Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

2-Diazo-1-(1,1-dioxothiomorpholin-4-yl)-ethanone

Åsmund Kaupang, Carl Henrik Görbitz* and Tore Hansen

Department of Chemistry, University of Oslo, PO Box 1033 Blindern, N-0315 Oslo, Norway
Correspondence e-mail: c.h.gorbitz@kjemi.uio.no

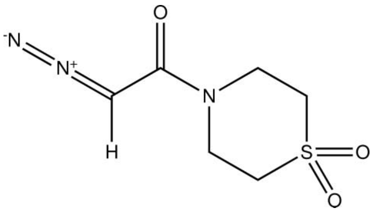
Received 7 June 2011; accepted 17 June 2011

Key indicators: single-crystal X-ray study; T = 105 K; mean σ(C–C) = 0.002 Å; disorder in main residue; R factor = 0.056; wR factor = 0.165; data-to-parameter ratio = 28.6.

In the molecule of the title compound, $C_6H_9N_3O_3S$, at 105 K, the six-membered ring is predominantly found in the chair conformation, with 1.89 (14)% in the boat conformation. In the crystal structure, there are five intermolecular $C—H\cdots O{=}C$ and $C—H\cdots O{=}S$ contacts less than 2.6 Å, as well as a weak $C—H\cdots N{=}N$ interaction to the diazo group.

Related literature

For related structures found in the Cambridge Structural Database (Version 5.32 of November 2010; Allen, 2002), see: Fenlon *et al.* (2007); Haynes *et al.* (2006); Wang *et al.* (2006); Miller *et al.* (1991); Foces-Foces *et al.* (1988); Ganguly *et al.* (1980); Herdklotz & Sass (1969). For details of the synthesis, see: Kaupang (2010); Toma *et al.* (2007) and for the synthesis of related diazoacetamides, see: Kaupang *et al.* (2010); Kaupang (2010); Ouihia *et al.* (1993). For quantum chemical calculations involving the acetamide analogue of the title compound, see: Fraenkel *et al.* (1992). For the Chemical Abstracts Service, see: American Chemical Society (2008). For hydrogen-bond graph-set notation, see: Etter *et al.* (1990).



Experimental

Crystal data

$C_6H_9N_3O_3S$
M_r = 203.22
Monoclinic, $P2_1/n$
a = 5.2729 (3) Å
b = 20.1349 (11) Å
c = 7.8683 (4) Å
β = 95.171 (2)°
V = 831.97 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.37 mm^{-1}
T = 105 K
0.80 × 0.30 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.849, T_{max} = 0.929
14742 measured reflections
3951 independent reflections
3029 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.165
S = 1.11
3951 reflections
138 parameters
13 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$C2—H2\cdots O2^{i}$	0.94 (2)	2.42 (2)	3.326 (2)	163 (2)
$C3—H32\cdots O1^{ii}$	0.99	2.47	3.372 (2)	152
$C5—H52\cdots O1^{iii}$	0.99	2.36	3.022 (2)	123
$C5—H51\cdots O3^{iv}$	0.99	2.56	3.445 (2)	149
$C5—H52\cdots N3^{v}$	0.99	2.59	3.417 (3)	141
$C6—H61\cdots O2^{vi}$	0.99	2.45	3.168 (2)	129

