Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

5-(Trifluoromethyl)uracil

Brendan Twamley,[a]* O. D. Gupta[b] and Jean'ne M. Shreeve[b]

[a]University Research Office, 114 Morrill Hall, University of Idaho, Moscow, ID 83844-3010, USA, and [b]Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, USA

Correspondence e-mail: btwamley@uidaho.edu

Key indicators

Single-crystal X-ray study
T = 213 K
Mean σ(C–N) = 0.003 Å
R factor = 0.049
wR factor = 0.105
Data-to-parameter ratio = 11.1

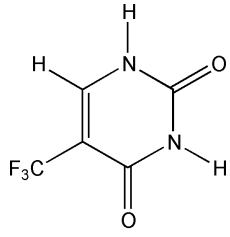
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 20 August 2002
Accepted 27 August 2002
Online 31 August 2002

The title compound, 5-trifluoromethyl-1*H*-pyrimidine-2,4-dione, 5-CF_3-$C_4H_3N_2O_2$ or $C_5H_3F_3N_2O_2$, (I), displays marked differences in packing compared to the non-fluorinated parent molecule, 5-CH_3-$C_4H_3N_2O_2$, *i.e.* thymine. Compound (I) forms a complicated three-dimensional array using hydrogen bonds [range 2.808 (3)–2.814 (3) Å], resulting in channels or voids parallel to [001], which are lined with F atoms from the CF_3 groups.

Comment

Compound (I), 5-CF_3-$C_4H_3N_2O_2$ (Fig. 1), is a partially fluorinated derivative of thymine. This compound has proven extremely useful in our continued research into fluorine chemistry (Gupta, Kirchmeier & Shreeve, 2000; Gupta, Twamley *et al.*, 2000).



(I)

The structure of non-fluorinated thymine is well known (Ozeki *et al.*, 1969; Portalone *et al.*, 1999); it crystallizes in the common space group $P2_1/c$. In the solid state, the structure consists of planar sheets of thymine molecules held together by hydrogen bonding, with the molecules facing head-to-head. Sheets are stacked on top of each other, forming a regular array. Hydrogen-bond values are in the range 2.810–2.836 Å.

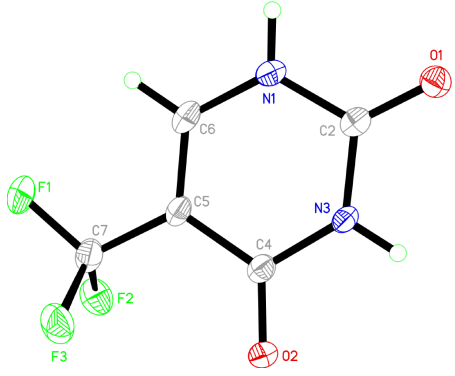


Figure 1
The molecular structure of (I). Atomic displacement ellipsoids are shown at the 30% probability level.

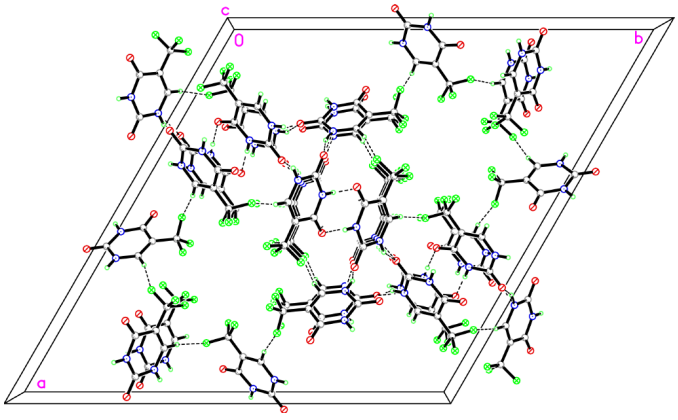


Figure 2
A ball-and-stick packing diagram of (I). Hydrogen bonding is indicated by dashed lines.

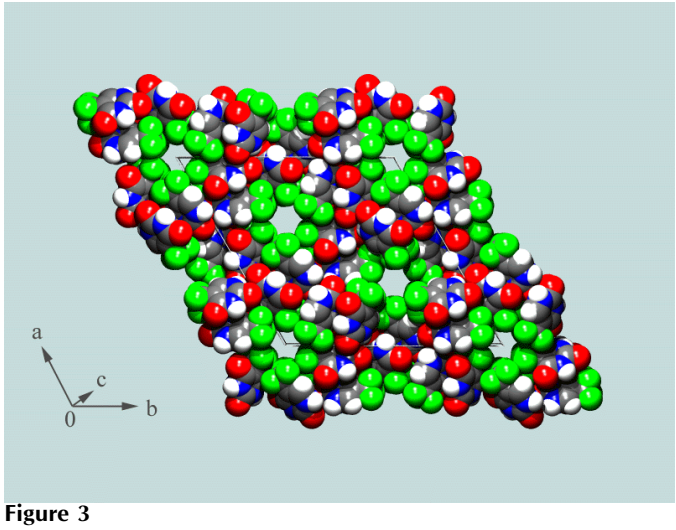


Figure 3
A space-filling representation of (I). F atoms are shown in green. The cell axes are shown separately for clarity.

