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7-Ethoxycarbonylmethyl-5-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine

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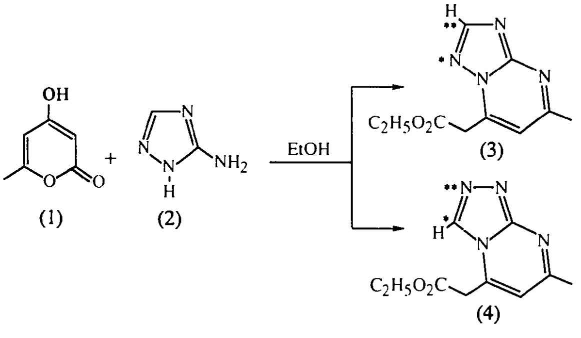
Abstract

The crystal structure of the title ester, ethyl 5-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine-7-acetate, $C_{10}H_{12}N_4O_2$, is described. In the field of heterocyclic chemistry, the prospects offered for the design of antiviral agents, as well as the chemistry of interaction of N-bridged purine analogue ligands with heavy metals, are of biological and environmental importance. This study has elucidated the isomeric structure of a heterocyclic product of the condensation of 3-amino-1,2,4-triazole and 4-hydroxy-6-methyl-2*H*-pyran-2-one (triacetic acid lactone).

Comment

The condensation of triacetic acid lactone, (1), with 3-amino-1,2,4-triazole, (2), in hot ethanol leads to two possible products, namely, ethyl 1,2,4-triazolo[1,5-*a*]-pyrimidine-7-acetate, (3), and ethyl 1,2,4-triazolo[4,3-*a*]pyrimidine-5-acetate, (4), depending to the orientation of the triacetic acid lactone attack and without consideration of the tautomeric form of each product. In the literature, several reports have been devoted to the synthesis of 1,2,4-triazolopyrimidines using other 1,3-difunctional synthons (Shaban & Nasr, 1990; Reiter, Pougo & Dvortsak, 1987; Moute, Kleschick, Meikle & Snider, 1989; Kuenstlinger & Breitmaier, 1983). Usual analytical and spectroscopic techniques do not permit identification of the isomeric compounds (3) and (4), and so, in order to resolve this problem, we undertook an X-ray diffraction study of the reaction product.



An *ORTEP* plot (Johnson, 1965) showing the atom-labeling scheme is presented in Fig. 1. Although the metric symmetry suggests an orthorhombic lattice, examination of equivalents in the *mmm* symmetry showed inconsistent results (R_{int} = 0.050). At this stage, a monoclinic cell with space group $P2_1/c$ was adopted from consideration of the systematic absences and a successful solution was then obtained with convergence parameters R_{int} = 0.012, R = 0.041 and wR = 0.059. The structures of compounds (3) and (4) differ only in the carbon and nitrogen occupation of the (*) and (**) sites (see scheme above) and owing to the strong resonance in this ring, the determination of both carbon and nitrogen positions would be possible only when the position of the bonded H atom was determined. Anisotropic refinement of the non-H atoms followed by difference Fourier synthesis gave unambiguous evidence of the majority of the H-atom positions, including a peak with a density of 0.50 e Å^{-3} ($\Delta\rho_{max}$ = 0.20 e Å^{-3}), and good geometrical parameters. The H atom indicated by this peak, correctly bonded to the atom in the (**) position, was systematically found when the refinement of non-H atoms was carried out for both hypotheses of the occupation of this pair of sites. A final refinement of the anisotropic parameters for the non-H atoms and the isotropic parameters for the H atoms gave a displacement parameter of B_{eq} = 4.6 (5) Å^2 for the H1 atom, confirming the structure of the title compound, (3).

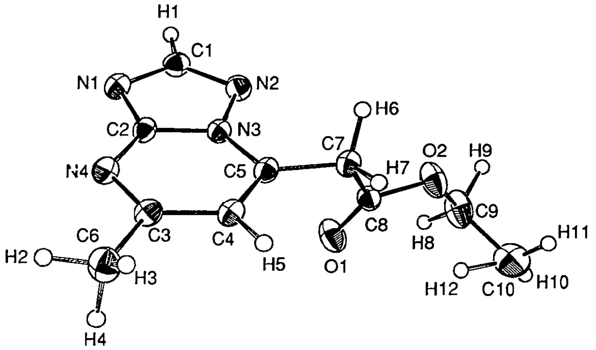


Fig. 1. *ORTEP* (Johnson, 1965) plot of the title compound with the atomic numbering scheme. Displacement ellipsoids are at the 20% probability level.

The two ring moieties are planar, with a maximum deviation from the mean plane of 0.028 (3) Å, for N3. The bond lengths and angles within the two rings are in good agreement with the values reported for DMTP (5,7-dimethyl-1,2,4-triazolo[1,5-*a*]pyrimidine) acting as a monodentate ligand in metal coordination complexes, in which the N1 atom is the most preferred binding site (Biagini, Manotti, Tiripicchio, Reedijk & Haasnoot, 1986; Salas, Romero, Rahmani & Faure, 1994).