Symmetry codes: (i) $x, y, z-1$; (ii) $x-1, y, z$; (iii) $-x+1, -y, -z+1$; (iv) $x+1, y, z$; (v) $x-1, y, z+1$; (vi) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2361).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
American Chemical Society (2008). Chemical Abstracts Service, American Chemical Society, Columbus, OH, USA; accessed Apr 27, 2010.
Bruker (2007). *APEX2*, *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Fenlon, T. W., Schwaebisch, D., Mayweg, A. V. W., Lee, V., Adlington, R. M. & Baldwin, J. E. (2007). *Synlett*, pp. 2679–2682.
Foces-Foces, M. C., Cano, F. H., Claramunt, R. M., Fruchier, A. & Elguero, J. (1988). *Bull. Soc. Chim. Belg.* **97**, 1055–1066.
Fraenkel, G., Kolp, C. J. & Chow, A. (1992). *J. Am. Chem. Soc.* **114**, 4307–4314.
Ganguly, A. K., Liu, Y.-T., Sarre, O., Jaret, R. S., McPhail, A. T. & Onan, K. D. (1980). *Tetrahedron Lett.* **21**, 49, 4699–4702.
Haynes, R. K., Fugmann, B., Stetter, J., Rieckmann, K., Heilmann, H.-D., Chan, H.-W., Cheung, M.-K., Lam, W.-L. & Wong, H.-N. (2006). *Angew. Chem. Int. Ed.* **45**, 2082–2088.
Herdklotz, J. & Sass, R. L. (1969). *Acta Cryst.* B**25**, 1614–1620.
Kaupang, Å. (2010). MSc thesis, University of Oslo, Norway. PDF available online at http://urn.nb.no/URN:NBN:no-26202 or through http://www.duo.uio.no/.
Kaupang, Å., Görbitz, C. H. & Hansen, T. (2010). *Acta Cryst.* E**66**, o1299.
Miller, R. D., Theis, W., Heilig, G. & Kirchmeyer, S. (1991). *J. Org. Chem.* **56**, 1453–1463.

Ouihia, A., Rene, L., Guilhem, J., Pascard, C. & Badet, B. (1993). *J. Org. Chem.* **58**, 1641–1642.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Toma, T., Shimokawa, J. & Fukuyama, T. (2007). *Org. Lett.* **9**, 3195–3197.

Wang, J., Zeng, T., Li, M.-L., Duan, E.-H. & Li, J.-S. (2006). *Acta Cryst.* E**62**, o2912–o2913.

Acta Cryst. (2011). E**67**, o1844–o1845 Kaupang *et al.* • $C_6H_9N_3O_3S$ **o1845**

supplementary materials

Acta Cryst. (2011). E**67**, o1844-o1845 [**doi:10.1107/S1600536811023774**]

2-Diazo-1-(1,1-dioxothiomorpholin-4-yl)ethanone

Å. Kaupang, C. H. Görbitz and **T. Hansen**

Comment

2-Diazo-1-(1,1-dioxido-4-thiomorpholinyl)ethanone (I) was prepared as part of a series of diazoacetamides used in the intramolecular C—H insertion reactions taking place upon thermolysis of their corresponding α-bromodiazoacetamides (Kaupang, 2010). The title compound was synthesized from 2-bromo-1-(1,1-dioxido-4-thiomorpholinyl)ethanone following a procedure reported by Toma *et al.* (2007), modified to employ 1,1,3,3-tetramethylguanidine as the base instead of 1,8-diazabicyclo[5.4.0]undec-7-ene. No previous reports of this compound were found in the Chemical Abstracts Service (CAS, American Chemical Society, 2008).

In the crystal (I) occurs in the expected chair conformation, with a very minor fraction [occupancy 0.0189 (14)] in a boat conformation as shown in Fig. 1. The unit cell and crystal packing are depicted in Fig. 2, while a list of six C—H···O/N interactions with H···O distance shorter than 2.60 Å are given in Table 1. The two shortest interactions, with C2—H2 and C5—H52 donors, form *C*(8) chains along the *a* axis and dimeric $R_2^2(12)$ ring motifs, respectively (Etter *et al.*, 1990). H52 is also close to the diazo N3 atom and thus participates in a three-center interaction. The interactions of (I) are different from those observed in our previous, related structure of *tert*-butyl 4-(2-diazoacetyl)piperazine-1-carboxylate (Kaupang *et al.*, 2010) where the H of the diazoacetyl group was accepted by the O atom of the same group.

Experimental

A solution of 4.0 mg of the title compound in 500 µ*L* of CH_2Cl_2 was placed in a 2.5 ml vial which was capped and a pinhole (0.5 mm) made in the cap to allow for slow evaporation in darkness at ambient temperature. A single cluster of pale yellow needles appeared after approximately 48 h.

