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

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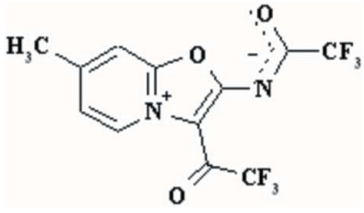
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.001 Å; disorder in main residue; R factor = 0.048; wR factor = 0.131; data-to-parameter ratio = 16.0.

The title compound, $C_{12}H_6F_6N_2O_3$, belongs to a class of mesoionic compounds. The crystal packing exhibits a short intermolecular N(heterobicycle)···O(*N*–trifluoroacetyl) contact of 2.8689 (11) Å, which indicates that the principal location of the negative charge is near the chain C and O atoms of the *N*–trifluoroacetyl group. The F atoms of one trifluoromethyl group are disordered over two positions, the site occupancy ratio being *ca* 3:2.

Related literature

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



Experimental

Crystal data

$C_{12}H_6F_6N_2O_3$
M_r = 340.19
Monoclinic, $P2_1/c$
a = 5.7996 (5) Å
b = 20.838 (2) Å
c = 10.4259 (8) Å
β = 91.100 (7)°
V = 1259.76 (19) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.19 mm^{-1}
T = 100 (2) K
0.6 × 0.2 × 0.1 mm

Data collection

Stoe IPDS diffractometer
Absorption correction: none
3851 measured reflections
3776 independent reflections
3247 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.131
S = 1.01
3776 reflections
236 parameters
12 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

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).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2281).

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supplementary materials

Acta Cryst. (2007). E**63**, o3619 [**doi:10.1107/S1600536807035611**]

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

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Comment

Earlier (Rybakov *et al.*, 2002, 2006; Babaev *et al.*, 2004, 2005), we described successful synthesis of previously unknown class of mesoionic compounds. Now we synthesized a new (Allen, 2002) one - see Scheme 1.

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 1.3926 (11) and 1.3467 (10) 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} = 3.2066 (11) Å, N1···O30^{i} = 2.8689 (11) Å and C5···O30^{i} = 2.9258 (12) Å [symmetry code: (i) $-x+1$, $-y+1$, $-z+2$]. Interestingly, the group C10═O10 seems to make a smaller contribution to the delocalization of the negative charge, since the C10—O10 distance are relatively long [1.2269 (11) Å].

Experimental

The slurry of 4-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.

[Scheme 2]

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. 7.63 g of 3,*N*-bis(trifluoroacetyl)-7-methyloxazolo[3,2-*a*]pyridinium-2-imidate was obtained. Yield 83%. *M*.p. 508–510 K (decomp.).

^{1}H-NMR spectrum: 9.61 (d, 1H, H_5, J_{56} = 6.6 Hz), 8.05 (s, 1H, H_8), 7.68 (d, 1H, H_6, J_{56} = 6.6 Hz), 2.67 (s, 3H, 7–CH_3).

Refinement

C-bound H-atoms were placed in calculated positions (C—H 0.95–0.99 Å) and refined as riding, with U_{iso}(H) = 1.2–1.5Ueq(C).

One CF_3-group (at C31) was treated as rotationally disordered between two orientations with the refined occupancies of 0.61 (1) and 0.39 (1), respectively. For this group, the bond restraints for the equality of C—F bond lengths and F···F distances have been applied using SADI option.

Figures

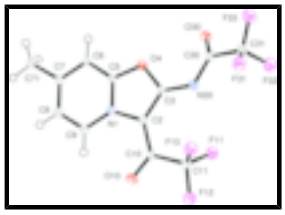

Fig. 1. The molecular structure of the title compound showing the atom–numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms presented as spheres with arbitrary radius. Only major part of the disordered CF_3–group is shown.

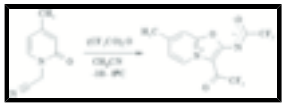

Fig. 2. Reaction scheme.

