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# 3-Methoxycarbonyl-1-methyl-4-trifluoromethylpyrazole†

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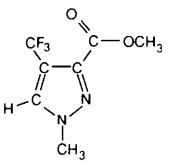
## Abstract

The crystallographic characterization of the title molecule, $C_7H_7F_3N_2O_2$, distinguishes it from its isomer, 5-methoxycarbonyl-1-methyl-4-trifluoromethylpyrazole, which is the major product in their joint synthesis. The bond lengths, except for C3—C4, are consistent with other molecules having substituents on the same ring positions. The pyrazole ring and the carboxy group plane are nearly coplanar.


† IUPAC name: methyl 1-methyl-4-trifluoromethyl-3-pyrazolecarboxylate.

## Comment

The title molecule (I) and its 5-methoxycarbonyl isomer are obtained, along with other cyclic products, by the reaction of 4,4,4-trifluorobut-1-ynoic acid and diazomethane (Tajammal, 1988, 1991; Tajammal & Tipping, 1990). The title molecule was recrystallized from dichloromethane after chromatographic separation.



(I)

The bond lengths in the pyrazole ring are typical of pyrazole molecules with substituents at the same ring positions (Becher, Brondum, Krake, Pluta, Simonsen, Molina & Begtrup, 1988; Cousson, Robert & Hubert-Habart, 1991; Lapasset & Falgueirettes, 1972), except for C3—C4 which is up to 0.05 Å shorter.

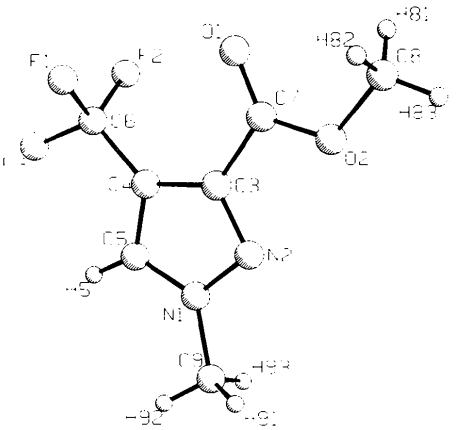


Fig. 1. View of the title molecule showing the atom-labelling scheme.

## Experimental

*Crystal data*

$C_7H_7F_3N_2O_2$
$M_r$ = 208.14
Monoclinic
$P2_1/c$
$a$ = 4.624 (2) Å
$b$ = 16.600 (2) Å
$c$ = 11.687 (2) Å
$\beta$ = 92.43 (2)°
$V$ = 896.3 (7) Å$^3$
$Z$ = 4
$D_x$ = 1.542 Mg m$^{-3}$
Mo $K\alpha$ radiation
$\lambda$ = 0.71069 Å
Cell parameters from 20 reflections
$\theta$ = 6.35-11.3°
$\mu$ = 0.146 mm$^{-1}$
$T$ = 296 K
Block
0.3 × 0.3 × 0.2 mm
Colourless

*Data collection*

Enraf-Nonius CAD-4 diffractometer
$R_{int}$ = 0.045
$\theta_{max}$ = 25°

$\omega/2\theta$ scans
Absorption correction: none
1284 measured reflections
721 independent reflections
522 observed reflections [$I > 2\sigma(I)$]
$h = -4 \rightarrow 4$
$k = 0 \rightarrow 16$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity variation: none