When the methyl group is fluorinated, the packing changes dramatically. Compound (I) now crystallizes in the trigonal space group $R\overline{3}$ and the hydrogen-bonded sheet motif is no longer observed. In this case, a complicated three-dimensional 'infinite' array is formed, with the uracil molecules hydrogen-bonding in pair-units, head-to-tail and side-by-side. These units are essentially planar with an out-of-plane r.m.s. deviation of 0.0241 Å (for all non-F atoms including H atoms). These pair-units then hydrogen bond to four other pair-units (Table 1). A section of the packing is shown in Fig. 2. This packing arrangement causes the CF_3 groups to form a symmetry-imposed pseudo-hexagonal channel. The F atoms become the lining for the channel, which is approximately 3.6 Å wide and extends parallel to [001]. The volume of these channels in the unit cell is approximately 50 Å^3. Fig. 3 displays these channels outlined in green. The orientation of the CF_3 groups brings an F atom into close proximity to an H atom [H6*A*···F3^{iii}; symmetry code: (iii) $x-y, x, 1-z$] of a neighboring molecule. There is also a close intramolecular contact with the same H atom (F1···H6*A*). These distances are recorded in Table 1. Although these values are within the sum of the van der Waals radii of both fluorine and hydrogen, whether these are weak interactions is questionable. Intermolecular distances of $d < 2.35$ Å (d = H···F intermolecular distance) are generally accepted to be 'true' weak hydrogen-bonding interactions (Desiraju & Steiner, 2001).

Experimental

The sample was obtained commercially from Fluorochem (Cat. No. 3333), and recrystallized from CH_3CN.

Crystal data

$C_5H_3F_3N_2O_2$
M_r = 180.09
Trigonal, $R\overline{3}$
a = 25.5695 (17) Å
c = 5.1934 (5) Å
V = 2940.5 (4) Å^3
Z = 18
D_x = 1.831 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2171 reflections
θ = 2.8–23.3°
μ = 0.20 mm^{-1}
T = 213 (2) K
Fragment, colorless
0.35 × 0.25 × 0.15 mm

Data collection

Bruker SMART 1K CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.935, T_{max} = 0.971
12 551 measured reflections
1208 independent reflections
896 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 25.5°
$h = -30 \rightarrow 27$
$k = -28 \rightarrow 30$
$l = -6 \rightarrow 6$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.105
S = 1.09
1208 reflections
109 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 5.2597P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*A*···O1^{i}	0.87	2.03	2.808 (3)	148
N3—H3*A*···O2^{ii}	0.87	1.94	2.814 (3)	176
C6—H6*A*···F1	0.94	2.35	2.697 (3)	101
C6—H6*A*···F3^{iii}	0.94	2.41	3.337 (3)	169

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

H atoms were positioned geometrically and refined using a riding model, with U_{iso} values constrained to be $1.2U_{eq}$ of the carrier atom.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT–Plus* (Bruker, 1999); program(s) used to solve structure: *XS* in *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XCIF* in *SHELXTL*.

The Bruker (Siemens) SMART CCD diffraction facility was established at the University of Idaho with the assistance of the NSF–EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA. The authors thank A. Vij for collecting the data.

References

Bruker (1999). *SMART* (Version 5.025) and *SAINT-Plus* (Version 5.01). Bruker AXS Inc., Madison, Wisconsin, USA.

Desiraju G. R. & Steiner, T. (2001). *The Weak Hydrogen Bond In Structural Chemistry and Biology*, IUCr Monograph No. 9. Oxford University Press.

Gupta, O. D., Kirchmeier, R. L. & Shreeve, J. M. (2000). *Inorg. Chem.* **39**, 117–120.

Gupta, O. D., Twamley, B., Kirchmeier, R. L. & Shreeve, J. M. (2000). *J. Fluorine Chem.* **106**, 199–204.

Ozeki, K., Sakabe, N. & Tanaka, J. (1969). *Acta Cryst.* B**25**, 1038–1045.

Portalone, G., Bencivenni, L., Colapietro, M., Pieretti, A. & Ramondo F. (1999). *Acta Chem. Scand.* **53**, 57–59.

Sheldrick, G. M. (2001). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2001). *SADABS*. Version 2.01. Bruker AXS Inc., Madison, Wisconsin, USA.