Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

8-Methyl-3,*N*-bis(trifluoroacetyl)-oxazolo[3,2-*a*]pyridinium-2-imidate

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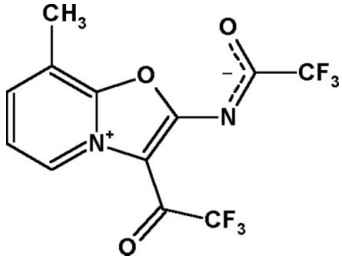
Received 18 July 2007; accepted 24 July 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.048; wR factor = 0.110; data-to-parameter ratio = 17.0.

The title compound, $C_{12}H_6F_6N_2O_3$, belongs to a class of mesoionic compounds. The crystal packing exibits a short intermolecular C(heterobicycle)···O(*N*-trifluoroacetyl) contact of 2.9573 (14) Å, which indicates the distribution of the positive charge in the N═C—O chain of the heterobicycle.

Related literature

For the crystal structures of related mesoionic compounds, see: Rybakov *et al.* (2002, 2006, 2007); Babaev *et al.* (2004, 2005).



Experimental

Crystal data

$C_{12}H_6F_6N_2O_3$
M_r = 340.19
Triclinic, $P\overline{1}$
a = 4.7470 (9) Å
b = 10.020 (2) Å
c = 13.121 (3) Å
α = 87.07 (2)°
β = 85.54 (2)°
γ = 79.16 (2)°
V = 610.7 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.19 mm^{-1}
T = 100 (2) K
0.5 × 0.2 × 0.1 mm

Data collection

Stoe IPDS diffractometer
Absorption correction: none
3647 measured reflections
3561 independent reflections
3033 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.110
S = 1.01
3561 reflections
209 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Table 1
Selected interatomic distances (Å).

C5···O30^{i}	2.9573 (14)	C2···O30^{i}	3.1842 (15)
N1···O30^{i}	3.1464 (14)		

Symmetry code: (i) $x+1, y, z$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors are indebted to the Russian Foundation for Basic Research for funding the licence fee for the use of the Cambridge Structural Database (Version 5.28; Allen, 2002).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2282).

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  doi:10.1107/S1600536807036227

supplementary materials

Acta Cryst. (2007). E**63**, o3620 [**doi:10.1107/S1600536807036227**]

8-Methyl-3,*N*-bis(trifluoroacetyl)oxazolo[3,2-*a*]pyridinium-2-imidate

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Comment

Earlier (Rybakov *et al.*, 2002, 2006, 2007; Babaev *et al.*, 2004, 2005), we described successful synthesis of new class of mesoionic compounds. Here we the title compound, (I), which belongs to this class.

The structure of the title compound is shown on Fig. 1. The main structural feature of this molecule is the difference in lengths of two C—O bonds in the oxazole ring, C3—O4 and C5—O4 of 1.3930 (12) and 1.3418 (12) Å, respectively. Additionally, the bond N1—C2 is longer than other two C—N bonds in the bicycle. These facts may demonstrate the separation of charges in the mesoionic system into two parts: N1 atom of the pyridine-2-one-like positively charged fragment and a negatively charged C2—C3—N30—C30—O30 unit. This conclusion also confirmed by relatively short interatomic contacts C2···O30^{i} = 3.1842 (15) Å Å, N1···O30^{i} = 3.1464 (14) Å and C5···O30^{i} = 2.9573 (14)Å [symmetry code: (i) *x* + 1, *y*, *z*]. Interestingly, the group C10═O10 seems to make a smaller contribution to the delocalization of the negative charge, since C10═O10 bond length is relatively long [1.2293(10 Å].

Experimental

The slurry of 3-methyl-*N*-(cyanomethyl)pyrid-2-one (3 g, 20.3 mmol) in 10 ml of acetonitrile was chilled to 228 K and then trifluoroacetic anhydride (10 ml, 15.1 g, 71.9 mmol) was added.

Immediately after addition the temperature of reaction mixture has risen to 263 K and then slowly decreased to 253 K. Reaction mixture was allowed to warm to RT. The formation of new precipitate was observed at 283 K. New precipitate was filtered off, washed with ether and dried. Mother liquor and ether washings were combined and, after staying overnight, new portion of product with identical mp was harvested. 7.17 g of 3,*N*-bis(trifluoroacetyl)-8-methyloxazolo[3,2-*a*]pyridinium-2-imidate was obtained. Yield 78%. Mp 485–487 K (decomp.).

