037 (6) | -0.0065 (7) | -0.0002 (6) |
| C3 | 0.0255 (8) | 0.0298 (8) | 0.0155 (8) | 0.0053 (6) | -0.0012 (6) | 0.0006 (6) |
| C4 | 0.0247 (8) | 0.0260 (7) | 0.0222 (8) | 0.0015 (6) | 0.0032 (6) | 0.0082 (6) |
| C5 | 0.0197 (7) | 0.0213 (7) | 0.0225 (8) | -0.0015 (6) | 0.0013 (6) | 0.0043 (6) |
| C6 | 0.0196 (7) | 0.0188 (6) | 0.0134 (7) | 0.0007 (5) | 0.0019 (5) | 0.0003 (5) |
| C7 | 0.0193 (7) | 0.0148 (6) | 0.0156 (7) | -0.0014 (5) | -0.0003 (5) | 0.0005 (5) |
| C8 | 0.0224 (7) | 0.0127 (6) | 0.0141 (7) | -0.0017 (5) | -0.0018 (6) | 0.0001 (5) |
| C9 | 0.0207 (7) | 0.0179 (6) | 0.0149 (7) | 0.0009 (5) | -0.0035 (6) | -0.0002 (5) |
| C10 | 0.0283 (8) | 0.0184 (7) | 0.0250 (8) | -0.0043 (6) | 0.0050 (7) | 0.0032 (6) |
| C11 | 0.0248 (8) | 0.0250 (7) | 0.0245 (9) | 0.0071 (6) | -0.0008 (6) | -0.0021 (6) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|------------|-------------|-------------|-------------|
| S1—C7 | 1.7356 (14) | C3—H3A | 0.9300 |
| S1—C6 | 1.7809 (15) | C4—C5 | 1.389 (2) |
| O1—C8 | 1.2648 (17) | C4—H4A | 0.9300 |
| N1—C9 | 1.3343 (19) | C5—C6 | 1.395 (2) |
| N1—N2 | 1.3801 (17) | C5—H5A | 0.9300 |
| N1—H1N1 | 0.94 (2) | C7—C9 | 1.3942 (19) |
| N2—C8 | 1.3708 (17) | C7—C8 | 1.428 (2) |
| N2—C10 | 1.4494 (19) | C9—C11 | 1.487 (2) |
| C1—C2 | 1.389 (2) | C10—H10A | 0.9600 |
| C1—C6 | 1.391 (2) | C10—H10B | 0.9600 |
| C1—H1A | 0.9300 | C10—H10C | 0.9600 |
| C2—C3 | 1.387 (2) | C11—H11A | 0.9600 |
| C2—H2A | 0.9300 | C11—H11B | 0.9600 |
| C3—C4 | 1.388 (2) | C11—H11C | 0.9600 |
| C7—S1—C6 | 103.83 (7) | C1—C6—S1 | 123.32 (11) |
| C9—N1—N2 | 108.92 (11) | C5—C6—S1 | 117.02 (11) |
| C9—N1—H1N1 | 129.0 (13) | C9—C7—C8 | 107.44 (12) |
| N2—N1—H1N1 | 121.9 (13) | C9—C7—S1 | 127.24 (12) |
| C8—N2—N1 | 109.70 (12) | C8—C7—S1 | 125.24 (10) |
| C8—N2—C10 | 127.39 (13) | O1—C8—N2 | 122.79 (13) |
| N1—N2—C10 | 121.97 (11) | O1—C8—C7 | 131.88 (13) |
| C2—C1—C6 | 119.79 (14) | N2—C8—C7 | 105.33 (12) |
| C2—C1—H1A | 120.1 | N1—C9—C7 | 108.57 (13) |
| C6—C1—H1A | 120.1 | N1—C9—C11 | 121.85 (13) |
| C3—C2—C1 | 120.80 (15) | C7—C9—C11 | 129.57 (14) |
| C3—C2—H2A | 119.6 | N2—C10—H10A | 109.5 |

