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Ethyl (2*E*)-3-dimethylamino-2-(5-methyl-1,2,4-triazolo[1,5-*a*]pyrimidin-7-yl)prop-2-enoate

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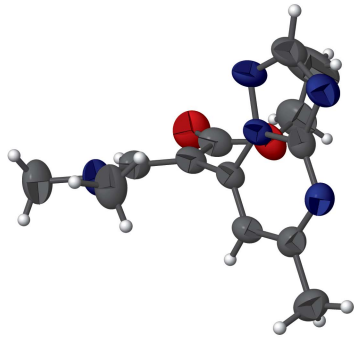
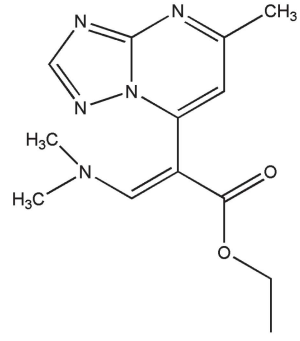
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecule, $C_{13}H_{17}N_5O_2$, the triazolopyrimidine ring system and the (dimethyamino)acrylate unit are nearly perpendicular to each other, subtending a dihedral angle of 78.55 (6)°. In the crystal, molecules are linked into a *C*(6) chain along the *b*-axis direction *via* C—H···O hydrogen bonds.

3D view



Chemical scheme



Structure description

Triazolopyrimidine derivatives possess a wide variety of interesting biological activities such as anti-tumor (Hiasa *et al.*, 1982), anti-inflammatory (Ashour *et al.*, 2013) and inhibition of KDR kinase (Fraley *et al.*, 2002). They have also proved to be promising anticancer agents (Lauria *et al.*, 2013). Formamide acetals are useful reagents in the synthesis of enaminones; these compounds are found to be useful precursors for the synthesis of several heterocyclic compounds (Abdulla & Brinkmeyer, 1979). The present work is a continuation of our work on triazolopyrimidine derivatives (Elotmani *et al.*, 2002).

In the crystal of the title compound (Fig. 1), the molecules are linked into a *C*(6) chain along the *b*-axis direction *via* C—H···O hydrogen bonds (Fig. 2 and Table 1).

Synthesis and crystallization

A mixture of ethyl 2-(5-methyl-[1,2,4]triazolo[1,5-*a*]pyrimidin-7-yl)acetate (1 g, 4,5 mmol) and *N*,*N*-dimethylformamide diethyl acetal (DMF/DEA) (0.94 ml, 5.4 mmol) was heated to 423 K in solvent-free conditions until completion (TLC). The reaction was

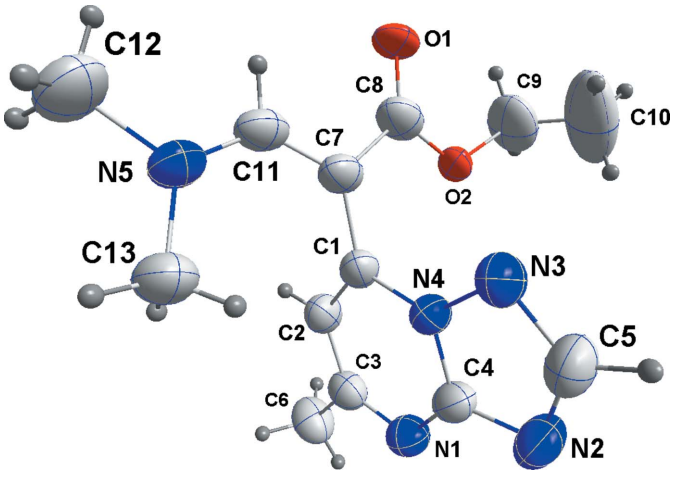


Figure 1
The molecular structure of the title compound, with the atom-labeling scheme and 50% probability ellipsoids.

cooled to room temperature and, after addition ethanol to the reaction, the solid obtained was purified by column chromatography on silica gel with ethyl acetate–hexane (4:1) as eluent. Colourless crystals were isolated when the solvent was allowed to evaporate (yield 67%, m.p. 453–455 K).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The appearance of the displacement ellipsoids for the ester group (atoms C9 and C10) is suggestive of a degree of disorder but this was not sufficiently severe as to produce resolved sites for these carbon atoms.

Acknowledgements

JTM thanks Tulane University for support of the Tulane Crystallography Laboratory.