^{1}H-NMR spectrum: 9.62 (d, 1H, H_5, J_{56} = 6.6 Hz), 8.18 (d, 1H, H_7, J_{67} = 8.0 Hz), 7.74 (m, 1H, H_6), 2.61 (s, 3H, 8-CH_3).

Refinement

C-bound H-atoms were placed in calculated positions (C—H 0.95–0.98 Å) and refined as riding, with U_{iso}(H) = 1.2–1.5Ueq(C).

Figures

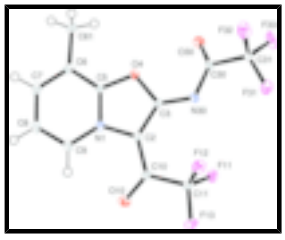

Fig. 1. The molecular structure of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms presented as spheres with arbitrary radius.

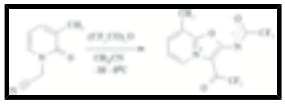

Fig. 2. Reaction scheme.

8-Methyl-3,*N*-bis(trifluoroacetyl)oxazolo[3,2-*a*]pyridinium-2-imidate

Crystal data

$C_{12}H_6F_6N_2O_3$	$Z = 2$
$M_r = 340.19$	$F_{000} = 340$
Triclinic, $P\overline{1}$	$D_x = 1.850$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 486 K
$a = 4.7470$ (9) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 10.020$ (2) Å	Cell parameters from 1533 reflections
$c = 13.121$ (3) Å	$\theta = 3.8$–29.6º
$\alpha = 87.07$ (2)º	$\mu = 0.19$ mm^{-1}
$\beta = 85.54$ (2)º	$T = 100$ (2) K
$\gamma = 79.16$ (2)º	Needle, colourless
$V = 610.7$ (2) Å^3	0.5 × 0.2 × 0.1 mm

Data collection

Stoe IPDS diffractometer	3033 reflections with $I > 2\sigma(I)$
Radiation source: Fine-focus sealed tube	$R_{int} = 0.026$
Monochromator: graphite	$\theta_{max} = 30.0$º
$T = 100$(2) K	$\theta_{min} = 1.6$º
ω scans	$h = -6 \rightarrow 6$
Absorption correction: none	$k = -14 \rightarrow 14$
3647 measured reflections	$l = 0 \rightarrow 18$
3561 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.048$	H-atom parameters constrained
$wR(F^2) = 0.110$	$w = 1/[\sigma^2(F_o^2) + (0.0886P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
3561 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
209 parameters	$\Delta\rho_{min} = -0.40$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.63108 (18)	1.01569 (9)	0.80548 (7)	0.01191 (17)
C2	0.5589 (2)	0.88933 (10)	0.84072 (8)	0.01249 (18)
C3	0.3972 (2)	0.85223 (10)	0.76503 (7)	0.01096 (18)
N30	0.29280 (19)	0.74182 (9)	0.75789 (7)	0.01295 (17)
C30	0.1122 (2)	0.73232 (10)	0.68501 (8)	0.01211 (18)
O30	−0.04146 (17)	0.82058 (8)	0.63682 (6)	0.01681 (16)
C31	0.1051 (2)	0.58336 (11)	0.66086 (8)	0.01484 (19)
F31	0.19537 (18)	0.49207 (7)	0.73456 (6)	0.02482 (17)
F32	0.27332 (18)	0.54922 (8)	0.57639 (6)	0.02720 (18)
F33	−0.15873 (16)	0.56834 (8)	0.64277 (7)	0.02651 (18)
O4	0.36896 (16)	0.95558 (7)	0.68932 (5)	0.01205 (15)
C5	0.5181 (2)	1.04911 (10)	0.71396 (7)	0.01127 (18)
C6	0.5524 (2)	1.16465 (10)	0.65525 (8)	0.01351 (19)
C61	0.4264 (3)	1.19068 (11)	0.55323 (8)	0.0187 (2)
H611	0.2354	1.1660	0.5578	0.028*
H612	0.5515	1.1357	0.5020	0.028*
H613	0.4098	1.2873	0.5332	0.028*
C7	0.7143 (2)	1.24746 (10)	0.69715 (8)	0.0158 (2)
H7	0.7454	1.3286	0.6610	0.019*
C8	0.8325 (2)	1.21334 (11)	0.79182 (9)	0.0166 (2)
H8	0.9425	1.2716	0.8188	0.020*
C9	0.7914 (2)	1.09688 (11)	0.84605 (8)	0.01452 (19)
H9	0.8722	1.0735	0.9100	0.017*
C10	0.6568 (2)	0.82430 (10)	0.93413 (7)	0.01208 (18)
O10	0.77976 (18)	0.87764 (9)	0.99513 (6)	0.01804 (17)
C11	0.6097 (2)	0.67686 (11)	0.96014 (8)	0.01464 (19)
F11	0.33178 (15)	0.66985 (7)	0.97317 (5)	0.01881 (15)
F12	0.73214 (15)	0.59253 (7)	0.88708 (5)	0.01939 (15)

