

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

1-Methyl-3-trifluoromethyl-1*H*-pyrazol-5-ol

 Jia-ying Xu,^{a*} Wei-hua Cheng,^b Jin-long Yan^a and Gui-xiang Quan^a

^aDepartment of Applied Chemistry, College of Chemical and Biological Engineering, Yancheng Institute of Technology, Yinbing Road No. 9 Yancheng, Yancheng 224051, People's Republic of China, and ^bDepartment of Chemical Engineering, Yancheng College of Textile Technology, Liberation Road S. No. 265 Yancheng, Yancheng 224005, People's Republic of China
Correspondence e-mail: xujiaying-1984@163.com

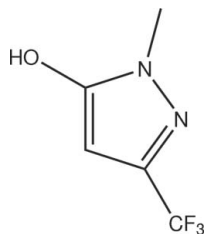
Received 2 September 2009; accepted 3 September 2009

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; disorder in main residue; R factor = 0.050; wR factor = 0.168; data-to-parameter ratio = 9.7.

In the title compound, $\text{C}_5\text{H}_5\text{F}_3\text{N}_2\text{O}$, the F atoms are disordered over two sets of sites in a 0.64 (3):0.36 (3) ratio. In the crystal structure, $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds link the molecules into chains and a short $\text{C}-\text{H}\cdots\text{F}$ contact also occurs.

Related literature

For background to fluorinated heterocycles, see: Marcos & Martins (2003). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_5\text{H}_5\text{F}_3\text{N}_2\text{O}$
 $M_r = 166.11$
Monoclinic, $P2_1/c$

$a = 7.5500$ (15) Å
 $b = 8.3530$ (17) Å
 $c = 11.371$ (2) Å

$\beta = 104.72$ (3)°
 $V = 693.6$ (2) Å³
 $Z = 4$
Mo $K\alpha$ radiation

$\mu = 0.17$ mm⁻¹
 $T = 293$ K
 $0.20 \times 0.10 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.968$, $T_{\max} = 0.984$
1357 measured reflections

1259 independent reflections
856 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.168$
 $S = 1.00$
1259 reflections
130 parameters

36 restraints
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.20$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}-\text{H}0\text{A}\cdots\text{N}1^i$	0.85	1.85	2.698 (3)	176
$\text{C}5-\text{H}5\text{B}\cdots\text{F}3^{\text{ii}}$	0.96	2.55	3.185 (12)	124

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5087).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Enraf–Nonius (1994). or (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Marcos, A. P. & Martins, X. X. (2003). *J. Fluorine Chem.* **123**, 261–265.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

supplementary materials

Acta Cryst. (2009). E65, o2377 [doi:10.1107/S1600536809035624]

1-Methyl-3-trifluoromethyl-1*H*-pyrazol-5-ol

J. Xu, W. Cheng, J. Yan and G. Quan

Comment

As part of the ongoing study of polyfluorinated heterocycles (Marcos & Martins, 2003), we report herein the crystal structure of the title compound.

In the molecule of the title compound (Fig 1), the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. Ring A (C4-C9) is, of course, planar. The intramolecular C-H \cdots O hydrogen bond (Table 1) results in the formation of a five-membered ring B (O1/C1-C3/H1A), having envelope conformation with C2 atom displaced by -0.668 (3) Å from the plane of the other ring atoms.

In the crystal structure, intermolecular O—H \cdots N hydrogen bonds (Table 1) link the molecules (Fig. 2), in which they may be effective in the stabilization of the structure.

Experimental

4,4-Diethoxy-1,1,1-trifluorobut-3-en-2-one (2 mmol) was added to a stirred solution of hydrazine (2.2 mmol) at room temperature in ethanol (15 ml). The mixture was stirred under reflux for 24 h. The solvent was evaporated and to the residue was added H₂O (10 ml) and the organic phase were extract with dichloromethane (15 ml). The organic extract was dried (Na₂SO₄) and the solvent was removed under reduced pressure to obtain the title compound (yield; 25%, m.p. 446 K). Colourless blocks of (I) were obtained by slow evaporation of an ethyl acetate solution.

