Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hydrogen-bonded chains in 5-methyl-2-trifluoromethyl-1,2,4-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one and hydrogen-bonded chains of rings in 5-amino-3-trifluoromethyl-1*H*-1,2,4-triazole–5-methyl-2-trifluoromethyl-1,2,4-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one (1/1), the co-crystal of a reaction product and one of its precursors

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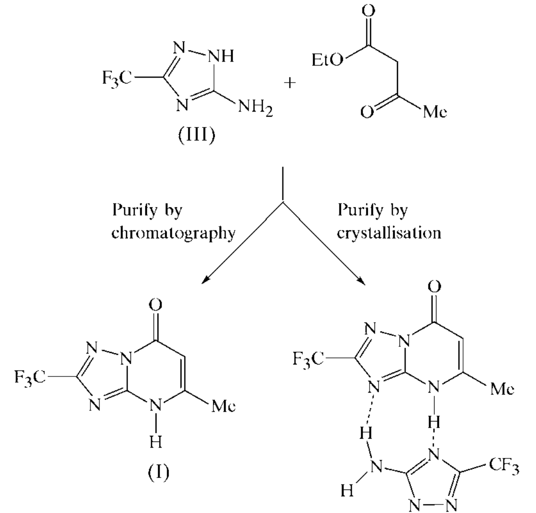
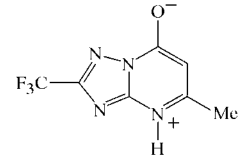
Received 11 August 2004
Accepted 16 August 2004
Online 18 September 2004

In the title compounds, $C_7H_5F_3N_4O$, (I), and $C_3H_3F_3N_4 \cdot C_7H_5F_3N_4O$, (II), all of the molecular components exhibit some polarization of their molecular–electronic structures. The molecules in (I) are linked into simple *C*(6) chains, while in (II), the components are linked by a combination of two-centre N—H···N and N—H···O, and three-centre N—H···(O,N) hydrogen bonds into chains containing $R^2_1(5)$, $R^1_2(6)$ and $R^2_2(8)$ rings.

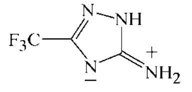
Comment

In the course of our studies of fluorinated triazole precursors of potential antimalarial compounds, we needed to prepare 3-methyl-5-(trifluoromethyl)-1,2,4-triazolo[1,5-*a*]pyrimidin-7-one, (I). The preparation of this compound by the reaction of 5-amino-3-trifluoromethyl-1*H*-1,2,4-triazole with ethyl acetoacetate has recently been reported (Zohdi, 1997), and use of the reported chromatographic purification readily affords pure (I). However, we have found that, when purification of the crude reaction product is attempted using recrystallization methods, the crystalline material obtained is not the expected triazolopyrimidinone, (I), but a co-crystal, (II), containing a 1:1 molar ratio of (I) with the starting triazole. We report here the molecular and supramolecular structures of both (I) and the co-crystal, (II).





(I*a*)



(III*a*)

In both (I) and (II) (Figs. 1 and 2), the bond lengths in the six-membered rings (Tables 1 and 3) indicate that the O14—C14—C15—C16—N17 fragment constitutes a vinylogous amide, with a significant contribution from the polarized form, (I*a*). The other bond distances and angles in (I) show no unexpected values. In particular, the five-membered ring of the bicyclic component shows very strong bond fixation with a clear distinction between single and double bonds.

Within the triazole component of (II), the N21—C25 and N25—C25 bonds are too similar in length to be convincingly represented as double and single bonds, respectively. In pure 5-amino-3-trifluoromethyl-1*H*-1,2,4-triazole itself, (III) (Borbulevych *et al.*, 1998), the corresponding bonds differ in length by only 0.022 (2) Å. The other C—N bond lengths within this ring are typical of their types (Allen *et al.*, 1987) in both (II) and (III), and the dimensions thus suggest that there is some contribution from the polarized form, (III*a*), in both (II) and (III).