3,*N*-Bis(trifluoroacetyl)-7-methyloxazolo[3,2-*a*]pyridinium-2-imidate

Crystal data

$C_{12}H_6F_6N_2O_3$	F_{000} = 680
M_r = 340.19	D_x = 1.794 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 509 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 5.7996 (5) Å	Cell parameters from 429 reflections
b = 20.838 (2) Å	θ = 3.0–29.5º
c = 10.4259 (8) Å	μ = 0.19 mm^{-1}
β = 91.100 (7)º	T = 100 (2) K
V = 1259.76 (19) Å^3	Needle, colourless
Z = 4	0.6 × 0.2 × 0.1 mm

Data collection

Stoe IPDS diffractometer	3247 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.026
Monochromator: graphite	θ_{max} = 30.4º
T = 100(2) K	θ_{min} = 2.0º
ω scans	h = −8→8
Absorption correction: none	k = 0→29
3851 measured reflections	l = 0→14
3776 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
$wR(F^2)$ = 0.131	$w = 1/[\sigma^2(F_o^2) + (0.0989P)^2]$

	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.008$
3776 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
236 parameters	$\Delta\rho_{min} = -0.40$ e Å^{-3}
12 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
N1	0.44604 (14)	0.48860 (4)	0.69681 (7)	0.01393 (16)	
C2	0.35449 (16)	0.54599 (4)	0.74712 (9)	0.01340 (17)	
C3	0.50625 (16)	0.56442 (4)	0.84737 (9)	0.01458 (18)	
O4	0.68186 (12)	0.51893 (3)	0.85528 (7)	0.01510 (15)	
C5	0.64170 (15)	0.47454 (4)	0.76367 (8)	0.01303 (17)	
C6	0.77826 (15)	0.42148 (4)	0.73918 (9)	0.01475 (17)	
H6	0.9158	0.4130	0.7872	0.018*	
C7	0.70315 (17)	0.38161 (4)	0.64112 (9)	0.01577 (18)	
C8	0.49988 (17)	0.39605 (5)	0.57260 (9)	0.01844 (19)	
H8	0.4502	0.3683	0.5052	0.022*	
C9	0.37070 (16)	0.44916 (4)	0.60035 (9)	0.01550 (18)	
H9	0.2323	0.4583	0.5536	0.019*	
C71	0.84132 (19)	0.32277 (5)	0.60798 (10)	0.0215 (2)	
H711	1.0047	0.3343	0.6025	0.032*	
H712	0.7868	0.3057	0.5253	0.032*	
H713	0.8223	0.2902	0.6747	0.032*	
C10	0.14649 (15)	0.57336 (4)	0.69798 (8)	0.01288 (17)	
O10	0.02315 (13)	0.54843 (4)	0.61505 (7)	0.02110 (17)	
C11	0.06580 (18)	0.63848 (4)	0.75063 (10)	0.0195 (2)	
F11	0.03658 (13)	0.63791 (3)	0.87753 (7)	0.02487 (16)	
F12	−0.13470 (12)	0.65525 (3)	0.69530 (7)	0.02538 (16)	
F13	0.21923 (13)	0.68456 (3)	0.72526 (7)	0.02507 (16)	
N30	0.50521 (14)	0.61598 (4)	0.91787 (8)	0.01664 (17)	
C30	0.64171 (15)	0.62233 (5)	1.02203 (8)	0.01487 (17)	
O30	0.73421 (13)	0.58246 (3)	1.09181 (7)	0.01776 (16)	
C31	0.66604 (13)	0.69364 (5)	1.06253 (7)	0.0247 (2)	
F31	0.6495 (3)	0.73418 (11)	0.96520 (19)	0.0263 (4)	0.61 (1)
F31A	0.7273 (4)	0.73278 (16)	0.9667 (3)	0.0281 (6)	0.39 (1)
F32	0.5059 (3)	0.71061 (10)	1.14445 (15)	0.0280 (4)	0.61 (1)
F32A	0.4601 (4)	0.71272 (16)	1.1051 (2)	0.0294 (6)	0.39 (1)
F33	0.8673 (3)	0.70461 (11)	1.11975 (15)	0.0290 (4)	0.61 (1)
F33A	0.8216 (5)	0.69982 (17)	1.1588 (2)	0.0323 (6)	0.39 (1)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0168 (3)	0.0119 (3)	0.0130 (3)	−0.0028 (2)	−0.0008 (3)	0.0015 (2)

