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Ethyl 3-methylimidazo[1,2-*a*]pyrimidine-2-carboxylate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.058
wR factor = 0.171
Data-to-parameter ratio = 17.3

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

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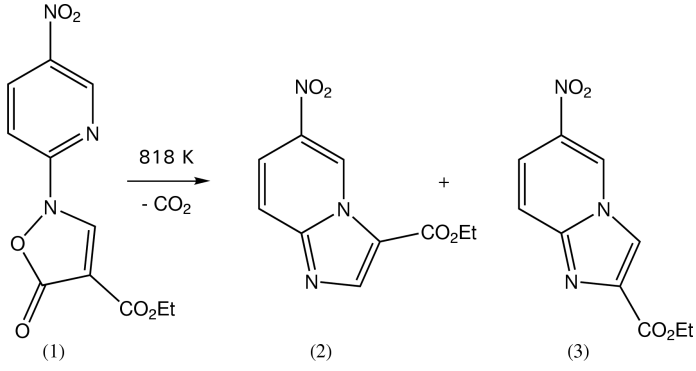
Two independent molecules comprise the asymmetric unit for the title compound, $C_{10}H_{11}N_3O_2$, and these differ in the relative orientations of the ester side chains. Molecules associate *via* π–π interactions forming stacks in the crystal structure.

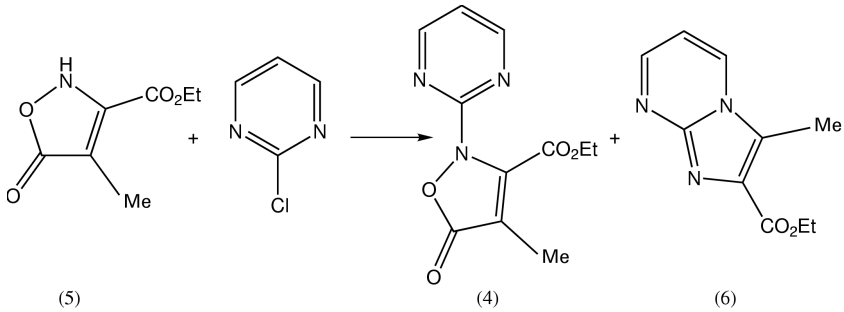
Comment

We have recently reported the conversion of heterocyclylisoxazol-5(2*H*)-ones to imidazoles by flash vacuum pyrolysis (Prager & Singh, 1993) or photolysis (Prager *et al.*, 1994). While these reactions, particularly the pyrolytic, proceeded in very high yields, in a few cases we noted minor amounts of products arising from rearrangement of the initially formed carbene. For instance, the 3-nitropyridylisoxazolone (1) gave 87% of the imidazopyridine (2), and 11% of the rearranged isomer (3) (Prager & Singh, 1993).



(1) (2) (3)

We have now subjected the pyrimidinylisoxazolone (4), prepared by reaction of the isoxazolone (5) with 2-chloropyrimidine, to flash vacuum pyrolysis at 813 K, and have isolated a single product in high yield. Initially, we were not convinced that it was the expected imidazole (6), even though



(5) (4) (6)

the spectral data were consistent with those of other derivatives, as the product was far less soluble than analogous

compounds, was much more polar, and was strongly fluorescent. Accordingly, we have determined the structure of the product by single-crystal X-ray analysis, and have confirmed that the product was indeed the imidazole (6). Since this work was completed, (6) has been reported in a patent application in which it was incorporated into the side chain of a β-lactam (Nakai *et al.*, 1993).

The asymmetric unit of (6) comprises two independent molecules, as illustrated in Fig. 1. The major difference between the two molecules is found in the conformation of the ester groups so that the imidazole nitrogen (N1) and carbonyl (O2) atoms are *anti* in molecule *A* and *syn* in molecule *B*. The fused ring system is effectively planar with a mean deviation of 0.002 Å for molecule *A*; 0.013 Å for molecule *B*. The side chain is coplanar with the aromatic group, as seen in the values of the O2′*A*—C2′*A*—C2*A*—N1*A*, O2*A*—C2′*A*—O2′*A*—C21*A* and C2′*A*—O2′*A*—C21*A*—C22*A* torsion angles of 176.5 (3), −4.0 (4) and 172.4 (2)°, respectively; the comparable angles for molecule *B* are −6.0 (5), −0.2 (5) and 168.1 (2)°, respectively.

The crystal structure is stabilized by π–π interactions. The average separation between the two five-membered ring systems of the two molecules comprising the asymmetric unit is 3.44 Å and the angle between them is 2.53 (7)°. Symmetry-related five-membered rings of molecule A are separated by 3.45 Å (symmetry code: $-1-x, 1-y, 1-z$) and, similarly, symmetry-related six-membered rings of molecule B are separated by 3.59 Å (symmetry code: $-x, 1-y, -z$). Such an arrangement leads to stacks of molecules approximately parallel to $(20\bar{2})$.