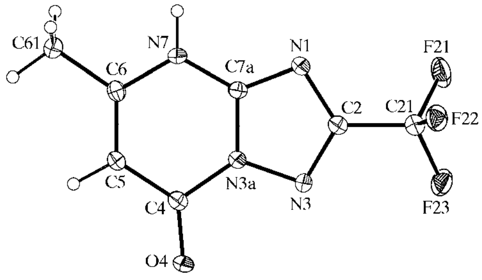


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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DOI: 10.1107/S0108270104020256

The molecules of (I) are linked into *C*(6) chains (Bernstein *et al.*, 1995) by a single, almost linear, N—H···O hydrogen bond (Table 2). Amine atom N7 in the molecule at (x, y, z) acts as donor to carbonyl atom O4 in the molecule at ($x - 1, \frac{3}{2} - y, z - \frac{1}{2}$), so forming a chain running parallel to the [201] direction and generated by the *c*-glide plane at $y = \frac{3}{4}$ (Fig. 3). Two such chains, which are related to one another by inversion and hence antiparallel to each other, pass through each unit cell, but there are no direction-specific interactions between adjacent chains.

Within the asymmetric unit of compound (II), the independent molecular components are linked by two nearly linear N—H···N hydrogen bonds (Table 4), forming an $R^2_2(8)$ motif. These units are linked into a chain by one two-centre N—H···O hydrogen bond and one three-centre N—H···(O,N) hydrogen bond. Atom N25 at (x, y, z) acts as hydrogen-bond donor, *via* atom H25*B*, to atom N11 at ($x - \frac{3}{2}, \frac{3}{2} - y, \frac{1}{2} + z$). At the same time, atom N24 at (x, y, z) acts as donor to both atoms O14 and N13 at ($x - \frac{3}{2}, \frac{3}{2} - y, \frac{1}{2} + z$), forming a markedly asymmetric, but planar, three-centre interaction. Propagation of these hydrogen bonds then forms a complex chain of rings, containing $[R^2_1(5)][R^1_2(6)][R^2_2(8)]$ sequences of three edge-fused rings (Fig. 4). This chain is generated by the *c*-glide plane at $y = \frac{3}{4}$ and runs parallel to the $[30\bar{1}]$ direction. Two chains of this type pass through each unit cell, but there are no direction-specific interactions between adjacent chains.

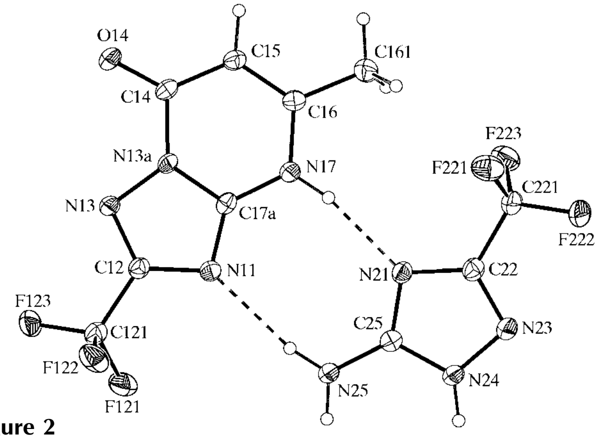

Figure 2
The independent molecular components of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

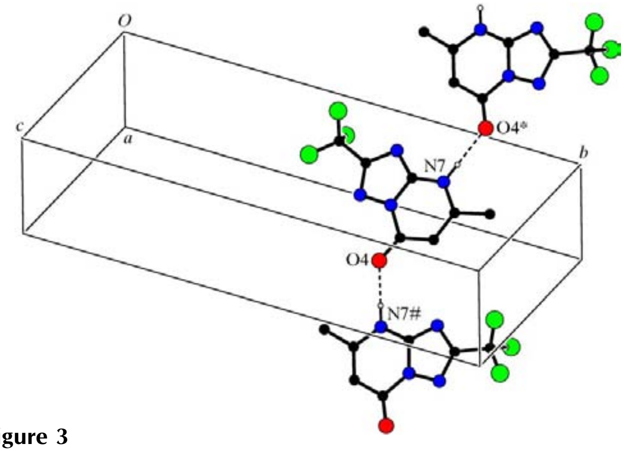

Figure 3
Part of the crystal structure of (I), showing the formation of a chain along [201]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($x - 1, \frac{3}{2} - y, z - \frac{1}{2}$) and ($1 + x, \frac{3}{2} - y, \frac{1}{2} + z$), respectively.

