Crystal structure of (*E*)-2-(1-methoxyimidazol-2-yl)-2-oxoacetaldehyde *O*-methyl oxime, $C_7H_9N_3O_3$

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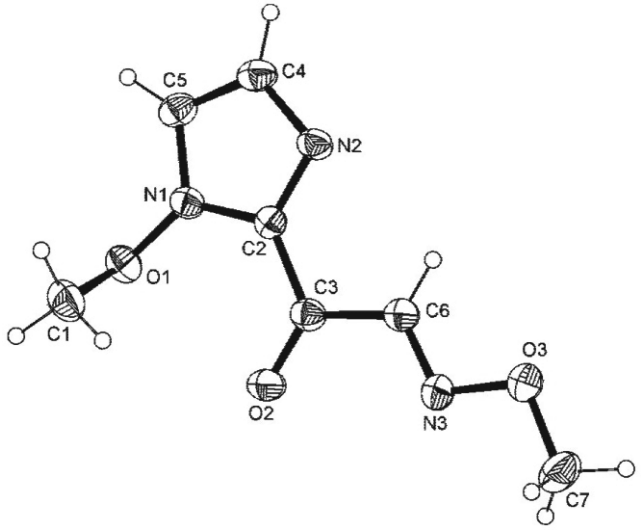

Abstract

$C_7H_9N_3O_3$, orthorhombic, $Pca2_1$ (no. 29), a = 17.3539(4) Å, b = 4.0243(1) Å, c = 12.3842(3) Å, V = 864.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.027, $wR_{ref}(F^2)$ = 0.069, T = 173 K.

Source of material

The title compound was synthesized conveniently from freshly prepared crude 1,3-dimethoxyimidazolium methylsulfate [1] (50 mmol) and $NaHCO_3$ (50 mmol) in H_2O (50 ml).

When other 1,3-dimethoxyimidazolium salts, i.e. the hexafluorophosphate [1] or the triflimide [1], were employed as starting materials, the reaction did not appreciably proceed, probably due to their low solubility in water. The solutions turned dark within a few days, and only traces (3 %) of the title compound could be extracted (CH_2Cl_2) after nine days from the reaction mixture and identified by ^{1}H and ^{13}C NMR. The PF_6 anion was not affected, as judged by ^{31}P NMR; the triflimide ion also remained intact, according to ^{13}C NMR. The use of Na_2CO_3 instead of $NaHCO_3$ gave a considerably faster reaction, but a more contaminated product mixture, and only tiny crystals were obtained. It is also noteworthy that the yield could not be increased by running the reaction at a higher concentration. Furthermore, under identical conditions the 2-methyl derivative [1] remained unchanged after four days (isolated as the PF_6 salt and spectroscopically identical with an authentical sample), obviously due to the impossibility of carbene formation. Even more forceful conditions, i.e. the use of NaOH (1 equ., 1 M), lead to total decomposition of these salts (which might be of interest for the degradation of ionic liquids in order to address ecological concerns [2]), but no products were identified.

Single crystals were obtained after 4 days at 20 °C as fine needles from this aqueous solution. They were washed with H_2O and dried (yield 23 %; m.p.: 119 °C).

^{1}H NMR, ^{13}C NMR (in $CDCl_3$ and DMSO-d_6) and IR spectroscopic data are available in the CIF file.

Experimental details

The Flack x parameter is 0.15(19) for this non-centrosymmetric crystal assembled from achiral molecules.

Discussion

Imidazolium salts with an N—O bond are rare [1,3-9]. Depending on the anion, e. g. triflimide [1,9] or tris(pentafluoroethyl)-trifluorophosphate (FAP) [1,10], they exhibit low melting points and may be regarded as 'ionic liquids'. It is known that imidazolium salts are sensitive to strong bases [11,12]. Only recently, the hydrolysis of imidazole-derived carbenes has been investigated in detail [13]. Now, the *N*-methoxy substitution allowed the isolation of this oxime as a product of the base-induced degradation. The mechanism of this reaction is not yet fully understood, but a tentative interpretation is attempted. So far, three facts can be safely stated: (1) two molecules of the starting material are required to yield one molecule of the product, (2) a ring-opening of the first molecule must occur to produce the precursor of the new side chain, and (3) the formation of a carbene from the second molecule is most likely involved, even in water [14]. The ring-opening is probably initiated by addition of a hydroxide ion to the 2-position of the imidazolium salt [11,12] or by hydrolysis of a preformed carbene [15]. Subsequently, the product of ring-opening is assumed to react with the carbene under concomitant loss of one *N*-methoxy group. A similar fragmentation of *N*-methoxybenzimidazolium salts has been reported [11].