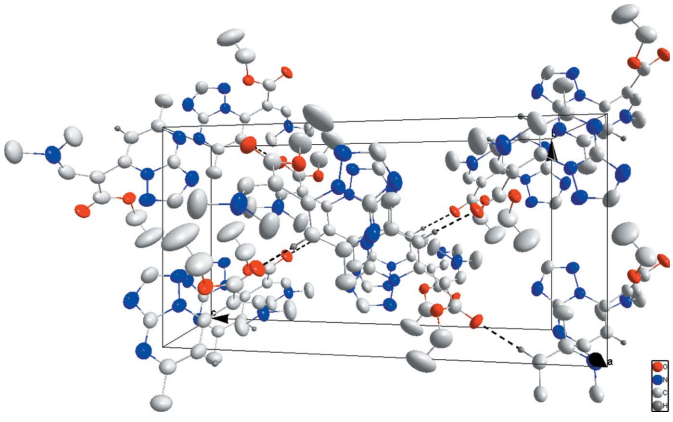


Figure 2
A packing diagram of the title compound, viewed along the *a* axis, with C—H···O hydrogen bonds shown as dotted lines. H atoms not involved in the hydrogen bonds have been omitted.

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O1^{i}	0.93	2.36	3.2461 (19)	159

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_{17}N_5O_2$
M_r	275.32
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	298
a, b, c (Å)	7.1482 (15), 10.306 (2), 19.705 (4)
β (°)	99.711 (3)
V (Å^3)	1430.9 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.30 × 0.15 × 0.14
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.84, 0.99
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26739, 3733, 1821
R_{int}	0.051
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.679
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.145, 0.87
No. of reflections	3733
No. of parameters	184
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.33, −0.24

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

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full crystallographic data

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Crystal data

$C_{13}H_{17}N_5O_2$
M_r = 275.32
Monoclinic, $P2_1/n$
a = 7.1482 (15) Å
b = 10.306 (2) Å
c = 19.705 (4) Å
β = 99.711 (3)°
V = 1430.9 (5) Å^3
Z = 4
$F(000)$ = 584
D_x = 1.278 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7291 reflections
θ = 2.9–28.7°
μ = 0.09 mm^{-1}
T = 298 K
Column, colourless
0.30 × 0.15 × 0.14 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
T_{min} = 0.84, T_{max} = 0.99
26739 measured reflections
3733 independent reflections
1821 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 28.8°, θ_{min} = 2.1°
h = −9→9
k = −13→13
l = −26→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.145
S = 0.87
3733 reflections
184 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0857P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω, collected at φ = 0.00, 90.00 and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ, collected at ω = –30.00 and 210.00°. The scan time was 25 sec/frame.

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 $F^2 > 2\text{sigma}(F^2)$ 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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.99 Å). All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.3200 (2)	0.87934 (14)	0.75398 (7)	0.0827 (4)
O2	0.14311 (19)	0.81319 (12)	0.65471 (6)	0.0724 (4)
N1	0.25961 (18)	0.52376 (13)	0.49261 (6)	0.0505 (4)
N2	0.3453 (2)	0.72746 (15)	0.44616 (6)	0.0594 (4)
N3	0.4499 (2)	0.82908 (12)	0.54873 (7)	0.0562 (4)
N4	0.38948 (17)	0.70581 (11)	0.55915 (6)	0.0423 (3)
N5	0.7588 (2)	0.63725 (14)	0.73030 (6)	0.0574 (4)
C1	0.3848 (2)	0.64585 (14)	0.62119 (7)	0.0426 (4)
C2	0.3167 (2)	0.52272 (15)	0.61611 (8)	0.0475 (4)
H2	0.3109	0.4760	0.6561	0.057*
C3	0.2544 (2)	0.46373 (15)	0.55158 (8)	0.0476 (4)
C4	0.3276 (2)	0.64584 (15)	0.49726 (7)	0.0453 (4)
C5	0.4170 (3)	0.83295 (18)	0.48033 (9)	0.0627 (5)
H5	0.4433	0.9073	0.4569	0.075*
C6	0.1744 (3)	0.32954 (16)	0.54899 (10)	0.0674 (5)
H6A	0.1217	0.3079	0.5023	0.101*
H6B	0.0767	0.3253	0.5769	0.101*
H6C	0.2733	0.2691	0.5661	0.101*
C7	0.4400 (2)	0.71961 (14)	0.68543 (7)	0.0482 (4)
C8	0.3019 (3)	0.81162 (16)	0.70288 (9)	0.0590 (5)
C9	0.0033 (3)	0.9128 (2)	0.65923 (13)	0.0949 (7)
H9A	−0.1229	0.8760	0.6471	0.114*
H9B	0.0176	0.9439	0.7063	0.114*
C10	0.0219 (5)	1.0159 (3)	0.61586 (16)	0.1600 (15)
H10A	−0.0727	1.0801	0.6201	0.240*
H10B	0.1458	1.0534	0.6283	0.240*
H10C	0.0055	0.9856	0.5692	0.240*
C11	0.6029 (3)	0.70522 (15)	0.73224 (8)	0.0511 (4)
H11	0.6044	0.7516	0.7728	0.061*
C12	0.9119 (3)	0.6354 (2)	0.78962 (9)	0.0810 (6)
H12A	1.0272	0.6652	0.7759	0.122*