F13	0.72892 (16)	0.63249 (7)	1.04720 (5)	0.02211 (16)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0122 (4)	0.0106 (4)	0.0132 (4)	−0.0028 (3)	−0.0007 (3)	−0.0005 (3)
C2	0.0142 (4)	0.0109 (4)	0.0130 (4)	−0.0042 (3)	−0.0013 (3)	0.0015 (3)
C3	0.0124 (4)	0.0097 (4)	0.0101 (4)	−0.0008 (3)	−0.0008 (3)	0.0013 (3)
N30	0.0146 (4)	0.0112 (4)	0.0140 (4)	−0.0040 (3)	−0.0032 (3)	0.0001 (3)
C30	0.0118 (4)	0.0118 (4)	0.0130 (4)	−0.0034 (3)	0.0011 (3)	−0.0014 (3)
O30	0.0179 (4)	0.0138 (3)	0.0191 (4)	−0.0021 (3)	−0.0057 (3)	−0.0003 (3)
C31	0.0150 (4)	0.0123 (4)	0.0183 (4)	−0.0045 (3)	−0.0019 (3)	−0.0020 (3)
F31	0.0372 (4)	0.0108 (3)	0.0269 (4)	−0.0040 (3)	−0.0086 (3)	0.0032 (3)
F32	0.0349 (4)	0.0206 (4)	0.0266 (4)	−0.0092 (3)	0.0119 (3)	−0.0122 (3)
F33	0.0187 (3)	0.0194 (3)	0.0449 (5)	−0.0090 (3)	−0.0077 (3)	−0.0046 (3)
O4	0.0146 (3)	0.0101 (3)	0.0121 (3)	−0.0035 (2)	−0.0029 (2)	0.0007 (2)
C5	0.0125 (4)	0.0092 (4)	0.0123 (4)	−0.0026 (3)	0.0003 (3)	−0.0017 (3)
C6	0.0152 (4)	0.0093 (4)	0.0151 (4)	−0.0005 (3)	−0.0002 (3)	0.0011 (3)
C61	0.0281 (5)	0.0136 (5)	0.0151 (5)	−0.0055 (4)	−0.0046 (4)	0.0037 (4)
C7	0.0176 (4)	0.0108 (4)	0.0192 (5)	−0.0045 (3)	0.0027 (4)	−0.0007 (3)
C8	0.0172 (4)	0.0140 (4)	0.0200 (5)	−0.0065 (3)	−0.0001 (4)	−0.0028 (4)
C9	0.0146 (4)	0.0150 (4)	0.0149 (4)	−0.0045 (3)	−0.0008 (3)	−0.0025 (3)
C10	0.0116 (4)	0.0118 (4)	0.0124 (4)	−0.0014 (3)	−0.0011 (3)	0.0005 (3)
O10	0.0203 (4)	0.0189 (4)	0.0165 (4)	−0.0056 (3)	−0.0072 (3)	0.0006 (3)
C11	0.0165 (4)	0.0142 (4)	0.0126 (4)	−0.0017 (3)	−0.0018 (3)	0.0018 (3)
F11	0.0165 (3)	0.0200 (3)	0.0206 (3)	−0.0065 (2)	−0.0002 (2)	0.0030 (2)
F12	0.0236 (3)	0.0121 (3)	0.0207 (3)	0.0007 (2)	0.0006 (3)	−0.0017 (2)
F13	0.0278 (4)	0.0203 (3)	0.0187 (3)	−0.0051 (3)	−0.0095 (3)	0.0081 (3)

Geometric parameters (Å, °)