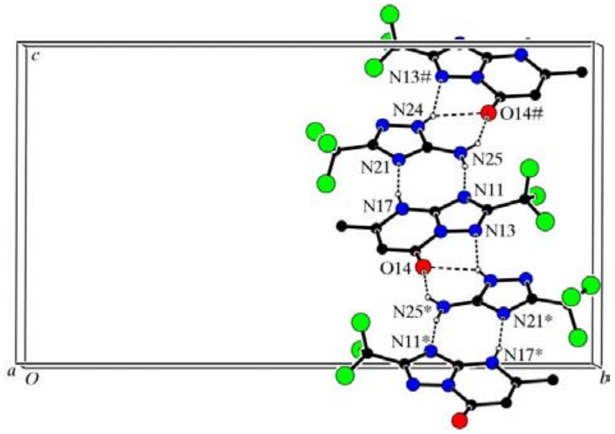

Figure 4
Part of the crystal structure of (II), showing the formation of a chain of rings along $[30\bar{1}]$. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($x - \frac{3}{2}, \frac{3}{2} - y, \frac{1}{2} + z$) and ($\frac{3}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$), respectively.

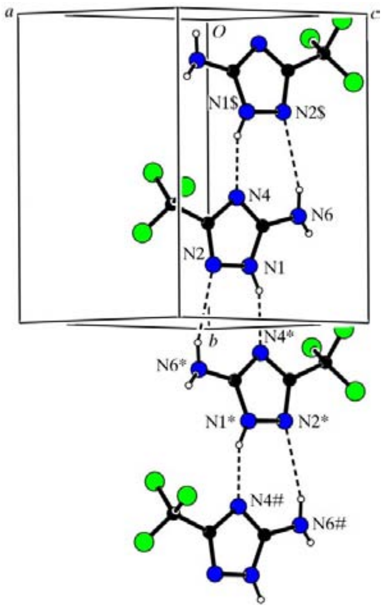

Figure 5
Part of the crystal structure of (III) (Borbulevych *et al.*, 1998), showing the formation of a chain of rings along [010]. The original atomic coordinates and atom-labelling scheme have been used. Atoms marked with an asterisk (*), a hash (#) or a dollar sign ($) are at the symmetry positions ($-x, \frac{1}{2} + y, \frac{1}{2} - z$), ($x, 1 + y, z$) and ($-x, y - \frac{1}{2}, \frac{1}{2} - z$), respectively.

It is pertinent to reconsider the supramolecular structure of the pure triazole component, (III). This was described (Borbulevych *et al.*, 1998) as forming hydrogen-bonded layers parallel to the *ab* plane. However, analysis of the original atom coordinates using *PLATON* (Spek, 2003) clearly shows that the supramolecular structure consists of a $C(4)C(5)[R_2^2(7)]$ chain of rings running parallel to the [010] direction (Fig. 5). The formation of this chain utilizes only two of the three available N—H bonds, but there are no plausible acceptors available within hydrogen-bonding range of the third N—H bond, so that the supramolecular structure of (III) is properly described as one-dimensional.

Experimental

For the preparation of (I) and (II), an equimolar mixture of 3-amino-5-trifluoromethyl-1,2,4-triazole and ethyl acetoacetate (1 mmol of each) in toluene (27 ml) was heated under reflux for 2 h. The mixture was cooled to ambient temperature and the resulting solid was collected. Chromatographic purification (Zohdi, 1997) gave pure (I), and crystals of (I) suitable for single-crystal X-ray diffraction were grown from a solution in ethanol. By contrast, successive recrystallizations of the crude reaction mixture from EtOH and then from Me_2CO–$CHCl_3$ (1:1 *v*/*v*) gave crystals of (II) suitable for single-crystal X-ray diffraction.

Compound (I)

Crystal data

$C_7H_5F_3N_4O$
$M_r = 218.15$
Monoclinic, $P2_1/c$
$a = 4.6152$ (4) Å
$b = 20.504$ (2) Å
$c = 8.7094$ (9) Å
$\beta = 91.378$ (7)°
$V = 823.93$ (14) Å^3
$Z = 4$

$D_x = 1.759$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1862 reflections
$\theta = 3.1$–$27.5°$
$\mu = 0.17$ mm^{-1}
$T = 120$ (2) K
Block, colourless
$0.42 \times 0.20 \times 0.12$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.922$, $T_{\max} = 0.980$
8410 measured reflections

1862 independent reflections
1288 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$
$\theta_{\max} = 27.5°$
$h = -5 \rightarrow 5$
$k = -26 \rightarrow 23$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.173$
$S = 1.02$
1862 reflections
138 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1146P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.65$ e Å^{-3}
$\Delta\rho_{\min} = -0.53$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.071 (10)

Table 1
Selected interatomic distances (Å) for (I).