H12B	0.9294	0.5484	0.8070	0.122*
H12C	0.8798	0.6912	0.8249	0.122*
C13	0.7933 (3)	0.5638 (2)	0.67024 (9)	0.0715 (6)
H13A	0.7484	0.6125	0.6292	0.107*
H13B	0.7273	0.4824	0.6685	0.107*
H13C	0.9269	0.5482	0.6736	0.107*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.1003 (11)	0.0832 (9)	0.0686 (9)	0.0129 (8)	0.0252 (8)	−0.0312 (7)
O2	0.0806 (9)	0.0744 (8)	0.0631 (8)	0.0308 (7)	0.0152 (7)	−0.0034 (6)
N1	0.0498 (8)	0.0552 (8)	0.0457 (8)	−0.0006 (6)	0.0061 (6)	−0.0050 (6)
N2	0.0736 (10)	0.0670 (9)	0.0373 (8)	−0.0023 (8)	0.0089 (7)	0.0082 (7)
N3	0.0760 (10)	0.0442 (8)	0.0502 (8)	−0.0021 (7)	0.0160 (7)	0.0060 (6)
N4	0.0533 (8)	0.0402 (7)	0.0347 (7)	0.0023 (6)	0.0111 (6)	0.0016 (5)
N5	0.0630 (9)	0.0706 (9)	0.0368 (8)	0.0077 (8)	0.0030 (6)	−0.0103 (6)
C1	0.0504 (9)	0.0430 (9)	0.0360 (8)	0.0070 (7)	0.0120 (7)	0.0022 (6)
C2	0.0549 (10)	0.0452 (9)	0.0442 (9)	0.0038 (7)	0.0137 (7)	0.0059 (7)
C3	0.0431 (9)	0.0463 (9)	0.0538 (10)	0.0036 (7)	0.0087 (7)	−0.0035 (7)
C4	0.0475 (9)	0.0519 (9)	0.0364 (8)	0.0046 (7)	0.0065 (7)	−0.0023 (7)
C5	0.0809 (13)	0.0601 (11)	0.0483 (11)	−0.0024 (10)	0.0142 (9)	0.0141 (9)
C6	0.0628 (12)	0.0512 (10)	0.0869 (14)	−0.0056 (9)	0.0090 (10)	−0.0038 (9)
C7	0.0667 (11)	0.0450 (9)	0.0351 (8)	0.0031 (8)	0.0149 (8)	−0.0011 (6)
C8	0.0789 (13)	0.0536 (10)	0.0495 (10)	0.0067 (9)	0.0251 (9)	−0.0031 (8)
C9	0.0960 (18)	0.0880 (16)	0.1076 (19)	0.0383 (14)	0.0372 (14)	0.0040 (14)
C10	0.181 (3)	0.126 (3)	0.189 (3)	0.084 (2)	0.076 (3)	0.070 (2)
C11	0.0699 (12)	0.0492 (9)	0.0360 (8)	−0.0026 (8)	0.0139 (8)	−0.0061 (7)
C12	0.0778 (14)	0.1117 (17)	0.0483 (11)	0.0085 (12)	−0.0044 (10)	−0.0136 (10)
C13	0.0686 (13)	0.0923 (14)	0.0525 (11)	0.0161 (11)	0.0066 (9)	−0.0211 (10)

Geometric parameters (Å, º)

O1—C8	1.2140 (19)	C5—H5	0.9300
O2—C8	1.351 (2)	C6—H6A	0.9600
O2—C9	1.446 (2)	C6—H6B	0.9600
N1—C3	1.3226 (19)	C6—H6C	0.9600
N1—C4	1.346 (2)	C7—C11	1.366 (2)
N2—C4	1.3343 (19)	C7—C8	1.451 (2)
N2—C5	1.335 (2)	C9—C10	1.384 (3)
N3—C5	1.329 (2)	C9—H9A	0.9700
N3—N4	1.3686 (17)	C9—H9B	0.9700
N4—C4	1.3722 (18)	C10—H10A	0.9600
N4—C1	1.3753 (17)	C10—H10B	0.9600
N5—C11	1.322 (2)	C10—H10C	0.9600
N5—C12	1.461 (2)	C11—H11	0.9300
N5—C13	1.461 (2)	C12—H12A	0.9600
C1—C2	1.357 (2)	C12—H12B	0.9600

