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4,6-Bis[5-methyl-3-(trifluoromethyl)-pyrazol-1-yl]pyrimidine

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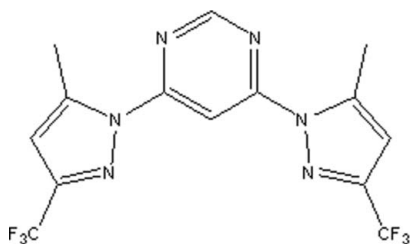
Received 19 October 2009; accepted 22 October 2009

Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.047; wR factor = 0.100; data-to-parameter ratio = 14.2.

The complete molecule of the the title compound, $\text{C}_{14}\text{H}_{10}\text{F}_6\text{N}_6$, is generated by crystallographic twofold symmetry, with two C atoms lying on the roatation axis. The dihedral angle between the central and peripheral rings is $25.97(8)^\circ$.

Related literature

For background to fluorine-containing heterocycles and their properties, see: Krishnaiah & Narsaiah (2002); Ohno *et al.* (2004).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{10}\text{F}_6\text{N}_6$
 $M_r = 376.28$
 Monoclinic, $C2/c$
 $a = 8.5387(14)$ Å
 $b = 16.110(6)$ Å
 $c = 11.022(5)$ Å
 $\beta = 99.295(5)^\circ$

$V = 1496.2(9)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.16$ mm⁻¹
 $T = 173$ K
 $0.41 \times 0.36 \times 0.26$ mm

Data collection

Rigaku Saturn724+ CCD
 diffractometer
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2008)
 $T_{\min} = 0.938$, $T_{\max} = 0.960$

8915 measured reflections
 1706 independent reflections
 1678 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.100$
 $S = 1.19$
 1706 reflections

120 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.23$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5156).

References

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supplementary materials

Acta Cryst. (2009). E65, o2865 [doi:10.1107/S1600536809043657]

4,6-Bis[5-methyl-3-(trifluoromethyl)pyrazol-1-yl]pyrimidine

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Comment

Strategically positioned fluorine in heterocyclic compounds, especially those containing trifluoromethyl groups plays an important role in medicines and agrochemicals (e.g. Krishnaiah & Narsaiah, 2002). Specifically, the fluorinated pyrazoles have been shown to possess high biological activities (e.g. Ohno *et al.* 2004) as herbicides, fungicides, insecticides, analgesics, antipyretics and antiinflammatories. Pyrazolopyrimidine and related fused heterocycles are of interest as potential bioactive molecules. Recently, the new title compound (I) was synthesized in our group with high herbicidal activity. The crystal structure of the compound (I) is shown in Fig. 1.

Experimental

The title compound (0.1 g) was dissolved in anhydrous methanol (20 ml) at room temperature. Colourless blocks of (I) were obtained through slow evaporation after two weeks.

Refinement

All the hydrogen atoms were placed in idealised positions with C—H = 0.93–0.98Å and $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{ep}}(\text{C})$.

Figures

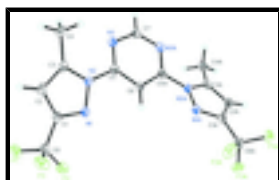


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids and atom-numbering scheme.

4,6-Bis[5-methyl-3-(trifluoromethyl)pyrazol-1-yl]pyrimidine

Crystal data

$\text{C}_{14}\text{H}_{10}\text{F}_6\text{N}_6$

$M_r = 376.28$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 8.5387 (14) \text{ \AA}$

$b = 16.110 (6) \text{ \AA}$

$c = 11.022 (5) \text{ \AA}$

$\beta = 99.295 (5)^\circ$

$F_{000} = 760$

$D_x = 1.670 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 648 reflections

$\theta = 2.2\text{--}27.5^\circ$

$\mu = 0.16 \text{ mm}^{-1}$

$T = 173 \text{ K}$

Block, colorless

supplementary materials

$V = 1496.2 (9) \text{ \AA}^3$
 $Z = 4$

$0.41 \times 0.36 \times 0.26 \text{ mm}$

Data collection

| | |
|--|--|
| Rigaku Saturn724+ CCD diffractometer | 1706 independent reflections |
| Radiation source: sealed tube | 1678 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.033$ |
| $T = 173 \text{ K}$ | $\theta_{\text{max}} = 27.5^\circ$ |
| ω scans at fixed $\chi = 45^\circ$ | $\theta_{\text{min}} = 2.7^\circ$ |
| Absorption correction: multi-scan (CrystalClear; Rigaku, 2008) | $h = -11 \rightarrow 11$ |
| $T_{\text{min}} = 0.938$, $T_{\text{max}} = 0.960$ | $k = -20 \rightarrow 20$ |
| 8915 measured reflections | $l = -14 \rightarrow 14$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.047$ | H-atom parameters constrained |
| $wR(F^2) = 0.100$ | $w = 1/[\sigma^2(F_o^2) + (0.0291P)^2 + 1.4916P]$ |
| $S = 1.19$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 1706 reflections | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 120 parameters | $\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$ |
| | 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.