| | | | |
|--------------|--------------|---------------|--------------|
| C1—C2—H2A | 119.6 | N2—C10—H10B | 109.5 |
| C2—C3—C4 | 119.26 (15) | H10A—C10—H10B | 109.5 |
| C2—C3—H3A | 120.4 | N2—C10—H10C | 109.5 |
| C4—C3—H3A | 120.4 | H10A—C10—H10C | 109.5 |
| C3—C4—C5 | 120.56 (14) | H10B—C10—H10C | 109.5 |
| C3—C4—H4A | 119.7 | C9—C11—H11A | 109.5 |
| C5—C4—H4A | 119.7 | C9—C11—H11B | 109.5 |
| C4—C5—C6 | 119.92 (14) | H11A—C11—H11B | 109.5 |
| C4—C5—H5A | 120.0 | C9—C11—H11C | 109.5 |
| C6—C5—H5A | 120.0 | H11A—C11—H11C | 109.5 |
| C1—C6—C5 | 119.66 (14) | H11B—C11—H11C | 109.5 |
| C9—N1—N2—C8 | -1.48 (17) | N1—N2—C8—O1 | -177.46 (13) |
| C9—N1—N2—C10 | -171.15 (14) | C10—N2—C8—O1 | -8.5 (2) |
| C6—C1—C2—C3 | 0.0 (2) | N1—N2—C8—C7 | 2.10 (16) |
| C1—C2—C3—C4 | 0.9 (2) | C10—N2—C8—C7 | 171.06 (14) |
| C2—C3—C4—C5 | -0.8 (2) | C9—C7—C8—O1 | 177.55 (16) |
| C3—C4—C5—C6 | -0.2 (2) | S1—C7—C8—O1 | -5.6 (2) |
| C2—C1—C6—C5 | -1.0 (2) | C9—C7—C8—N2 | -1.96 (16) |
| C2—C1—C6—S1 | 178.43 (12) | S1—C7—C8—N2 | 174.91 (11) |
| C4—C5—C6—C1 | 1.1 (2) | N2—N1—C9—C7 | 0.18 (17) |
| C4—C5—C6—S1 | -178.38 (12) | N2—N1—C9—C11 | 179.36 (13) |
| C7—S1—C6—C1 | 7.87 (15) | C8—C7—C9—N1 | 1.12 (17) |
| C7—S1—C6—C5 | -172.70 (12) | S1—C7—C9—N1 | -175.67 (11) |
| C6—S1—C7—C9 | -100.38 (14) | C8—C7—C9—C11 | -177.97 (15) |
| C6—S1—C7—C8 | 83.36 (14) | S1—C7—C9—C11 | 5.2 (2) |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|----------|-------------|-------------|---------------|
| N1—H1N1 \cdots O1 ⁱ | 0.94 (2) | 1.71 (2) | 2.6446 (16) | 173 (2) |
| C3—H3A \cdots O1 ⁱⁱ | 0.93 | 2.53 | 3.2549 (19) | 135 |

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

Fig. 1

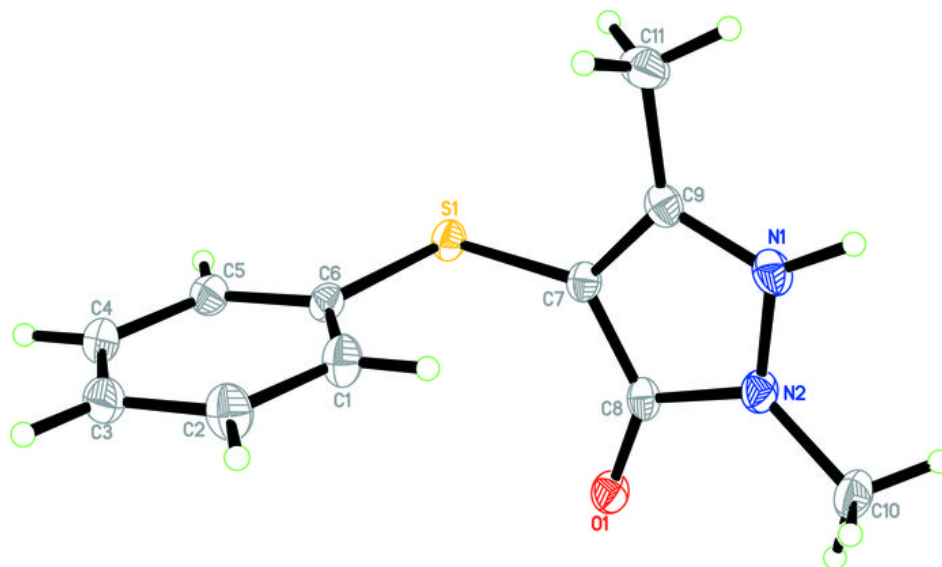


Fig. 2

