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## Key indicators

Single-crystal X-ray study  
T = 150 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$   
R factor = 0.038  
wR factor = 0.088  
Data-to-parameter ratio = 12.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## Ethyl 5-oxo-2,5-dihydro-4-isoxazolecarboxylate hydroxylamine salt

The isoxazole proton is sufficiently acidic to give the title salt, hydroxylammonium 4-(ethyloxycarbonyl)-5-oxo-2,5-dihydroisoxazolidine,  $\text{NH}_3\text{OH}^+ \cdot \text{C}_6\text{H}_6\text{NO}_4^-$ , in the presence of hydroxylamine. The deprotonation of the heterocyclic ring has a profound effect on its geometry, notably increasing the N—O distance by 0.05 Å to 1.433 (2) Å.

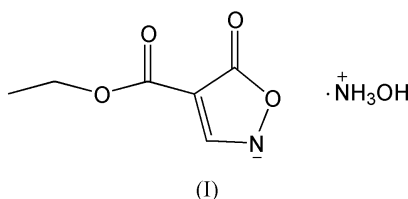
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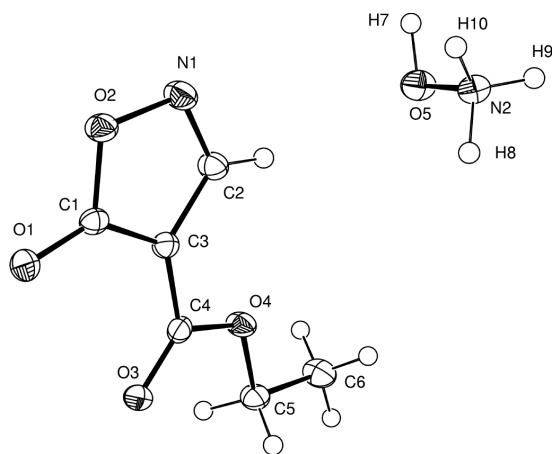
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## Comment

As part of a search for biologically active heterocyclic compounds, the title compound, (I), was prepared. Isoxazoles have a plethora of biological activities, for instance antibacterial and antifungal activity (Kang *et al.*, 2000; Tsubotani *et al.*, 1991) and anti-inflammatory activity (Pathak & Jindal, 1998). They are also known to suppress the immune system (Millan *et al.*, 2000). Heterocyclic compounds of this sort are also incorporated in the synthesis of DNA minor-groove binders, such as analogues of the well known anticancer and antibiotic drugs distamycin and netropsin (Khalaf *et al.*, 2002).



The vicinal O atom and double bond of (I) appears to make the amine proton more acidic than in other isoxazoles and so the compound isolated is a salt with the proton found on the hydroxylamine group. We know of no other crystal structure of a deprotonated isoxazole. The loss of a proton has a major effect on the bonding within the planar heterocycle. Compared to its closest relative (a neutral amide-substituted isoxazole; Tsubotani *et al.*, 1991), (I) has lengthened N1—O2, C2=C3 and C1=O1 bonds [1.433 (2), 1.409 (2) and 1.257 (2) Å in (I) compared with 1.385, 1.385 and 1.226 Å in the neutral compound] and shortened N1—C2, C1—C3 and C1—O2 distances [1.302 (2), 1.394 (2) and 1.370 (2) Å compared with 1.346, 1.402 and 1.404 Å]. The longer N—O bond must be due to repulsion from the increased negative charge on N1, whilst the other changes can be rationalized by resonance effects caused by the extra electron-pushing ability of N1. The  $\text{NH}_3\text{OH}^+$  cation utilizes all four H atoms in acting as a hydrogen-bond donor to all the possible acceptor atoms of the anion, with the exception of O4. The shortest, most linear, and hence presumably the strongest of these interactions is between the hydroxy H atom and O1.