C2	0.0163 (4)	0.0098 (3)	0.0141 (3)	−0.0003 (3)	−0.0017 (3)	0.0007 (3)
C3	0.0181 (4)	0.0096 (4)	0.0160 (4)	−0.0024 (3)	−0.0028 (3)	0.0008 (3)
O4	0.0161 (3)	0.0110 (3)	0.0181 (3)	0.0005 (2)	−0.0032 (2)	−0.0012 (2)
C5	0.0158 (4)	0.0092 (3)	0.0140 (4)	−0.0021 (3)	−0.0012 (3)	−0.0007 (3)
C6	0.0136 (4)	0.0118 (3)	0.0187 (4)	−0.0007 (3)	−0.0025 (3)	0.0004 (3)
C7	0.0220 (4)	0.0094 (3)	0.0159 (4)	−0.0016 (3)	0.0005 (3)	−0.0004 (3)
C8	0.0227 (4)	0.0135 (4)	0.0191 (4)	−0.0028 (3)	−0.0008 (3)	−0.0023 (3)
C9	0.0176 (4)	0.0133 (4)	0.0155 (4)	−0.0034 (3)	−0.0021 (3)	0.0002 (3)
C71	0.0282 (5)	0.0160 (4)	0.0203 (4)	0.0028 (3)	−0.0003 (4)	−0.0025 (3)
C10	0.0132 (4)	0.0135 (4)	0.0119 (3)	−0.0005 (3)	−0.0017 (3)	−0.0010 (3)
O10	0.0216 (3)	0.0195 (3)	0.0219 (3)	0.0003 (3)	−0.0083 (3)	−0.0024 (3)
C11	0.0208 (4)	0.0125 (4)	0.0251 (5)	0.0039 (3)	−0.0062 (3)	−0.0038 (3)
F11	0.0279 (3)	0.0207 (3)	0.0259 (3)	0.0021 (2)	−0.0035 (3)	−0.0020 (2)
F12	0.0275 (3)	0.0199 (3)	0.0286 (3)	0.0035 (2)	−0.0041 (3)	−0.0015 (2)
F13	0.0295 (3)	0.0178 (3)	0.0278 (3)	0.0029 (2)	−0.0030 (3)	−0.0008 (2)
N30	0.0194 (4)	0.0132 (3)	0.0171 (4)	−0.0020 (3)	−0.0039 (3)	−0.0033 (3)
C30	0.0135 (4)	0.0181 (4)	0.0130 (4)	−0.0021 (3)	−0.0013 (3)	−0.0033 (3)
O30	0.0227 (3)	0.0138 (3)	0.0167 (3)	0.0002 (2)	−0.0034 (2)	0.0021 (2)
C31	0.0335 (6)	0.0145 (4)	0.0258 (5)	0.0068 (4)	−0.0095 (4)	−0.0071 (3)
F31	0.0327 (10)	0.0164 (6)	0.0297 (7)	0.0029 (8)	0.0008 (7)	0.0000 (5)
F31A	0.0301 (14)	0.0181 (9)	0.0360 (11)	0.0028 (11)	−0.0014 (11)	−0.0019 (7)
F32	0.0322 (8)	0.0193 (6)	0.0323 (9)	0.0046 (6)	−0.0026 (6)	−0.0001 (7)
F32A	0.0287 (12)	0.0245 (10)	0.0351 (15)	0.0085 (9)	0.0029 (10)	0.0041 (11)
F33	0.0347 (9)	0.0193 (7)	0.0329 (9)	0.0020 (6)	−0.0064 (7)	−0.0016 (7)
F33A	0.0375 (14)	0.0210 (10)	0.0380 (16)	−0.0007 (9)	−0.0095 (11)	0.0006 (12)

Geometric parameters (Å, °)