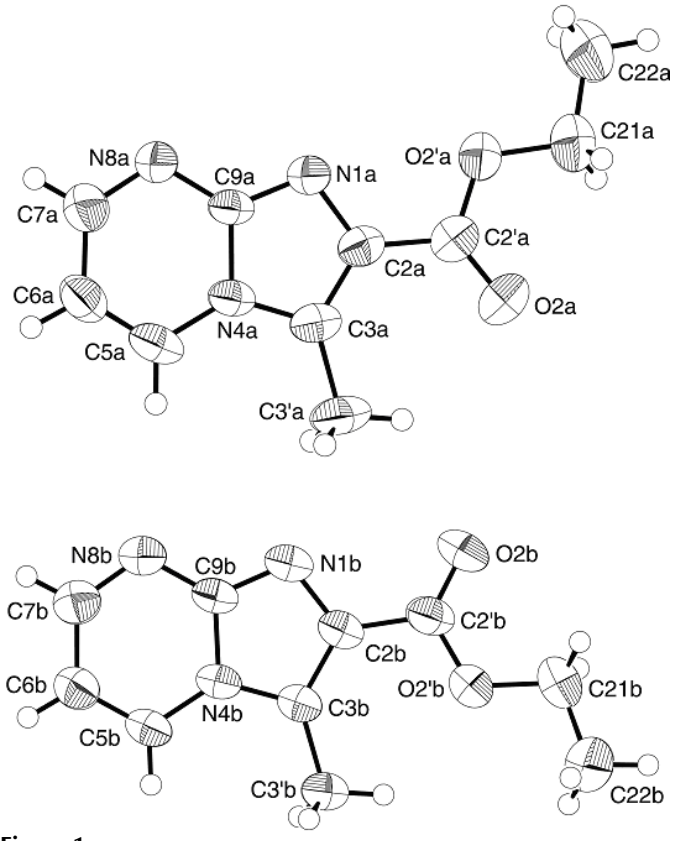


Figure 1
The molecular structure and crystallographic numbering scheme for (6). Displacement ellipsoids are shown at the 50% probability level (Johnson, 1976).

Experimental

For the preparation of ethyl 4-methyl-5-oxo-2-(pyrimidin-2-yl)-2,5-dihydroisoxazole-3-carboxylate, (4), the isoxazolone (5) (Adembri & Tedeschi, 1965) (500 mg, 2.9 mmol) and 2-chloropyrimidine (340 mg, 0.29 mmol) were refluxed in dichloroethane (20 ml) for 16 h. The solvent was removed and the resulting solid was recrystallized from *tert*-butyl methyl ether to give (4) as yellow needles in 80% yield (m.p. 335–337 K). Analysis found: C 53.01, H 4.45, N 16.86%; $C_{11}H_{11}N_3O_4$ requires: C 52.82, H 4.47, N 16.87%. ^{1}H NMR: δ 1.34 (*t, J* = 7 Hz, 3H), 4.23 (*q, J* = 7 Hz, 2H), 7.15 (*t, J* = 5 Hz, 1H), 8.64 (*d, J* = 5 Hz, 2H). ^{13}C NMR: δ 7.4 (*q*), 13.8 (*q*), 62.6 (*t*), 109.6 (*s*), 118.3 (*d*), 148.0 (*d*), 156.8 (*s*), 158.5 (*s*), 159.3 (*s*), 168.8 (*s*). IR ν_{max}: 1763, 1740, 1571, 1406, 1237 cm^{-1}. MS *m*/*z*: 249 (M^+, 100%), 204 (12), 188 (11), 176 (15), 160 (34), 133 (22), 79 (91), 67 (19), 53 (91). For the pyrolysis of (4); the isoxazolone (4) (200 mg, 0.8 mmol) was pyrolysed under FVP conditions (813 K, 393 K, 0.05 mmHg, 2 h). A solid was collected from the pyrolysis tube and recrystallized from ethanol to give colourless needles of ethyl 3-methylimidazo[1,2-*a*]pyrimidine-2-carboxylate, (6), in 90% yield (m.p. 468–469 K). Analysis found: C 58.54, H 5.40, N 20.48%; $C_9H_{11}N_3O_2$ requires: C 58.64, H 5.31, N 20.40%. ^{1}H NMR: δ 1.28 (*t, J* = 7 Hz, 3H), 2.65 (*s*, 3H), 4.29 (*q, J* = 7 Hz, 2H), 6.90 (*dd*, *J*′ = 7, *J*″ = 4 Hz, 1H), 8.34 (*dd*, *J*′ = 7, *J*″ = 2 Hz, 1H), 8.46 (*dd*, *J*′ = 4, *J*″ = 2 Hz, 1H). ^{13}C NMR: δ 8.7 (*q*), 14.1 (*q*), 60.6 (*t*), 109.3 (*d*), 124.7 (*s*), 131.6 (*s*), 132.7 (*s*), 146.3 (*s*), 154.2 (*d*), 163.5 (*s*). IR ν_{max}: 1702, 1503, 1196, 1086, 786, 768 cm^{-1}. MS *m*/*z*: 205 (M^+, 11%), 158 (4), 133 (100), 132 (77), 78 (14).

Crystal data

$C_{10}H_{11}N_3O_2$
M_r = 205.22
Triclinic, $P\bar{1}$
a = 9.910 (1) Å
b = 11.653 (2) Å
c = 9.000 (2) Å
α = 100.93 (1)°
β = 95.31 (1)°
γ = 89.24 (1)°
V = 1016.0 (3) Å^3
Z = 4
D_x = 1.341 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 19.8–22.0°
μ = 0.10 mm^{-1}
T = 293 K
Block, colourless
0.32 × 0.32 × 0.24 mm

Data collection

Rigaku AFC-6*R* diffractometer
ω–2θ scans
4967 measured reflections
4696 independent reflections
2373 reflections with $I > 2\sigma(I)$
R_{int} = 0.059
θ_{max} = 27.6°
$h = 0 \rightarrow 12$
$k = -15 \rightarrow 15$
$l = -11 \rightarrow 11$
3 standard reflections
every 400 reflections
intensity decay: 5.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.171
S = 1.03
4696 reflections
272 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0827P)^2 + 0.0227P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

The H atoms were placed in geometrically calculated positions and included in the final refinement in the riding model approximation with an overall displacement parameter.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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