Refinement

H atoms were positioned with idealized geometry and with fixed C—H distances at 0.99 Å, except H atoms bonded to C2 and C4 for which coordinates were refined, as too short intramolecular H···H distances resulted from putting these H atoms in theoretical positions. Distance restraints were imposed on the C2—H2 and C4—H41/H42 bonds utilizing *SHELX DFIX* 0.95 0.02 and *DFIX* 0.99 0.02 commands, respectively. Heavy atoms were refined anisotropically, except S11, O12 and O13 associated with the minor boat conformation of the six-membered ring with an occupancy 0.0189 (14). The first two were assigned U_{iso}-values equal to the U_{eq}-values of the corresponding atoms of the major chair conformation, while O13 received the same set of anisotropic thermal parameters as O2, from which it is separated by 0.35 Å. Failure to include the 2% minor conformation in the refinement increases the *R*-factor from 0.056 to 0.058 for 138 *versus*. 127 refinement parameters.

Initial checkCIF/PLATON results indicated possible twinning; introduction of the suggested command TWIN -1 0 0 0 - 1 0 0.269 0 1 during refinement gave a very modest decrease in the *R*-factor, from 0.057 to 0.056, with BASF = 0.00248.

Figures

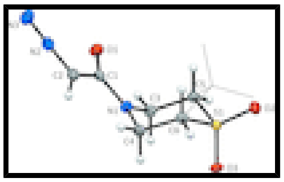


Fig. 1. The asymmetric unit of (I) with atomic numbering indicated. Displacement ellipsoids are shown at the 50% probability level with H atoms as spheres of arbitrary size. The wire-frame structure represents the minor boat conformation [occupancy 0.189 (14)].

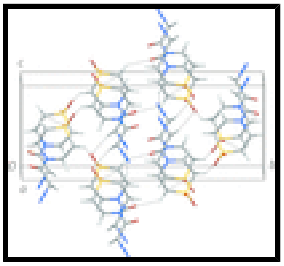


Fig. 2. The unit cell and crystal packing of (I) viewed approximately along the *a* axis. A three-dimensional network of weak intermolecular C=O···H, S=O···H and N=N···H contacts with O/N···H < 2.6 Å are shown as dotted lines.

2-Diazo-1-(1,1-dioxothiomorpholin-4-yl)ethanone

Crystal data

$C_6H_9N_3O_3S$

M_r = 203.22

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

a = 5.2729 (3) Å

b = 20.1349 (11) Å

c = 7.8683 (4) Å

β = 95.171 (2)°

V = 831.97 (8) Å^3

Z = 4

$F(000)$ = 424

D_x = 1.622 Mg m^{-3}

Melting point = 438–449 K

Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 5309 reflections

θ = 2.8–36.6°

μ = 0.37 mm^{-1}

T = 105 K

Needle, yellow

0.80 × 0.30 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer

Radiation source: fine-focus sealed tube

graphite

Detector resolution: 8.3 pixels mm^{-1}

Sets of exposures each taken over 0.5° ω rotation scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2007)

T_{min} = 0.849, T_{max} = 0.929

14742 measured reflections

3951 independent reflections

3029 reflections with $I > 2\sigma(I)$

R_{int} = 0.031

θ_{max} = 36.8°, θ_{min} = 2.0°

$h = -8 \rightarrow 8$

$k = -30 \rightarrow 32$

$l = -11 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.165$

$S = 1.11$

3951 reflections

138 parameters

13 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0728P)^2 + 1.0103P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 1.24$ e Å^{-3}

$\Delta\rho_{min} = -0.71$ e Å^{-3}

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.12602 (8)	0.17713 (2)	0.58307 (5)	0.01306 (11)	0.9811 (14)
O3	−0.1485 (2)	0.17127 (7)	0.56520 (19)	0.0176 (3)	0.9811 (14)
O2	0.2367 (3)	0.21336 (7)	0.73056 (18)	0.0194 (3)	0.9811 (14)
C5	0.2645 (3)	0.09728 (9)	0.5781 (2)	0.0152 (3)	0.9811 (14)
H51	0.4524	0.1012	0.5913	0.018*	0.9811 (14)
H52	0.2115	0.0703	0.6739	0.018*	0.9811 (14)
C6	0.2280 (3)	0.21174 (9)	0.3937 (2)	0.0156 (3)	0.9811 (14)
H61	0.1529	0.2565	0.3747	0.019*	0.9811 (14)
H62	0.4157	0.2163	0.4051	0.019*	0.9811 (14)
S11	0.385 (3)	0.1792 (3)	0.5843 (11)	0.013*	0.0189 (14)
O12	0.6562 (19)	0.1779 (9)	0.569 (4)	0.018*	0.0189 (14)
O13	0.302 (7)	0.2139 (3)	0.7308 (6)	0.0194 (3)	0.0189 (14)
C15	0.2645 (3)	0.09728 (9)	0.5781 (2)	0.0152 (3)	0.0189 (14)
H151	0.3969	0.0687	0.6379	0.018*	0.0189 (14)
H152	0.1168	0.0968	0.6474	0.018*	0.0189 (14)
C16	0.2280 (3)	0.21174 (9)	0.3937 (2)	0.0156 (3)	0.0189 (14)
H161	0.0734	0.2348	0.4255	0.019*	0.0189 (14)

