

4-[[3,5-Bis(methoxycarbonyl)-4,5-dihydro-1H-pyrazol-5-yl]methylamino]pyridine 1-oxide monohydrate

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Key indicators

Single-crystal X-ray study

T = 150 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.046

wR factor = 0.131

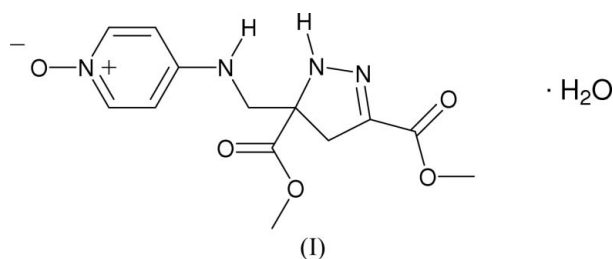
Data-to-parameter ratio = 9.1

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

The title compound, $\text{C}_{13}\text{H}_{16}\text{N}_4\text{O}_5 \cdot \text{H}_2\text{O}$, was isolated following the cycloaddition reaction of 4-azidopyridine 1-oxide with an excess of methyl acrylate. The compound arises from a reaction sequence whereby the expected triazoline product undergoes rearrangement and a second cycloaddition reaction to yield the title pyrazoline product without the presence of a strong base which is usually required for such transformations.

Comment

The title compound, (I), is formed by the thermal reaction of 4-azidopyridine 1-oxide with methyl acrylate. 1,3-Dipolar cycloaddition reactions of aryl azides, particularly phenyl azide and its derivatives, with alkenes and alkynes have been well studied. In general terms, the expected outcome of such a reaction is a triazole (in the case of alkynes) or triazoline (in the case of alkenes) compound (Patai, 1971; Sustmann & Trill, 1972). However, under the reaction conditions employed, the triazoline compound generated from this reaction undergoes rearrangement to generate an diazoalkane intermediate, which in turn undergoes a second 1,3-cycloaddition reaction with methyl acrylate to generate the pyrazoline product. The X-ray crystal structure indicates that water co-crystallizes with the title compound, (I), in association with the *N*-oxide compound.



The tautomer shown in the *ORTEP* (Johnson, 1976) representation of the structure (Fig. 1) is consistent with the NMR data obtained for this compound. Peaks observed at 8.88 and 6.73 p.p.m. in *d*₆-dimethyl sulfoxide (DMSO) are not observed in *d*₄-methanol, indicating that these resonances correspond to labile N—H protons (at the N1 position of the pyrazoline ring, and N position of the aminopyridine 1-oxide fragment, respectively, confirmed by two-dimensional NMR experiments). Such reactions have been observed in substituted phenyl azides, but these have required the presence of a moderately strong base, such as 1,4-diazabicyclo[2.2.2]octane (DABCO), to catalyse the triazoline–diazoalkane rearrangement (Yadav *et al.*, 2002). In this particular case, either water itself is sufficiently basic to catalyse the reaction, or no such base-catalysis is required.

Experimental

A solution of 4-azidopyridine 1-oxide in methyl acrylate and acetonitrile (approximate 1:1 ratio) was deoxygenated by a thin stream of bubbling argon and heated at 333 K overnight. Slow evaporation of the solvent yielded crystalline chunks of the title compound which were isolated from the supernatant and characterized.

Crystal data

$C_{13}H_{16}N_4O_5 \cdot H_2O$	$V = 742.57 (15) \text{ \AA}^3$
$M_r = 326.31$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.459 \text{ Mg m}^{-3}$
$a = 6.0678 (7) \text{ \AA}$	Mo - $K\alpha$ radiation
$b = 8.7476 (9) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 15.0449 (18) \text{ \AA}$	$T = 150 \text{ K}$
$\alpha = 104.435 (6)^\circ$	Chunk, colourless
$\beta = 94.885 (6)^\circ$	$0.40 \times 0.35 \times 0.29 \text{ mm}$
$\gamma = 103.676 (6)^\circ$	

Data collection

Nonius KappaCCD diffractometer	8766 measured reflections
ω scans	2559 independent reflections
Absorption correction: multi-scan (Otwinowski & Minor, 1997)	1906 reflections with $I > 2.0\sigma(I)$
$T_{\min} = 0.936$, $T_{\max} = 0.969$	$R_{\text{int}} = 0.029$
	$\theta_{\max} = 27.8^\circ$

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.0806P)^2]$
$wR(F^2) = 0.131$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{\max} < 0.001$
2559 reflections	$\Delta\rho_{\max} = 0.47 \text{ e \AA}^{-3}$
280 parameters	$\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$

Coordinates and isotropic displacement parameters for all H atoms were refined [C–H = 0.86 (5)–1.02 (2) Å].

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and local programs.

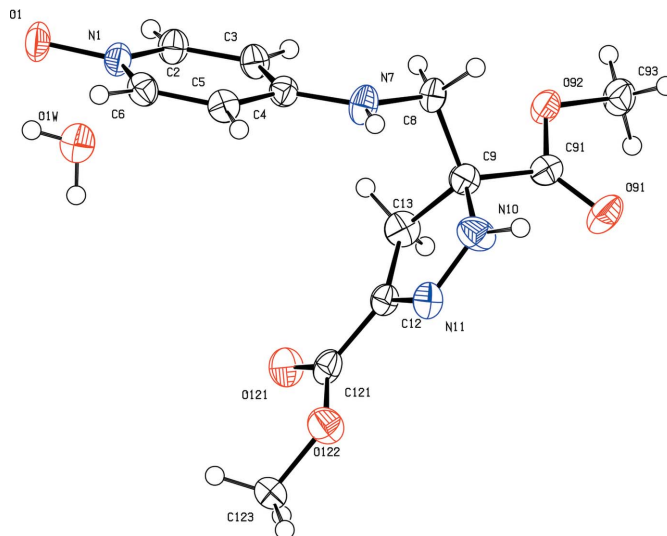


Figure 1
View of (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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