

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

7-Methyl-3,*N*-bis(trifluoroacetyl)-oxazolo[3,2-*a*]pyridinium-2-imidateVictor B. Rybakov,^{a*} Alexander A. Bush,^a Sergei I. Troyanov,^a Eugene V. Babaev^a and Erhard Kemnitz^b^aDepartment of Chemistry, Moscow State University, 119992 Moscow, Russian Federation, and ^bInstitut für Chemie, Mathematisch-Naturwissenschaftliche Fakultät, Humboldt-Universität zu Berlin, D-12489 Berlin, Germany

Correspondence e-mail: rybakov20021@yandex.ru

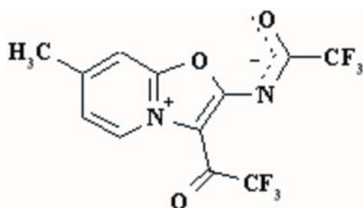
Received 17 July 2007; accepted 20 July 2007

Key indicators: single-crystal X-ray study; *T* = 100 K; mean $\sigma(\text{C}-\text{C})$ = 0.001 Å; disorder in main residue; *R* factor = 0.048; *wR* factor = 0.131; data-to-parameter ratio = 16.0.

The title compound, C₁₂H₆F₆N₂O₃, 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

C₁₂H₆F₆N₂O₃
M_r = 340.19
 Monoclinic, *P*2₁/*c*
a = 5.7996 (5) Å
b = 20.838 (2) Å
c = 10.4259 (8) Å
 β = 91.100 (7)°

V = 1259.76 (19) Å³
Z = 4
 Mo *K*α 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* > 2σ(*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
 $\Delta\rho_{\text{max}}$ = 0.41 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -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).

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: CV2281).

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Babaev, E. V., Bush, A. A., Orlova, I. A., Rybakov, V. B. & Iwataki, I. (2005). *Russ. Chem. Bull.* **54**, 231–237.
 Babaev, E. V., Rybakov, V. B., Orlova, I. A., Bush, A. A., Maerle, K. V. & Nasonov, A. F. (2004). *Russ. Chem. Bull.* **53**, 176–180.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
 Rybakov, V. B., Babaev, E. V., Pasechnichenko, K. Yu. & Sonneveld, E. (2002). *Crystallogr. Rep.* **47**, 76–81.
 Rybakov, V. B., Bush, A. A., Troyanov, S. I., Babaev, E. V. & Kemnitz, E. (2006). *Acta Cryst.* **E62**, o1673–o1675.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.

supplementary materials

Acta Cryst. (2007). E63, o3619 [doi:10.1107/S1600536807035611]

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

V. B. Rybakov, A. A. Bush, S. I. Troyanov, E. V. Babaev and E. Kemnitz

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 $C2\cdots O30^i = 3.2066$ (11) Å, $N1\cdots O30^i = 2.8689$ (11) Å and $C5\cdots O30^i = 2.9258$ (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.).

¹H-NMR spectrum: 9.61 (d, 1H, H₅, *J*₅₆ = 6.6 Hz), 8.05 (s, 1H, H₈), 7.68 (d, 1H, H₆, *J*₅₆ = 6.6 Hz), 2.67 (s, 3H, 7-CH₃).

Refinement

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

One CF₃-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

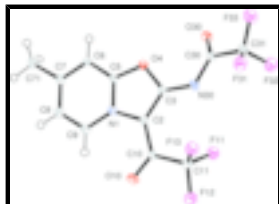


Fig. 1. The molecular structure of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms presented as spheres with arbitrary radius. Only major part of the disordered CF₃-group is shown.



Fig. 2. Reaction scheme.

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

Crystal data

C₁₂H₆F₆N₂O₃

M_r = 340.19

Monoclinic, *P*2₁/*c*

Hall symbol: -*P* 2ybc

a = 5.7996 (5) Å

b = 20.838 (2) Å

c = 10.4259 (8) Å

β = 91.100 (7)°

V = 1259.76 (19) Å³

Z = 4

*F*₀₀₀ = 680

D_x = 1.794 Mg m⁻³

Melting point: 509 K

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 429 reflections

θ = 3.0–29.5°

μ = 0.19 mm⁻¹

T = 100 (2) K

Needle, colourless

0.6 × 0.2 × 0.1 mm

Data collection

Stoe IPDS
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 100(2) K

ω scans

Absorption correction: none

3851 measured reflections

3776 independent reflections

3247 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.026

θ_{max} = 30.4°

θ_{min} = 2.0°

h = -8→8

k = 0→29

l = 0→14

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.048

wR(*F*²) = 0.131

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.0989*P*)²]

$S = 1.01$
 3776 reflections
 236 parameters
 12 restraints
 Primary atom site location: structure-invariant direct methods

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.008$
 $\Delta\rho_{\max} = 0.41 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	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 (\AA^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)

supplementary materials

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)

supplementary materials

C3—C2—C10—O10

-174.13 (10)

Fig. 1

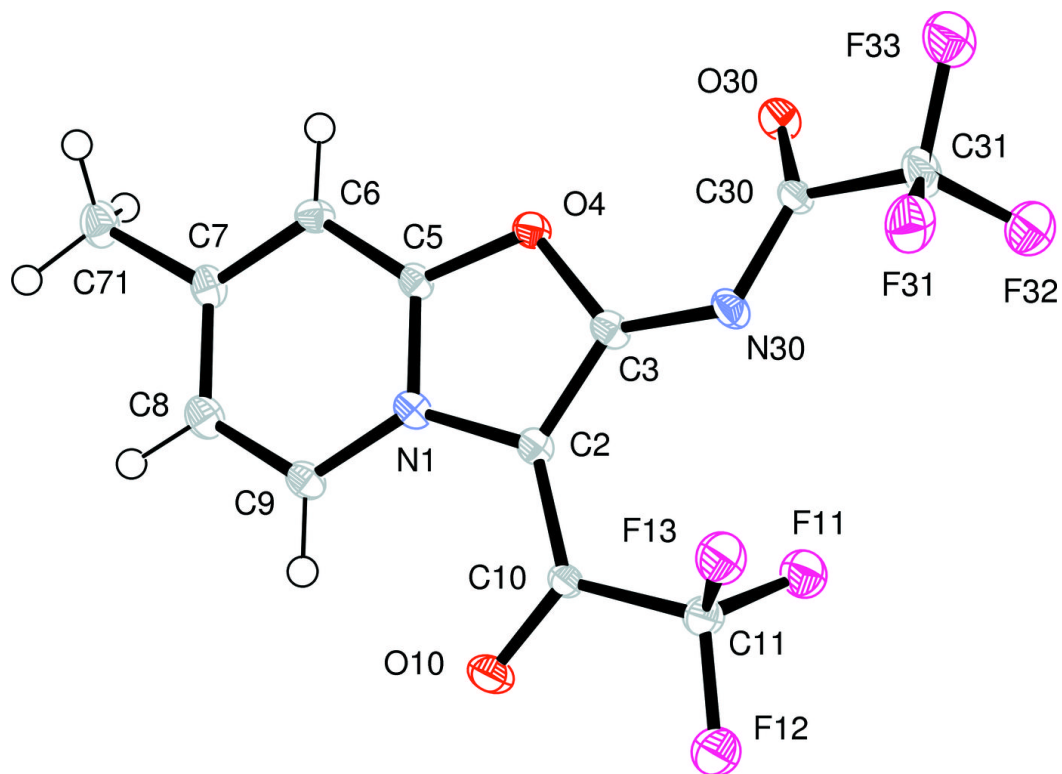


Fig. 2