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)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|--------------|-------------|--------------|----------------------------------|
| F1 | 0.53252 (12) | 0.61885 (7) | 0.61601 (11) | 0.0484 (3) |
| F2 | 0.39212 (17) | 0.66320 (8) | 0.45033 (11) | 0.0610 (4) |
| F3 | 0.31154 (14) | 0.67824 (7) | 0.62363 (12) | 0.0544 (3) |

| | | | | |
|-----|--------------|--------------|--------------|------------|
| N1 | 0.22004 (15) | 0.52452 (8) | 0.43231 (12) | 0.0284 (3) |
| N2 | 0.16127 (15) | 0.44751 (8) | 0.45125 (11) | 0.0269 (3) |
| N3 | 0.07685 (16) | 0.32384 (8) | 0.35077 (13) | 0.0311 (3) |
| C1 | 0.30268 (18) | 0.54413 (10) | 0.54059 (14) | 0.0288 (3) |
| C2 | 0.29725 (19) | 0.48203 (10) | 0.62924 (14) | 0.0310 (4) |
| H2A | 0.3470 | 0.4829 | 0.7128 | 0.037* |
| C3 | 0.20539 (18) | 0.42006 (10) | 0.57018 (14) | 0.0289 (3) |
| C4 | 0.1508 (2) | 0.34123 (11) | 0.62036 (16) | 0.0369 (4) |
| H4A | 0.1750 | 0.3423 | 0.7103 | 0.055* |
| H4B | 0.2054 | 0.2942 | 0.5892 | 0.055* |
| H4C | 0.0360 | 0.3353 | 0.5945 | 0.055* |
| C5 | 0.07580 (17) | 0.40647 (10) | 0.34787 (13) | 0.0266 (3) |
| C6 | 0.0000 | 0.45258 (14) | 0.2500 | 0.0265 (4) |
| H6A | 0.0000 | 0.5115 | 0.2500 | 0.032* |
| C7 | 0.0000 | 0.28736 (15) | 0.2500 | 0.0331 (5) |
| H7A | 0.0000 | 0.2284 | 0.2500 | 0.040* |
| C8 | 0.3840 (2) | 0.62608 (11) | 0.55639 (15) | 0.0342 (4) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|-------------|-------------|-------------|
| F1 | 0.0298 (5) | 0.0524 (7) | 0.0594 (7) | -0.0036 (5) | -0.0038 (5) | -0.0096 (5) |
| F2 | 0.0863 (10) | 0.0544 (7) | 0.0384 (6) | -0.0291 (7) | -0.0011 (6) | 0.0066 (5) |
| F3 | 0.0461 (7) | 0.0431 (6) | 0.0754 (9) | 0.0017 (5) | 0.0146 (6) | -0.0206 (6) |
| N1 | 0.0275 (6) | 0.0310 (7) | 0.0259 (6) | -0.0002 (5) | 0.0011 (5) | -0.0002 (5) |
| N2 | 0.0254 (6) | 0.0302 (7) | 0.0242 (6) | 0.0013 (5) | 0.0014 (5) | 0.0006 (5) |
| N3 | 0.0300 (7) | 0.0313 (7) | 0.0311 (7) | 0.0019 (5) | 0.0023 (5) | 0.0010 (6) |
| C1 | 0.0251 (7) | 0.0353 (8) | 0.0256 (7) | 0.0034 (6) | 0.0027 (6) | -0.0028 (6) |
| C2 | 0.0288 (8) | 0.0393 (9) | 0.0239 (7) | 0.0063 (6) | 0.0013 (6) | -0.0011 (6) |
| C3 | 0.0270 (7) | 0.0350 (8) | 0.0244 (7) | 0.0070 (6) | 0.0038 (6) | 0.0024 (6) |
| C4 | 0.0432 (10) | 0.0373 (9) | 0.0296 (8) | 0.0035 (7) | 0.0044 (7) | 0.0062 (7) |
| C5 | 0.0223 (7) | 0.0324 (8) | 0.0252 (7) | 0.0012 (6) | 0.0043 (6) | -0.0016 (6) |
| C6 | 0.0236 (10) | 0.0292 (11) | 0.0262 (10) | 0.000 | 0.0028 (8) | 0.000 |
| C7 | 0.0341 (12) | 0.0291 (11) | 0.0352 (12) | 0.000 | 0.0032 (9) | 0.000 |
| C8 | 0.0318 (8) | 0.0394 (9) | 0.0304 (8) | 0.0008 (7) | 0.0014 (6) | -0.0031 (7) |