C1—C7	1.472 (2)	C12—H12C	0.9600
C2—C3	1.412 (2)	C13—H13A	0.9600
C2—H2	0.9300	C13—H13B	0.9600
C3—C6	1.494 (2)	C13—H13C	0.9600

C8—O2—C9	118.22 (15)	C11—C7—C1	126.79 (14)
C3—N1—C4	116.15 (13)	C8—C7—C1	116.53 (15)
C4—N2—C5	102.12 (13)	O1—C8—O2	122.34 (17)
C5—N3—N4	100.00 (13)	O1—C8—C7	126.19 (18)
N3—N4—C4	110.32 (12)	O2—C8—C7	111.46 (14)
N3—N4—C1	127.31 (12)	C10—C9—O2	111.6 (2)
C4—N4—C1	122.36 (13)	C10—C9—H9A	109.3
C11—N5—C12	120.37 (14)	O2—C9—H9A	109.3
C11—N5—C13	123.80 (14)	C10—C9—H9B	109.3
C12—N5—C13	115.81 (15)	O2—C9—H9B	109.3
C2—C1—N4	114.63 (13)	H9A—C9—H9B	108.0
C2—C1—C7	125.96 (13)	C9—C10—H10A	109.5
N4—C1—C7	119.28 (13)	C9—C10—H10B	109.5
C1—C2—C3	121.60 (14)	H10A—C10—H10B	109.5
C1—C2—H2	119.2	C9—C10—H10C	109.5
C3—C2—H2	119.2	H10A—C10—H10C	109.5
N1—C3—C2	122.58 (15)	H10B—C10—H10C	109.5
N1—C3—C6	118.06 (15)	N5—C11—C7	131.64 (15)
C2—C3—C6	119.35 (15)	N5—C11—H11	114.2
N2—C4—N1	128.08 (14)	C7—C11—H11	114.2
N2—C4—N4	109.24 (14)	N5—C12—H12A	109.5
N1—C4—N4	122.68 (13)	N5—C12—H12B	109.5
N3—C5—N2	118.31 (15)	H12A—C12—H12B	109.5
N3—C5—H5	120.8	N5—C12—H12C	109.5
N2—C5—H5	120.8	H12A—C12—H12C	109.5
C3—C6—H6A	109.5	H12B—C12—H12C	109.5
C3—C6—H6B	109.5	N5—C13—H13A	109.5
H6A—C6—H6B	109.5	N5—C13—H13B	109.5
C3—C6—H6C	109.5	H13A—C13—H13B	109.5
H6A—C6—H6C	109.5	N5—C13—H13C	109.5
H6B—C6—H6C	109.5	H13A—C13—H13C	109.5
C11—C7—C8	116.56 (14)	H13B—C13—H13C	109.5

C5—N3—N4—C4	0.53 (16)	C1—N4—C4—N1	−0.6 (2)
C5—N3—N4—C1	−178.47 (14)	N4—N3—C5—N2	−0.7 (2)
N3—N4—C1—C2	179.68 (14)	C4—N2—C5—N3	0.5 (2)
C4—N4—C1—C2	0.8 (2)	C2—C1—C7—C11	76.7 (2)
N3—N4—C1—C7	3.5 (2)	N4—C1—C7—C11	−107.55 (18)
C4—N4—C1—C7	−175.41 (14)	C2—C1—C7—C8	−99.24 (19)
N4—C1—C2—C3	−0.7 (2)	N4—C1—C7—C8	76.51 (19)
C7—C1—C2—C3	175.20 (15)	C9—O2—C8—O1	9.6 (3)
C4—N1—C3—C2	−0.3 (2)	C9—O2—C8—C7	−171.17 (15)
C4—N1—C3—C6	178.14 (14)	C11—C7—C8—O1	2.3 (3)

C1—C2—C3—N1	0.5 (2)	C1—C7—C8—O1	178.67 (16)
C1—C2—C3—C6	−177.89 (15)	C11—C7—C8—O2	−176.93 (14)
C5—N2—C4—N1	179.27 (16)	C1—C7—C8—O2	−0.6 (2)
C5—N2—C4—N4	−0.10 (18)	C8—O2—C9—C10	97.9 (3)
C3—N1—C4—N2	−178.96 (15)	C12—N5—C11—C7	−177.77 (18)
C3—N1—C4—N4	0.3 (2)	C13—N5—C11—C7	4.1 (3)
N3—N4—C4—N2	−0.28 (17)	C8—C7—C11—N5	−175.16 (17)
C1—N4—C4—N2	178.77 (13)	C1—C7—C11—N5	8.9 (3)
N3—N4—C4—N1	−179.69 (14)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O1^{i}	0.93	2.36	3.2461 (19)	159

Symmetry code: (i) −*x*+1/2, *y*−1/2, −*z*+3/2.