H162	0.3408	0.2463	0.3519	0.019*	0.0189 (14)
O1	0.5857 (3)	0.02988 (7)	0.23496 (18)	0.0199 (3)	
N1	0.2562 (3)	0.10078 (8)	0.26290 (19)	0.0153 (3)	
C3	0.1799 (3)	0.06335 (9)	0.4088 (2)	0.0158 (3)	
H31	0.2552	0.0183	0.4081	0.019*	
H32	−0.0077	0.0585	0.3982	0.019*	
C4	0.1452 (4)	0.16671 (9)	0.2410 (2)	0.0175 (3)	
H41	−0.042 (3)	0.1625 (15)	0.232 (4)	0.021*	
H42	0.197 (5)	0.1864 (13)	0.135 (3)	0.021*	
C1	0.4582 (3)	0.07843 (9)	0.1828 (2)	0.0146 (3)	
C2	0.5141 (4)	0.11299 (10)	0.0274 (2)	0.0173 (3)	
H2	0.410 (5)	0.1428 (12)	−0.039 (3)	0.021*	
N2	0.7103 (3)	0.08892 (9)	−0.0445 (2)	0.0200 (3)	
N3	0.8809 (4)	0.06859 (12)	−0.1020 (2)	0.0294 (4)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01136 (17)	0.01274 (19)	0.01499 (19)	0.00030 (13)	0.00065 (12)	−0.00052 (13)
O3	0.0102 (5)	0.0198 (6)	0.0230 (6)	0.0005 (4)	0.0021 (4)	0.0000 (5)
O2	0.0209 (6)	0.0185 (6)	0.0182 (6)	−0.0011 (5)	−0.0011 (5)	−0.0042 (5)
C5	0.0151 (7)	0.0143 (7)	0.0163 (7)	0.0017 (5)	0.0013 (5)	0.0016 (5)
C6	0.0160 (7)	0.0132 (7)	0.0175 (7)	0.0001 (5)	0.0010 (5)	0.0017 (5)
O13	0.0209 (6)	0.0185 (6)	0.0182 (6)	−0.0011 (5)	−0.0011 (5)	−0.0042 (5)
C15	0.0151 (7)	0.0143 (7)	0.0163 (7)	0.0017 (5)	0.0013 (5)	0.0016 (5)
C16	0.0160 (7)	0.0132 (7)	0.0175 (7)	0.0001 (5)	0.0010 (5)	0.0017 (5)
O1	0.0195 (6)	0.0180 (6)	0.0224 (6)	0.0039 (5)	0.0026 (5)	0.0040 (5)
N1	0.0182 (6)	0.0130 (6)	0.0151 (6)	0.0021 (5)	0.0032 (5)	0.0019 (5)
C3	0.0177 (7)	0.0132 (7)	0.0168 (7)	−0.0010 (5)	0.0036 (5)	0.0008 (5)
C4	0.0207 (8)	0.0146 (8)	0.0169 (7)	0.0038 (6)	0.0005 (6)	0.0013 (5)
C1	0.0151 (7)	0.0144 (7)	0.0140 (7)	−0.0013 (5)	−0.0003 (5)	−0.0004 (5)
C2	0.0186 (7)	0.0190 (8)	0.0143 (7)	−0.0008 (6)	0.0013 (5)	0.0007 (6)
N2	0.0199 (7)	0.0243 (8)	0.0160 (7)	−0.0043 (6)	0.0022 (5)	0.0005 (5)
N3	0.0240 (8)	0.0410 (11)	0.0245 (9)	0.0015 (8)	0.0087 (7)	0.0003 (7)