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

| | | | |
|-------|-------------|--------------------|-------------|
| F1—C8 | 1.3359 (19) | C2—C3 | 1.368 (2) |
| F2—C8 | 1.325 (2) | C2—H2A | 0.9500 |
| F3—C8 | 1.336 (2) | C3—C4 | 1.490 (2) |
| N1—C1 | 1.323 (2) | C4—H4A | 0.9800 |
| N1—N2 | 1.3668 (19) | C4—H4B | 0.9800 |
| N2—C3 | 1.377 (2) | C4—H4C | 0.9800 |
| N2—C5 | 1.414 (2) | C5—C6 | 1.3815 (19) |
| N3—C5 | 1.331 (2) | C6—C5 ⁱ | 1.3815 (19) |
| N3—C7 | 1.3319 (17) | C6—H6A | 0.9500 |
| C1—C2 | 1.404 (2) | C7—N3 ⁱ | 1.3319 (17) |

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| | | | |
|-------------|--------------|--------------------------|--------------|
| C1—C8 | 1.489 (2) | C7—H7A | 0.9500 |
| C1—N1—N2 | 103.56 (13) | H4A—C4—H4C | 109.5 |
| N1—N2—C3 | 112.71 (12) | H4B—C4—H4C | 109.5 |
| N1—N2—C5 | 117.12 (12) | N3—C5—C6 | 123.83 (15) |
| C3—N2—C5 | 130.02 (14) | N3—C5—N2 | 116.59 (13) |
| C5—N3—C7 | 114.87 (15) | C6—C5—N2 | 119.57 (15) |
| N1—C1—C2 | 112.63 (15) | C5 ⁱ —C6—C5 | 114.9 (2) |
| N1—C1—C8 | 119.21 (14) | C5 ⁱ —C6—H6A | 122.5 |
| C2—C1—C8 | 128.13 (15) | C5—C6—H6A | 122.5 |
| C3—C2—C1 | 105.64 (14) | N3—C7—N3 ⁱ | 127.6 (2) |
| C3—C2—H2A | 127.2 | N3—C7—H7A | 116.2 |
| C1—C2—H2A | 127.2 | N3 ⁱ —C7—H7A | 116.2 |
| C2—C3—N2 | 105.44 (14) | F2—C8—F1 | 107.01 (15) |
| C2—C3—C4 | 129.45 (15) | F2—C8—F3 | 107.49 (16) |
| N2—C3—C4 | 124.98 (15) | F1—C8—F3 | 105.65 (14) |
| C3—C4—H4A | 109.5 | F2—C8—C1 | 112.77 (14) |
| C3—C4—H4B | 109.5 | F1—C8—C1 | 111.59 (14) |
| H4A—C4—H4B | 109.5 | F3—C8—C1 | 111.93 (14) |
| C3—C4—H4C | 109.5 | | |
| C1—N1—N2—C3 | 0.68 (16) | N1—N2—C5—N3 | 152.46 (14) |
| C1—N1—N2—C5 | -175.36 (13) | C3—N2—C5—N3 | -22.8 (2) |
| N2—N1—C1—C2 | -0.63 (17) | N1—N2—C5—C6 | -26.16 (18) |
| N2—N1—C1—C8 | -179.10 (13) | C3—N2—C5—C6 | 158.62 (13) |
| N1—C1—C2—C3 | 0.37 (18) | N3—C5—C6—C5 ⁱ | -0.48 (11) |
| C8—C1—C2—C3 | 178.67 (15) | N2—C5—C6—C5 ⁱ | 178.03 (15) |
| C1—C2—C3—N2 | 0.07 (17) | C5—N3—C7—N3 ⁱ | -0.43 (10) |
| C1—C2—C3—C4 | -175.86 (16) | N1—C1—C8—F2 | -14.0 (2) |
| N1—N2—C3—C2 | -0.47 (17) | C2—C1—C8—F2 | 167.76 (16) |
| C5—N2—C3—C2 | 174.92 (14) | N1—C1—C8—F1 | -134.52 (15) |
| N1—N2—C3—C4 | 175.69 (14) | C2—C1—C8—F1 | 47.3 (2) |
| C5—N2—C3—C4 | -8.9 (3) | N1—C1—C8—F3 | 107.31 (17) |
| C7—N3—C5—C6 | 0.9 (2) | C2—C1—C8—F3 | -70.9 (2) |
| C7—N3—C5—N2 | -177.66 (11) | | |

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

Fig. 1