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Experimental

Crystals of the title compound were obtained by slow evaporation of an ethanol solution.

Crystal data

$C_{10}H_{12}N_4O_2$
$M_r = 220.23$
Monoclinic
$P2_1/c$
$a = 11.507\,(6)$ Å
$b = 12.179\,(1)$ Å
$c = 7.928\,(10)$ Å
$\beta = 90.03\,(3)^\circ$
$V = 1111.1\,(5)$ Å^3
$Z = 4$
$D_x = 1.317$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7–12^\circ$
$\mu = 0.089$ mm^{-1}
$T = 298$ K
Block
0.6 × 0.25 × 0.2 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2596 measured reflections
2238 independent reflections
1152 observed reflections $[I > 6\sigma(I)]$

$R_{\rm int} = 0.012$
$\theta_{\max} = 27^\circ$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity decay: <4%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.059$
$S = 1.55$
1152 reflections
194 parameters
$w = 4F_o^2/[\sigma^2(I) + (0.07F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.200$ e Å^{-3}
$\Delta\rho_{\min} = -0.179$ e Å^{-3}

Extinction correction: secondary (Stout & Jensen, 1968)
Extinction coefficient: 8.182×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$
O1	0.1679 (2)	0.5071 (2)	0.2023 (2)	6.44 (5)
O2	0.1376 (2)	0.5996 (2)	0.4412 (2)	6.62 (5)
N1	0.3301 (2)	0.1304 (2)	0.3149 (3)	4.31 (4)
N2	0.2353 (2)	0.2766 (2)	0.4320 (2)	4.18 (4)
N3	0.3318 (1)	0.3103 (1)	0.3455 (2)	3.50 (4)
N4	0.4861 (2)	0.2311 (2)	0.1858 (3)	4.06 (4)
C1	0.2408 (2)	0.1691 (2)	0.4085 (3)	4.44 (5)
C2	0.3877 (2)	0.2217 (2)	0.2765 (3)	3.62 (4)
C3	0.5281 (2)	0.3322 (2)	0.1703 (3)	4.08 (5)
C4	0.4740 (2)	0.4249 (2)	0.2435 (3)	3.89 (5)
C5	0.3744 (2)	0.4148 (2)	0.3338 (3)	3.65 (4)
C6	0.6378 (2)	0.3460 (2)	0.0710 (4)	5.70 (6)
C7	0.3110 (2)	0.5041 (2)	0.4232 (3)	4.14 (5)
C8	0.1986 (2)	0.5354 (2)	0.3392 (2)	4.13 (5)
C9	0.0272 (3)	0.6433 (3)	0.3756 (5)	7.51 (8)
C10	0.0399 (3)	0.7603 (3)	0.3356 (4)	8.01 (9)

Table 2. *Selected geometric parameters (Å, °)*

O1—C8	1.192 (3)	N4—C2	1.347 (3)
O2—C8	1.326 (3)	N4—C3	1.328 (3)
O2—C9	1.472 (4)	C3—C4	1.414 (3)
N1—C1	1.352 (3)	C3—C6	1.497 (4)
N1—C2	1.329 (3)	C4—C5	1.357 (3)
N2—N3	1.368 (3)	C5—C7	1.490 (3)
N2—C1	1.323 (3)	C7—C8	1.503 (3)
N3—C2	1.371 (3)	C9—C10	1.467 (5)
N3—C5	1.366 (3)		
C8—O2—C9	117.0 (2)	N4—C3—C6	117.4 (2)
C1—N1—C2	102.3 (2)	C4—C3—C6	119.8 (2)
N3—N2—C1	100.8 (2)	C3—C4—C5	121.1 (2)
N2—N3—C2	110.1 (2)	N3—C5—C4	115.0 (2)
N2—N3—C5	127.2 (2)	N3—C5—C7	118.2 (2)
C2—N3—C5	122.6 (2)	C4—C5—C7	126.8 (2)
C2—N4—C3	115.8 (2)	C5—C7—C8	113.3 (2)
N1—C1—N2	117.3 (2)	O1—C8—O2	124.7 (2)
N1—C2—N3	109.5 (2)	O1—C8—C7	125.7 (2)
N1—C2—N4	127.8 (2)	O2—C8—C7	109.5 (2)
N3—C2—N4	122.7 (2)	O2—C9—C10	110.0 (3)
N4—C3—C4	122.8 (2)		

The crystal structure was solved by direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). The refinement were performed by full-matrix least-squares methods employing anisotropic displacement parameters for non-H atoms. The H atoms were found by Fourier synthesis, placed in computed positions and refined isotropically. All calculations were performed on a MicroVAX 3100 computer using the *MolEN* package (Fair, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1204). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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