The molecules in the title crystal structure are almost planar, with one exception: the C1 methyl group is twisted out of the molecular plane by 1.25 Å. A weak hydrogen bond is observed between the carbonyl oxygen atom O2 and the ring proton C4–H^i (d(H···acceptor) = 2.61 Å and d(donor···acceptor) = 3.177(2) Å, ∠donor–H···acceptor = 118°). The nitrogen atom N3 of the side chain accepts another hydrogen bond from the ring proton C5–H^i (2.47 Å and 3.408(2) Å, 167°). These hydrogen bonds form an infinite ribbon-shaped structure (symmetry code i: ½–x,1+y,½+z).

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Table 1. Data collection and handling.

Crystal:	colourless needle, size 0.1 × 0.36 × 0.4 mm
Wavelength:	Cu K_α radiation (1.5418 Å)
μ:	9.56 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Ruby, Gemini ultra, ω
$2\theta_{max}$:	134.66°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7486, 1525
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1494
$N(param)_{refined}$:	120
Programs:	SIR2002 [16], SHELXL-97 [17]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(6)	4*a*	0.0714	0.7073	0.5567	0.045
H(5)	4*a*	0.3116	0.2888	0.2910	0.042
H(1A)	4*a*	0.3506	0.5311	0.6109	0.064
H(1B)	4*a*	0.4345	0.6015	0.5623	0.064
H(1C)	4*a*	0.3879	0.2765	0.5265	0.064
H(4)	4*a*	0.1718	0.1574	0.2792	0.041
H(7A)	4*a*	0.0142	1.0142	0.8606	0.077
H(7B)	4*a*	–0.0576	1.1974	0.8056	0.077
H(7C)	4*a*	0.0262	1.3630	0.8009	0.077

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*a*	0.34889(5)	0.6947(3)	0.45840(8)	0.0338(5)	0.0378(5)	0.0364(5)	–0.0050(4)	–0.0032(4)	0.0018(4)
O(2)	4*a*	0.24240(7)	0.9458(3)	0.62012(9)	0.0406(6)	0.0492(6)	0.0350(5)	–0.0028(5)	–0.0011(5)	–0.0135(5)
O(3)	4*a*	0.01315(6)	0.9813(3)	0.7001(1)	0.0343(6)	0.0648(7)	0.0483(6)	0.0026(5)	0.0035(6)	–0.0147(6)
N(1)	4*a*	0.27965(7)	0.5513(3)	0.4279(1)	0.0322(6)	0.0315(5)	0.0279(6)	–0.0011(4)	–0.0026(5)	–0.0003(5)
N(2)	4*a*	0.15576(7)	0.4361(3)	0.4165(1)	0.0371(7)	0.0335(6)	0.0254(5)	0.0007(4)	–0.0052(5)	0.0010(5)
N(3)	4*a*	0.09217(7)	0.9836(3)	0.6821(1)	0.0310(6)	0.0407(6)	0.0357(7)	0.0020(5)	0.0011(5)	–0.0018(6)
C(6)	4*a*	0.10960(9)	0.8167(4)	0.5985(1)	0.0370(7)	0.0416(8)	0.0335(7)	0.0006(6)	–0.0009(5)	–0.0046(6)
C(2)	4*a*	0.20908(8)	0.5981(3)	0.4733(1)	0.0338(7)	0.0286(6)	0.0251(6)	0.0012(5)	–0.0015(6)	0.0038(5)
C(5)	4*a*	0.27215(9)	0.3596(4)	0.3390(1)	0.0441(8)	0.0341(7)	0.0261(6)	0.0037(6)	0.0015(5)	–0.0001(5)
C(1)	4*a*	0.3832(1)	0.5111(4)	0.5467(1)	0.0405(8)	0.0443(8)	0.0424(8)	0.0006(6)	–0.0110(7)	0.0029(7)
C(3)	4*a*	0.19261(8)	0.8003(3)	0.5691(1)	0.0389(7)	0.0305(7)	0.0260(6)	0.0014(6)	–0.0017(6)	0.0012(5)
C(4)	4*a*	0.19503(8)	0.2902(3)	0.3337(1)	0.0445(8)	0.0335(7)	0.0241(6)	0.0005(5)	–0.0047(5)	–0.0031(5)
C(7)	4*a*	–0.0022(1)	1.1526(5)	0.7998(2)	0.0462(9)	0.059(1)	0.0489(9)	0.0052(8)	0.0149(8)	–0.0132(8)

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