**Figure 1**  
The molecular structure of (I), with 50% probability ellipsoids.

## Experimental

A mixture of triethyl orthoformate (44.5 g, 0.300 mol), acetic anhydride (68.0 g, 0.666 mmol), ethyl malonate (50.6 g, 0.316 mmol) and zinc chloride (0.200 g) was placed in a three-necked flask equipped with a thermometer and a (30 cm) column. The column was attached to a still head and a condenser. The reaction mixture was well stirred and then heated as follows: 375–388 K for 2.5 h, 388–400 K for 12 h, 400–418 K for 2 h, and 418–428 K for 2 h, after which time, acetic anhydride (13.5 g, 0.123 mol) and triethyl orthoformate (8.9 g, 0.060 mol) were added. The mixture was cooled to room temperature, filtered and distilled under reduced pressure. 2-(Ethoxymethylene)-malonate was boiled at 383–391 K at 1.0 mmHg and was collected as a colourless oil (31.1 g, 46% yield) [literature 381–383 K at 0.25 mmHg (Fuson *et al.*, 1946)]. Hydroxylamine hydrochloride (0.965 g, 13.8 mmol) was dissolved in a mixture of water (5 ml) and ethanol (5 ml). Potassium hydroxide (0.776 g, 13.8 mmol) was dissolved in ethanol (10 ml). These were then added to the hydroxylamine hydrochloride solution with stirring. Potassium chloride precipitated and was filtered off. The filtrate was added to diethyl 2-(ethoxymethylene)malonate (Fuson *et al.*, 1946) (1.004 g, 4.629 mmol). The reaction mixture was left stirring at room temperature overnight. The resultant mixture was heated on a water bath for 2 h, then the solvents were removed under reduced pressure. The product so obtained was recrystallized from acetone/*n*-hexane to give a colourless crystalline solid (0.705 g, 97% yield), m.p. > 503 K [literature m.p. 433–438 K; (Claisen, 1893) and 473–478 K (Claisen, 1897)]. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): 1.13–1.16 (3H, *t*, *J* = 7.0 Hz, CH<sub>3</sub>); 3.95–4.01 (2H, *q*, *J* = 7.0 Hz, CH<sub>2</sub>); 7.93 (1H, *s*, CH); 9.83 (1H, *br*); 10.08 (3H, *br*); IR (KBr): 3097, 2998, 2702, 1686, 1647, 1544, 1499, 1210, 1170, 1070 cm<sup>-1</sup>.

## Crystal data

NH<sub>4</sub>O<sup>+</sup>·C<sub>6</sub>H<sub>6</sub>NO<sub>4</sub><sup>-</sup>  
*M<sub>r</sub>* = 190.16  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 4.6788 (2) Å  
*b* = 13.3277 (6) Å  
*c* = 13.5380 (7) Å  
 $\beta$  = 97.212 (2)°  
*V* = 837.52 (7) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.508 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 1706 reflections  
 $\theta$  = 1.0–27.5°  
 $\mu$  = 0.13 mm<sup>-1</sup>  
*T* = 150 (2) K  
 Needle, colourless  
 0.55 × 0.20 × 0.10 mm

## Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: none  
 5375 measured reflections  
 1894 independent reflections  
 1536 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$   
 $\theta_{\text{max}} = 27.4^\circ$   
 $h = 0 \rightarrow 6$   
 $k = -17 \rightarrow 16$   
 $l = -17 \rightarrow 17$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.088$   
 $S = 1.05$   
 1894 reflections  
 158 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 0.4766P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

O1—C1	1.2574 (17)	O5—N2	1.4143 (16)
O2—C1	1.3698 (17)	N1—C2	1.3022 (19)
O2—N1	1.4326 (16)	C1—C3	1.394 (2)
O3—C4	1.2270 (18)	C2—C3	1.409 (2)
O4—C4	1.3414 (17)	C3—C4	1.4395 (19)
O4—C5	1.4533 (17)		
C1—O2—N1	109.12 (10)	O2—C1—C3	107.70 (12)
C2—N1—O2	105.17 (12)	N1—C2—C3	113.09 (14)
O1—C1—O2	118.01 (13)	C1—C3—C2	104.92 (13)
O1—C1—C3	134.28 (14)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H7...O1 <sup>i</sup>	0.98 (3)	1.66 (3)	2.6244 (15)	170 (2)
O5—H7...O2 <sup>i</sup>	0.98 (3)	2.62 (3)	3.2753 (15)	124.8 (19)
N2—H8...N1 <sup>ii</sup>	0.98 (2)	1.90 (2)	2.8657 (19)	166.2 (17)
N2—H9...O1 <sup>iii</sup>	0.94 (2)	1.93 (2)	2.8019 (17)	153.6 (17)
N2—H10...O3 <sup>iv</sup>	0.93 (2)	2.00 (2)	2.8750 (17)	154.8 (17)
N2—H10...O1 <sup>v</sup>	0.93 (2)	2.51 (2)	3.0696 (17)	118.9 (15)

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

All H atoms were refined isotropically.

Data collection: *DENZO* and *COLLECT* (Otwinowski & Minor, 1997; Nonius, 1988); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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