N1—C5	1.3539 (13)	C6—C7	1.3904 (15)
N1—C9	1.3654 (13)	C6—C61	1.4994 (15)
N1—C2	1.4188 (13)	C61—H611	0.9800
C2—C3	1.4060 (14)	C61—H612	0.9800
C2—C10	1.4269 (13)	C61—H613	0.9800
C3—N30	1.3048 (13)	C7—C8	1.4027 (15)
C3—O4	1.3930 (12)	C7—H7	0.9500
N30—C30	1.3512 (13)	C8—C9	1.3731 (15)
C30—O30	1.2190 (13)	C8—H8	0.9500
C30—C31	1.5486 (15)	C9—H9	0.9500
C31—F33	1.3300 (12)	C10—O10	1.2250 (13)
C31—F32	1.3346 (13)	C10—C11	1.5525 (15)
C31—F31	1.3350 (13)	C11—F11	1.3314 (13)
O4—C5	1.3418 (12)	C11—F13	1.3330 (12)
C5—C6	1.3858 (14)	C11—F12	1.3350 (13)
C5···O30^{i}	2.9573 (14)	C2···O30^{i}	3.1842 (15)
N1···O30^{i}	3.1464 (14)		

C5—N1—C9	120.67 (9)	C7—C6—C61	124.81 (9)
C5—N1—C2	107.92 (8)	C6—C61—H611	109.5
C9—N1—C2	131.37 (9)	C6—C61—H612	109.5
C3—C2—N1	105.57 (8)	H611—C61—H612	109.5
C3—C2—C10	133.05 (9)	C6—C61—H613	109.5
N1—C2—C10	121.34 (9)	H611—C61—H613	109.5
N30—C3—O4	122.04 (9)	H612—C61—H613	109.5
N30—C3—C2	130.07 (9)	C6—C7—C8	121.19 (9)
O4—C3—C2	107.85 (8)	C6—C7—H7	119.4
C3—N30—C30	120.87 (9)	C8—C7—H7	119.4
O30—C30—N30	130.63 (10)	C9—C8—C7	120.87 (10)
O30—C30—C31	116.50 (9)	C9—C8—H8	119.6
N30—C30—C31	112.87 (9)	C7—C8—H8	119.6
F33—C31—F32	107.08 (9)	N1—C9—C8	118.14 (10)
F33—C31—F31	107.14 (9)	N1—C9—H9	120.9
F32—C31—F31	107.10 (9)	C8—C9—H9	120.9
F33—C31—C30	111.25 (9)	O10—C10—C2	123.73 (10)
F32—C31—C30	109.40 (9)	O10—C10—C11	117.61 (9)
F31—C31—C30	114.52 (9)	C2—C10—C11	118.66 (9)
C5—O4—C3	108.08 (8)	F11—C11—F13	107.55 (8)
O4—C5—N1	110.48 (8)	F11—C11—F12	108.62 (9)
O4—C5—C6	125.43 (9)	F13—C11—F12	107.90 (9)
N1—C5—C6	124.09 (9)	F11—C11—C10	112.01 (9)
C5—C6—C7	115.04 (10)	F13—C11—C10	109.26 (9)
C5—C6—C61	120.12 (9)	F12—C11—C10	111.35 (8)
C5—N1—C2—C3	−0.33 (11)	C2—N1—C5—O4	2.26 (11)
C9—N1—C2—C3	−177.92 (10)	C9—N1—C5—C6	−0.22 (15)
C5—N1—C2—C10	177.68 (9)	C2—N1—C5—C6	−178.13 (9)
C9—N1—C2—C10	0.08 (16)	O4—C5—C6—C7	179.38 (9)
N1—C2—C3—N30	175.92 (10)	N1—C5—C6—C7	−0.18 (14)
C10—C2—C3—N30	−1.75 (19)	O4—C5—C6—C61	−2.32 (15)
N1—C2—C3—O4	−1.62 (10)	N1—C5—C6—C61	178.12 (9)
C10—C2—C3—O4	−179.29 (10)	C5—C6—C7—C8	0.32 (15)
O4—C3—N30—C30	−10.94 (15)	C61—C6—C7—C8	−177.89 (10)
C2—C3—N30—C30	171.82 (10)	C6—C7—C8—C9	−0.07 (16)
C3—N30—C30—O30	−22.33 (17)	C5—N1—C9—C8	0.47 (14)
C3—N30—C30—C31	157.68 (9)	C2—N1—C9—C8	177.81 (10)
O30—C30—C31—F33	−37.38 (13)	C7—C8—C9—N1	−0.33 (15)
N30—C30—C31—F33	142.61 (9)	C3—C2—C10—O10	−174.34 (11)
O30—C30—C31—F32	80.73 (12)	N1—C2—C10—O10	8.29 (16)
N30—C30—C31—F32	−99.28 (11)	C3—C2—C10—C11	6.48 (17)
O30—C30—C31—F31	−159.06 (10)	N1—C2—C10—C11	−170.89 (9)
N30—C30—C31—F31	20.94 (12)	O10—C10—C11—F11	116.61 (10)
N30—C3—O4—C5	−174.77 (9)	C2—C10—C11—F11	−64.16 (12)
C2—C3—O4—C5	3.01 (10)	O10—C10—C11—F13	−2.45 (13)
C3—O4—C5—N1	−3.29 (10)	C2—C10—C11—F13	176.78 (9)
C3—O4—C5—C6	177.10 (9)	O10—C10—C11—F12	−121.54 (10)
C9—N1—C5—O4	−179.84 (8)	C2—C10—C11—F12	57.70 (12)