*Refinement*

Refinement on $F$
$R = 0.071$
$wR = 0.040$
$S = 3.00$
522 reflections
127 parameters
H-atom parameters not refined
Weights as default in *TEXSAN*
$(\Delta/\sigma)_{max} = 0.04$
$\Delta\rho_{max} = 0.33$ e Å$^{-3}$
$\Delta\rho_{min} = -0.30$ e Å$^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: CAD-4 *Software* (Enraf-Nonius, 1989). Cell refinement: CAD-4 *Software*. Data reduction: *SHELX*76 (Sheldrick, 1976). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation,1985). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *CIF* (Hall, Allen & Brown, 1991).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å$^2$)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| F1 | 0.4080 (13) | 0.1649 (4) | 0.6144 (5) | 6.1 (4) |
| F2 | 0.0379 (13) | 0.1554 (4) | 0.7181 (6) | 6.5 (4) |
| F3 | −0.0007 (13) | 0.1211 (4) | 0.5448 (5) | 6.9 (4) |
| O1 | 0.425 (2) | 0.2980 (4) | 0.7814 (7) | 6.4 (5) |
| O2 | 0.329 (2) | 0.4275 (5) | 0.7495 (6) | 5.8 (5) |
| N1 | −0.189 (2) | 0.3563 (6) | 0.4962 (7) | 4.0 (5) |
| N2 | −0.028 (2) | 0.3941 (5) | 0.5784 (8) | 4.2 (5) |
| C3 | 0.101 (2) | 0.3325 (7) | 0.6307 (9) | 3.8 (7) |
| C4 | 0.029 (2) | 0.2585 (7) | 0.5834 (9) | 3.7 (7) |
| C5 | −0.159 (2) | 0.2769 (6) | 0.4951 (9) | 4.0 (7) |
| C6 | 0.126 (3) | 0.1765 (8) | 0.6155 (11) | 4.8 (8) |
| C7 | 0.303 (3) | 0.3503 (8) | 0.7312 (10) | 4.6 (8) |
| C8 | 0.536 (3) | 0.4523 (7) | 0.8382 (10) | 7.5 (9) |
| C9 | −0.379 (2) | 0.4066 (6) | 0.4156 (9) | 5.3 (7) |

Table 2. *Geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| F1—C6 | 1.32 (1) | N1—C5 | 1.33 (1) |
| F2—C6 | 1.33 (1) | N1—C9 | 1.51 (1) |
| F3—C6 | 1.35 (1) | N2—C3 | 1.32 (1) |
| O1—C7 | 1.18 (1) | C3—C4 | 1.38 (1) |
| O2—C7 | 1.30 (1) | C3—C7 | 1.50 (1) |
| O2—C8 | 1.44 (1) | C4—C5 | 1.35 (1) |
| N1—N2 | 1.35 (1) | C4—C6 | 1.48 (1) |
| C7—O2—C8 | 116.9 (9) | N1—C5—C4 | 106 (1) |
| N2—N1—C5 | 114.4 (9) | F1—C6—F2 | 108 (1) |
| N2—N1—C9 | 118.5 (9) | F1—C6—F3 | 107 (1) |
| C5—N1—C9 | 127 (1) | F1—C6—C4 | 115 (1) |
| N1—N2—C3 | 101.2 (8) | F2—C6—F3 | 103 (1) |
| N2—C3—C4 | 114.1 (9) | F2—C6—C4 | 112 (1) |
| N2—C3—C7 | 118 (1) | F3—C6—C4 | 111 (1) |
| C4—C3—C7 | 128 (1) | O1—C7—O2 | 127 (1) |
| C3—C4—C5 | 103.8 (9) | O1—C7—C3 | 121 (1) |
| C3—C4—C6 | 131 (1) | O2—C7—C3 | 112 (1) |
| C5—C4—C6 | 125 (1) | | |



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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry including torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71507 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1068]

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# *meso*- and *rac*-2,7-Diphenyl-3,5-octadiyne-2,7-diol, $C_{20}H_{18}O_2$

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## Abstract

The stereoisomeric forms of 2,7-diphenyl-3,5-octadiyne-2,7-diol (I) have been identified; *meso*- and *rac*-(I) exhibit different crystal packing, reflecting very different hydrogen-bonding networks.

## Comment

Copper(I)-induced oxidative coupling of terminal acetylenes, the so-called Glaser reaction, provides a