Refinement

H atoms were positioned geometrically, with C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H, respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.5$ for methyl H and $x = 1.2$ for all other H atoms.

Figures

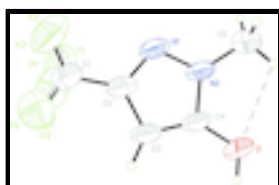


Fig. 1. The molecular structure of (I).

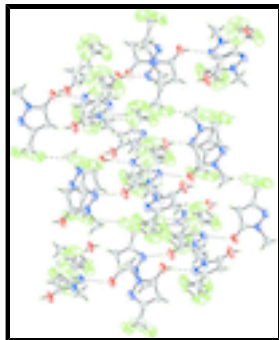


Fig. 2. A partial packing diagram of (I). Hydrogen bonds are shown as dashed lines.

1-Methyl-3-trifluoromethyl-1H-pyrazol-5-ol

Crystal data

$C_5H_5F_3N_2O$

$M_r = 166.11$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.5500$ (15) Å

$b = 8.3530$ (17) Å

$c = 11.371$ (2) Å

$\beta = 104.72$ (3)°

$V = 693.6$ (2) Å³

$Z = 4$

$F_{000} = 336$

$D_x = 1.591$ Mg m⁻³

Melting point: 446 K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 9\text{--}13^\circ$

$\mu = 0.17$ mm⁻¹

$T = 293$ K

Block, colourless

$0.20 \times 0.10 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ K

$\omega/2\theta$ scans

Absorption correction: ψ scan
(North *et al.*, 1968)

$T_{\min} = 0.968$, $T_{\max} = 0.984$

1357 measured reflections

1259 independent reflections

856 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.041$

$\theta_{\max} = 25.3^\circ$

$\theta_{\min} = 2.8^\circ$

$h = 0 \rightarrow 9$

$k = 0 \rightarrow 10$

$l = -13 \rightarrow 13$

3 standard reflections

every 200 reflections

intensity decay: 1%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.168$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.12P]$

$S = 1.00$	where $P = (F_o^2 + 2F_c^2)/3$
1259 reflections	$(\Delta/\sigma)_{\max} < 0.001$
130 parameters	$\Delta\rho_{\max} = 0.20 \text{ e } \text{\AA}^{-3}$
36 restraints	$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ Extinction coefficient: 0.062 (13)

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 $F^2 > 2\sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O	0.6146 (3)	0.1822 (3)	0.22551 (16)	0.0812 (8)	
H0A	0.5735	0.1988	0.2874	0.097*	
N1	0.4722 (3)	0.2582 (3)	-0.08398 (18)	0.0562 (7)	
C1	0.1757 (5)	0.3877 (5)	-0.1412 (3)	0.0701 (9)	
N2	0.5857 (3)	0.2020 (3)	0.02028 (18)	0.0549 (7)	
C2	0.3341 (4)	0.3246 (3)	-0.0489 (2)	0.0540 (8)	
C3	0.3563 (4)	0.3122 (4)	0.0765 (2)	0.0609 (8)	
H3A	0.2783	0.3492	0.1220	0.073*	
C4	0.5184 (4)	0.2333 (4)	0.1169 (2)	0.0585 (8)	
C5	0.7551 (4)	0.1216 (5)	0.0201 (3)	0.0697 (9)	
H5A	0.8043	0.0723	0.0978	0.105*	
H5B	0.8414	0.1981	0.0046	0.105*	
H5C	0.7323	0.0411	-0.0422	0.105*	
F1	0.0666 (15)	0.2656 (12)	-0.1980 (10)	0.117 (3)	0.64 (3)
F2	0.2287 (15)	0.4689 (17)	-0.2294 (11)	0.107 (3)	0.64 (3)
F3	0.057 (2)	0.458 (3)	-0.0997 (12)	0.093 (5)	0.36 (3)
F3'	0.1113 (17)	0.5237 (14)	-0.0992 (8)	0.103 (2)	0.64 (3)
F2'	0.202 (2)	0.412 (2)	-0.2461 (11)	0.077 (4)	0.36 (3)
F1'	0.0325 (19)	0.309 (3)	-0.157 (2)	0.105 (5)	0.36 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O	0.0761 (14)	0.143 (2)	0.0277 (11)	0.0173 (14)	0.0192 (9)	0.0057 (11)