Symmetry codes: (i) *x*+1, *y*, *z*.

Fig. 1

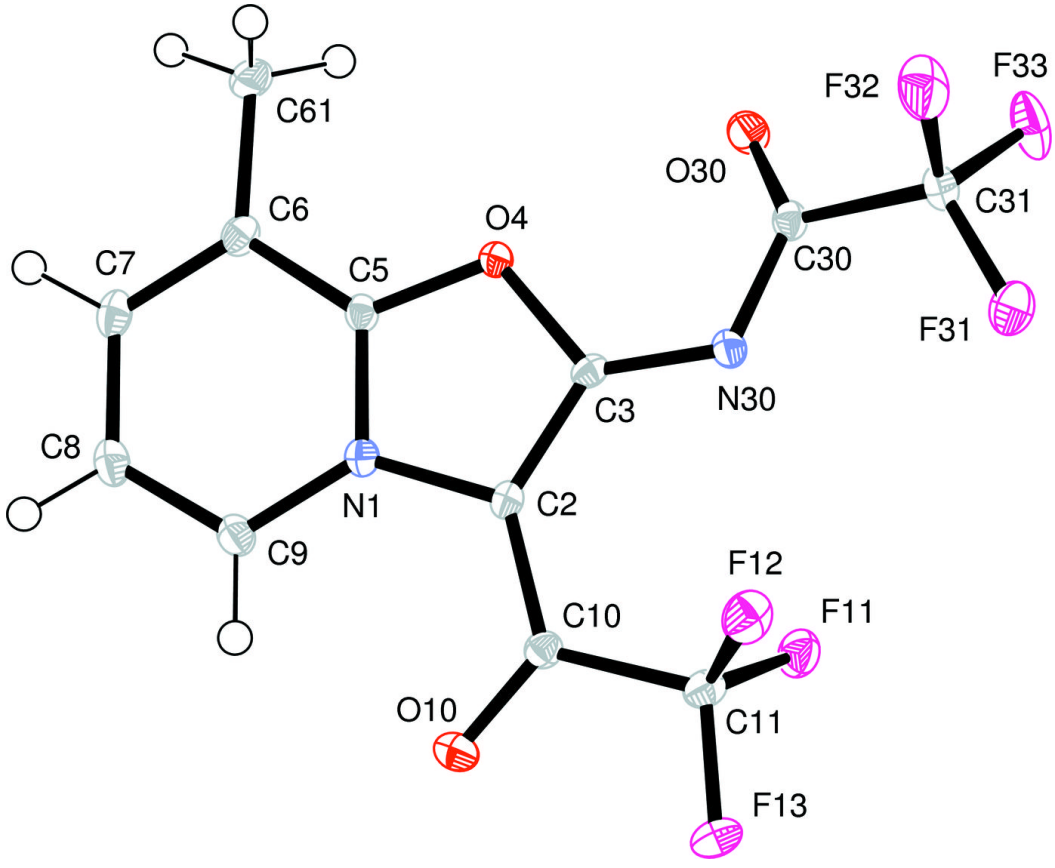
C61
C6
C7
C5
O4
C8
N1
C9
C3
N30
C2
C10
O10
O30
C30
C31
F32
F33
F31
F12
F11
C11
F13

Fig. 2