Crystal structure of ethyl (Z)-2-hydroxyimino-2-(methylsulfanyl)acetate, $C_5H_9NO_3$

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Abstract

$C_5H_9NO_3$, triclinic, $P\bar{1}$ (No. 2), $a = 5.278(3)$ Å, $b = 8.235(4)$ Å, $c = 9.667(2)$ Å, $\alpha = 95.26(4)^\circ$, $\beta = 103.68(4)^\circ$, $\gamma = 102.16(4)^\circ$, $V = 394.6$ Å³, $Z = 2$, $R_g(F) = 0.066$, $wR(F) = 0.079$, $T = 293$ K.

Source of material

Ethyl nitroacetate was dissolved in triflic acid at 273 K – 278 K. After about 30 minute reaction time, the solution was quenched by a mixture of methanethiol and CH_2Cl_2 at 193 K – 213 K. Extraction with CH_2Cl_2 and flash-chromatography afforded the title compound [1]. The compound was crystallized from dichloromethane/petroleum ether.

Discussion

Ethyl nitroacetate is readily dissolved in triflic acid, sulfuric acid or $HF-SbF_5$. In these very acidic media, ethyl nitroacetate is doubly protonated and form a conjugated hydroxynitrilium ion that can be trapped by aromatics [2] or MeSH to affords the title compound [1]. The present X-ray analysis of the title compound shows that the molecule has a nearly planar conformation, with a maximum deviation from the best plane of 0.554 Å. The torsion

angle $C-S-C=N$, with a value of $\tau_1 = -157.94^\circ$, indicates a *s-cis* conformation for the $-S-C=$ single bond. The conjugated bonds $N=C-C=O$ are nearly coplanar ($\tau_2 = -157.86^\circ$), which allows delocalization of the π -electronic system, affording a better electronic stabilization. The planar $S-C=N-O(H)$ system ($\tau_3 = 1.59^\circ$ value) is *Z* configured with MeS and $N-OH$ in the *cis* geometrical position. This last feature is in agreement with theoretical considerations concerning nucleophilic addition on triple bond [3, 4] and, in the present case, of MeSH on the CN triple bond of the hydroxynitrilium ion formed from ethyl nitroacetate.

Table 1. Data collection and handling.

Crystal:	colorless prism, size $0.15 \times 0.20 \times 0.25$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	34.5 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{\text{max}}$:	50°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	2776, 925
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 3 \sigma(I_{\text{obs}})$, 925
$N(\text{param})_{\text{refined}}$:	94
Programs:	SHELXS-86 [5], CRYSTALS [6], CAMERON [7]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1)	2i	−0.2625	−0.0567	0.3825	0.172(8)
H(11)	2i	0.9856	0.3952	0.861	0.131(8)
H(12)	2i	0.6579	0.3547	0.8134	0.131(8)
H(13)	2i	0.8099	0.2023	0.8032	0.131(8)
H(21)	2i	0.8332	0.4672	0.6327	0.109(8)
H(22)	2i	0.9852	0.3149	0.6225	0.109(8)
H(51)	2i	0.3608	0.2164	−0.0263	0.107(8)
H(52)	2i	0.5307	0.3298	0.1283	0.107(8)
H(53)	2i	0.5227	0.1299	0.1008	0.107(8)

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
S(1)	2i	0.1246(2)	0.1687(2)	0.1469(1)	0.0534(7)	0.0761(9)	0.0507(7)	0.0108(6)	0.0131(5)	0.0088(5)
C(1)	2i	0.817(1)	0.3228(8)	0.7917(6)	0.108(5)	0.071(4)	0.063(3)	0.013(3)	0.000(3)	−0.001(3)
C(2)	2i	0.828(1)	0.3466(6)	0.6435(5)	0.051(3)	0.043(2)	0.068(3)	0.004(2)	0.002(2)	−0.004(2)
C(3)	2i	0.5087(9)	0.2836(5)	0.4169(5)	0.054(2)	0.028(2)	0.056(2)	0.011(2)	0.016(2)	0.004(2)
C(4)	2i	0.2463(8)	0.1747(5)	0.3311(4)	0.053(2)	0.026(2)	0.051(2)	0.014(2)	0.016(2)	0.004(2)
C(5)	2i	0.415(1)	0.2178(8)	0.0806(6)	0.070(3)	0.104(5)	0.061(3)	0.018(3)	0.029(3)	0.009(3)
N(1)	2i	0.1031(7)	0.0974(4)	0.4058(4)	0.052(2)	0.036(2)	0.051(2)	0.005(1)	0.012(2)	0.002(1)
O(1)	2i	−0.1504(6)	0.0071(4)	0.3257(3)	0.051(2)	0.051(2)	0.059(2)	−0.002(1)	0.012(1)	0.007(1)
O(2)	2i	0.5837(6)	0.2410(3)	0.5456(3)	0.057(2)	0.035(2)	0.055(2)	0.003(1)	0.007(1)	0.004(1)
O(3)	2i	0.6322(8)	0.3986(4)	0.3744(4)	0.073(2)	0.055(2)	0.075(2)	−0.009(2)	0.012(2)	0.017(2)

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