supplementary materials

N1	0.0633 (14)	0.0805 (17)	0.0266 (11)	-0.0061 (12)	0.0150 (10)	-0.0014 (10)
C1	0.075 (2)	0.089 (2)	0.0477 (18)	0.003 (2)	0.0183 (16)	0.0058 (16)
N2	0.0585 (13)	0.0824 (16)	0.0266 (11)	-0.0018 (12)	0.0162 (9)	-0.0031 (10)
C2	0.0632 (17)	0.0676 (18)	0.0346 (13)	-0.0069 (14)	0.0190 (12)	-0.0019 (12)
C3	0.0642 (17)	0.090 (2)	0.0338 (14)	-0.0021 (16)	0.0221 (12)	-0.0070 (13)
C4	0.0606 (17)	0.090 (2)	0.0277 (13)	-0.0054 (16)	0.0164 (12)	-0.0050 (13)
C5	0.0675 (18)	0.100 (2)	0.0454 (16)	0.0037 (18)	0.0219 (14)	-0.0017 (15)
F1	0.096 (4)	0.120 (4)	0.104 (5)	-0.001 (3)	-0.033 (3)	-0.017 (3)
F2	0.118 (4)	0.122 (6)	0.076 (4)	-0.003 (4)	0.016 (3)	0.042 (4)
F3	0.088 (6)	0.120 (10)	0.074 (4)	0.036 (6)	0.027 (4)	-0.009 (6)
F3'	0.112 (5)	0.099 (5)	0.095 (3)	0.028 (4)	0.020 (3)	0.000 (3)
F2'	0.091 (6)	0.114 (8)	0.030 (3)	0.019 (5)	0.024 (3)	0.011 (4)
F1'	0.073 (5)	0.114 (9)	0.110 (8)	-0.029 (5)	-0.008 (5)	0.014 (6)

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

O—C4	1.334 (3)	C1—C2	1.474 (4)
O—H0A	0.8501	N2—C4	1.348 (3)
N1—C2	1.328 (3)	N2—C5	1.445 (4)
N1—N2	1.358 (3)	C2—C3	1.397 (4)
C1—F1'	1.238 (13)	C3—C4	1.363 (4)
C1—F3	1.257 (12)	C3—H3A	0.9300
C1—F2'	1.274 (12)	C5—H5A	0.9600
C1—F2	1.352 (10)	C5—H5B	0.9600
C1—F1	1.366 (9)	C5—H5C	0.9600
C1—F3'	1.369 (9)		
C4—O—H0A	119.2	F1—C1—C2	110.6 (5)
C2—N1—N2	104.6 (2)	F3'—C1—C2	110.2 (5)
F1'—C1—F3	68 (2)	C4—N2—N1	111.1 (2)
F1'—C1—F2'	106.6 (10)	C4—N2—C5	127.5 (2)
F3—C1—F2'	124.7 (11)	N1—N2—C5	121.5 (2)
F1'—C1—F2	124.7 (8)	N1—C2—C3	112.1 (3)
F3—C1—F2	114.7 (14)	N1—C2—C1	119.5 (2)
F2'—C1—F2	23.0 (8)	C3—C2—C1	128.2 (3)
F1'—C1—F1	30.3 (9)	C4—C3—C2	104.2 (2)
F3—C1—F1	97.0 (17)	C4—C3—H3A	127.9
F2'—C1—F1	84.1 (8)	C2—C3—H3A	127.9
F2—C1—F1	106.3 (6)	O—C4—N2	117.6 (3)
F1'—C1—F3'	96.6 (18)	O—C4—C3	134.3 (2)
F3—C1—F3'	29.9 (8)	N2—C4—C3	108.1 (2)
F2'—C1—F3'	110.2 (11)	N2—C5—H5A	109.5
F2—C1—F3'	92.4 (11)	N2—C5—H5B	109.5
F1—C1—F3'	124.0 (11)	H5A—C5—H5B	109.5
F1'—C1—C2	115.8 (7)	N2—C5—H5C	109.5
F3—C1—C2	115.2 (6)	H5A—C5—H5C	109.5
F2'—C1—C2	115.7 (7)	H5B—C5—H5C	109.5
F2—C1—C2	111.6 (5)		
C2—N1—N2—C4	0.0 (3)	F2'—C1—C2—C3	168.0 (11)
C2—N1—N2—C5	-179.4 (3)	F2—C1—C2—C3	143.2 (8)