N1—C5	1.3524 (11)	C71—H712	0.9800
N1—C9	1.3641 (11)	C71—H713	0.9800
N1—C2	1.4135 (11)	C10—O10	1.2269 (11)
C2—C3	1.4068 (12)	C10—C11	1.5401 (13)
C2—C10	1.4210 (12)	C11—F12	1.3346 (11)
C3—N30	1.3018 (11)	C11—F11	1.3371 (13)
C3—O4	1.3926 (11)	C11—F13	1.3389 (13)
O4—C5	1.3467 (10)	N30—C30	1.3380 (11)
C5—C6	1.3868 (12)	C30—O30	1.2215 (12)
C6—C7	1.3813 (12)	C30—C31	1.5506 (13)
C6—H6	0.9500	C31—F33	1.3205 (18)
C7—C8	1.3994 (13)	C31—F31	1.3223 (17)
C7—C71	1.5085 (14)	C31—F32	1.3218 (18)
C8—C9	1.3705 (13)	C31—F32A	1.342 (3)
C8—H8	0.9500	C31—F33A	1.343 (3)
C9—H9	0.9500	C31—F31A	1.342 (3)
C71—H711	0.9800		
C5—N1—C9	120.21 (8)	C7—C71—H713	109.5
C5—N1—C2	108.02 (7)	H711—C71—H713	109.5
C9—N1—C2	131.76 (8)	H712—C71—H713	109.5
C3—C2—N1	105.82 (8)	O10—C10—C2	124.31 (9)

C3—C2—C10	132.30 (8)	O10—C10—C11	116.56 (8)
N1—C2—C10	121.87 (8)	C2—C10—C11	119.13 (8)
N30—C3—O4	122.66 (8)	F12—C11—F11	107.71 (9)
N30—C3—C2	129.43 (9)	F12—C11—F13	107.68 (8)
O4—C3—C2	107.73 (7)	F11—C11—F13	107.41 (8)
C5—O4—C3	108.01 (7)	F12—C11—C10	110.17 (8)
O4—C5—N1	110.41 (7)	F11—C11—C10	112.96 (8)
O4—C5—C6	125.92 (8)	F13—C11—C10	110.72 (8)
N1—C5—C6	123.66 (8)	C3—N30—C30	122.05 (9)
C7—C6—C5	116.28 (8)	O30—C30—N30	131.48 (9)
C7—C6—H6	121.9	O30—C30—C31	116.93 (8)
C5—C6—H6	121.9	N30—C30—C31	111.41 (8)
C6—C7—C8	119.94 (8)	F33—C31—F31	106.66 (10)
C6—C7—C71	119.80 (9)	F33—C31—F32	106.71 (10)
C8—C7—C71	120.26 (8)	F31—C31—F32	106.47 (10)
C9—C8—C7	121.63 (9)	F32A—C31—F33A	108.30 (13)
C9—C8—H8	119.2	F32A—C31—F31A	108.42 (13)
C7—C8—H8	119.2	F33A—C31—F31A	108.32 (13)
N1—C9—C8	118.26 (9)	F33—C31—C30	111.34 (12)
N1—C9—H9	120.9	F31—C31—C30	113.47 (13)
C8—C9—H9	120.9	F32—C31—C30	111.77 (12)
C7—C71—H711	109.5	F32A—C31—C30	107.27 (16)
C7—C71—H712	109.5	F33A—C31—C30	110.59 (17)
H711—C71—H712	109.5	F31A—C31—C30	113.80 (17)
C5—N1—C2—C3	−0.38 (10)	N1—C2—C10—O10	4.53 (14)
C9—N1—C2—C3	179.12 (9)	C3—C2—C10—C11	5.72 (15)
C5—N1—C2—C10	−179.35 (8)	N1—C2—C10—C11	−175.62 (8)
C9—N1—C2—C10	0.14 (15)	O10—C10—C11—F12	1.46 (13)
N1—C2—C3—N30	175.15 (10)	C2—C10—C11—F12	−178.40 (8)
C10—C2—C3—N30	−6.03 (17)	O10—C10—C11—F11	121.96 (10)
N1—C2—C3—O4	0.01 (10)	C2—C10—C11—F11	−57.91 (12)
C10—C2—C3—O4	178.83 (9)	O10—C10—C11—F13	−117.54 (9)
N30—C3—O4—C5	−175.19 (9)	C2—C10—C11—F13	62.60 (11)
C2—C3—O4—C5	0.36 (10)	O4—C3—N30—C30	−15.46 (14)
C3—O4—C5—N1	−0.61 (10)	C2—C3—N30—C30	170.04 (9)
C3—O4—C5—C6	179.43 (9)	C3—N30—C30—O30	−23.29 (16)
C9—N1—C5—O4	−178.94 (8)	C3—N30—C30—C31	161.80 (8)
C2—N1—C5—O4	0.62 (10)	O30—C30—C31—F33	33.75 (11)
C9—N1—C5—C6	1.02 (13)	N30—C30—C31—F33	−150.53 (9)
C2—N1—C5—C6	−179.42 (8)	O30—C30—C31—F31	154.09 (9)
O4—C5—C6—C7	179.30 (8)	N30—C30—C31—F31	−30.19 (11)
N1—C5—C6—C7	−0.65 (14)	O30—C30—C31—F32	−85.50 (10)
C5—C6—C7—C8	0.23 (13)	N30—C30—C31—F32	90.23 (10)
C5—C6—C7—C71	179.99 (9)	O30—C30—C31—F32A	−107.33 (12)
C6—C7—C8—C9	−0.19 (14)	N30—C30—C31—F32A	68.40 (12)
C71—C7—C8—C9	−179.95 (9)	O30—C30—C31—F33A	10.58 (13)
C5—N1—C9—C8	−0.92 (13)	N30—C30—C31—F33A	−173.70 (12)
C2—N1—C9—C8	179.64 (9)	O30—C30—C31—F31A	132.76 (12)
C7—C8—C9—N1	0.53 (14)	N30—C30—C31—F31A	−51.51 (12)