N1—C2	1.362 (3)	C6—N7	1.368 (3)
C2—N3	1.316 (3)	N7—C7a	1.350 (3)
N3—N3a	1.369 (3)	C7a—N1	1.312 (3)
N3a—C4	1.405 (3)	N3a—C7a	1.363 (3)
C4—C5	1.424 (3)	C4—O4	1.235 (3)
C5—C6	1.361 (3)	C2—C21	1.496 (3)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N7—H7···O4$^{\rm i}$	0.88	1.83	2.713 (2)	179

Symmetry code: (i) $x-1, \frac{3}{2}-y, z-\frac{1}{2}$.

Compound (II)

Crystal data

$C_3H_3F_3N_4 \cdot C_7H_5F_3N_4O$
$M_r = 370.24$
Monoclinic, Cc
$a = 5.0752$ (4) Å
$b = 22.182$ (2) Å
$c = 12.3960$ (11) Å
$\beta = 91.3200$ (5)°
$V = 1395.2$ (2) Å^3
$Z = 4$

$D_x = 1.763$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1596 reflections
$\theta = 3.3$–$27.5°$
$\mu = 0.18$ mm^{-1}
$T = 120$ (2) K
Plate, colourless
$0.55 \times 0.18 \times 0.04$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.948$, $T_{\max} = 0.993$
8977 measured reflections

1596 independent reflections
1176 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\max} = 27.5°$
$h = -6 \rightarrow 6$
$k = -28 \rightarrow 28$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.110$
$S = 1.03$
1596 reflections
227 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0677P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Table 3
Selected interatomic distances (Å) for (II).

N11—C12	1.361 (5)	C14—O14	1.235 (5)
C12—N13	1.312 (5)	C12—C121	1.498 (6)
N13—N13a	1.369 (5)	C22—C221	1.488 (6)
N13a—C14	1.404 (5)	N21—C22	1.363 (5)
C14—C15	1.417 (6)	C22—N23	1.298 (5)
C15—C16	1.372 (6)	N23—N24	1.358 (5)
C16—N17	1.364 (5)	N24—C25	1.356 (5)
N17—C17a	1.351 (5)	C25—N21	1.329 (5)
C17a—N11	1.323 (5)	C25—N25	1.342 (5)
N13a—C17a	1.355 (5)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N17—H17···N21	0.88	2.00	2.868 (4)	168
N25—H25A···N11	0.88	2.12	2.987 (5)	167
N24—H24···N13$^{\rm i}$	0.88	2.41	3.193 (4)	149
N24—H24···O14$^{\rm i}$	0.88	2.16	2.860 (5)	136
N25—H25B···O14$^{\rm i}$	0.88	2.10	2.853 (4)	143

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

For compound (I), the space group $P2_1/c$ was uniquely assigned from the systematic absences. Crystals of (II) are monoclinic and the systematic absences permitted Cc and $C2/c$ as possible space groups. Consideration of the unit-cell volume suggested space group Cc, and this was confirmed by the subsequent structure analysis. All H atoms were located from difference maps and then treated as riding atoms, with C—H distances of 0.95 (ring CH) or 0.98 Å (CH_3) and N—H distances of 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$, or $1.5U_{eq}(C)$ for the methyl group. In the absence of any significant anomalous scattering, the Flack (1983) parameter was indeterminate (Flack & Bernardinelli, 2000) and it was not possible to establish the correct orientation of the structure of (II) relative to the polar-axis directions (Jones, 1986). Accordingly, the Friedel-equivalent reflections were merged prior to the final refinements. However, although the data are 99.2% complete to $\theta = 27.47°$, with merged equivalents the ratio of data to parameters is rather low at only 7.0.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*. For compound (I), program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). For compound (II), program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997). For both compounds, molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. NB, KDBD and SMSVW thank CNPq for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1761). Services for accessing these data are described at the back of the journal.

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