N2—N1—C2—C3	-0.1 (3)	F1—C1—C2—C3	-98.6 (8)
N2—N1—C2—C1	-175.2 (3)	F3'—C1—C2—C3	42.1 (8)
F1'—C1—C2—N1	108.2 (15)	N1—C2—C3—C4	0.1 (3)
F3—C1—C2—N1	-175.6 (14)	C1—C2—C3—C4	174.7 (3)
F2'—C1—C2—N1	-17.7 (11)	N1—N2—C4—O	178.9 (3)
F2—C1—C2—N1	-42.5 (8)	C5—N2—C4—O	-1.7 (5)
F1—C1—C2—N1	75.7 (8)	N1—N2—C4—C3	0.0 (3)
F3'—C1—C2—N1	-143.6 (7)	C5—N2—C4—C3	179.4 (3)
F1'—C1—C2—C3	-66.1 (16)	C2—C3—C4—O	-178.7 (4)
F3—C1—C2—C3	10.1 (15)	C2—C3—C4—N2	0.0 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O-H0A\cdots N1^i$	0.85	1.85	2.698 (3)	176
$C5-H5B\cdots F3^{iii}$	0.96	2.55	3.185 (12)	124

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

Fig. 1

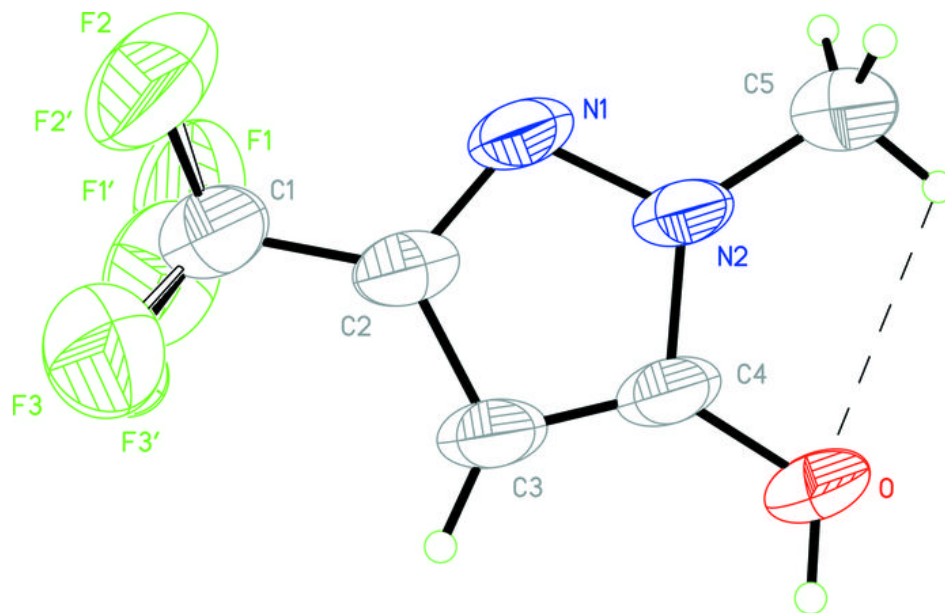


Fig. 2