C3—C2—C10—O10	−174.13 (10)

Fig. 1

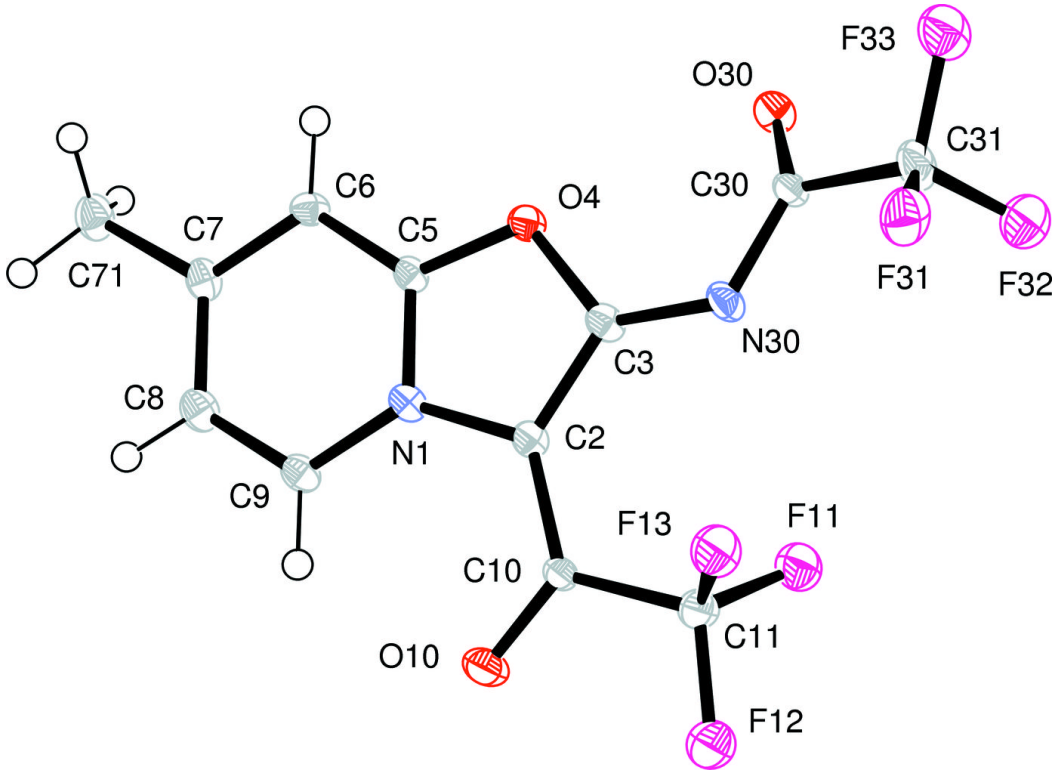

Fig. 2