Geometric parameters (Å, °)

S1—O3	1.4463 (13)	O1—C1	1.235 (2)
S1—O2	1.4482 (14)	N1—C1	1.362 (2)
S1—C5	1.7679 (18)	N1—C4	1.455 (2)
S1—C6	1.7718 (18)	N1—C3	1.460 (2)
C5—C3	1.528 (3)	C3—H31	0.9900
C5—H51	0.9900	C3—H32	0.9900
C5—H52	0.9900	C4—H41	0.984 (17)
C6—C4	1.537 (3)	C4—H42	0.983 (16)
C6—H61	0.9900	C1—C2	1.460 (2)
C6—H62	0.9900	C2—N2	1.316 (2)
S11—O12	1.446 (2)	C2—H2	0.940 (17)
S11—O13	1.448 (2)	N2—N3	1.120 (2)

O3—S1—O2	116.52 (9)	C4—N1—C3	115.30 (14)
O3—S1—C5	109.59 (8)	N1—C3—C5	112.05 (14)
O2—S1—C5	109.77 (9)	N1—C3—H31	109.2
O3—S1—C6	109.11 (9)	C5—C3—H31	109.2
O2—S1—C6	110.17 (9)	N1—C3—H32	109.2
C5—S1—C6	100.48 (8)	C5—C3—H32	109.2
C3—C5—S1	109.70 (12)	H31—C3—H32	107.9
C3—C5—H51	109.7	N1—C4—C6	111.28 (15)
S1—C5—H51	109.7	N1—C4—H41	108.6 (17)
C3—C5—H52	109.7	C6—C4—H41	108.7 (17)
S1—C5—H52	109.7	N1—C4—H42	109.1 (17)
H51—C5—H52	108.2	C6—C4—H42	110.1 (17)
C4—C6—S1	109.81 (12)	H41—C4—H42	109 (2)
C4—C6—H61	109.7	O1—C1—N1	122.16 (16)
S1—C6—H61	109.7	O1—C1—C2	120.72 (16)
C4—C6—H62	109.7	N1—C1—C2	117.09 (16)
S1—C6—H62	109.7	N2—C2—C1	114.24 (17)
H61—C6—H62	108.2	N2—C2—H2	116.1 (17)
O12—S11—O13	116.5 (3)	C1—C2—H2	128.1 (18)
C1—N1—C4	124.74 (15)	N3—N2—C2	178.3 (2)
C1—N1—C3	118.42 (15)		

O3—S1—C5—C3	59.85 (14)	C3—N1—C4—C6	62.7 (2)
O2—S1—C5—C3	−170.98 (12)	S1—C6—C4—N1	−60.49 (17)
C6—S1—C5—C3	−54.93 (13)	C4—N1—C1—O1	161.34 (18)
O3—S1—C6—C4	−59.84 (14)	C3—N1—C1—O1	−3.9 (3)
O2—S1—C6—C4	171.06 (12)	C4—N1—C1—C2	−20.7 (3)
C5—S1—C6—C4	55.31 (13)	C3—N1—C1—C2	174.07 (15)
C1—N1—C3—C5	103.74 (18)	O1—C1—C2—N2	−1.7 (3)
C4—N1—C3—C5	−62.8 (2)	N1—C1—C2—N2	−179.68 (16)
S1—C5—C3—N1	60.09 (17)	C1—C2—N2—N3	−53 (8)
C1—N1—C4—C6	−102.9 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O2^{i}	0.94 (2)	2.42 (2)	3.326 (2)	163 (2)
C3—H32···O1^{ii}	0.99	2.47	3.372 (2)	152
C5—H52···O1^{iii}	0.99	2.36	3.022 (2)	123
C5—H51···O3^{iv}	0.99	2.56	3.445 (2)	149
C5—H52···N3^{v}	0.99	2.59	3.417 (3)	141
C6—H61···O2^{vi}	0.99	2.45	3.168 (2)	129

Symmetry codes: (i) *x*, *y*, *z*−1; (ii) *x*−1, *y*, *z*; (iii) −*x*+1, −*y*, −*z*+1; (iv) *x*+1, *y*, *z*; (v) *x*−1, *y*, *z*+1; (vi) *x*−1/2, −*y*+1/2, *z*−1/2.

Fig. 1

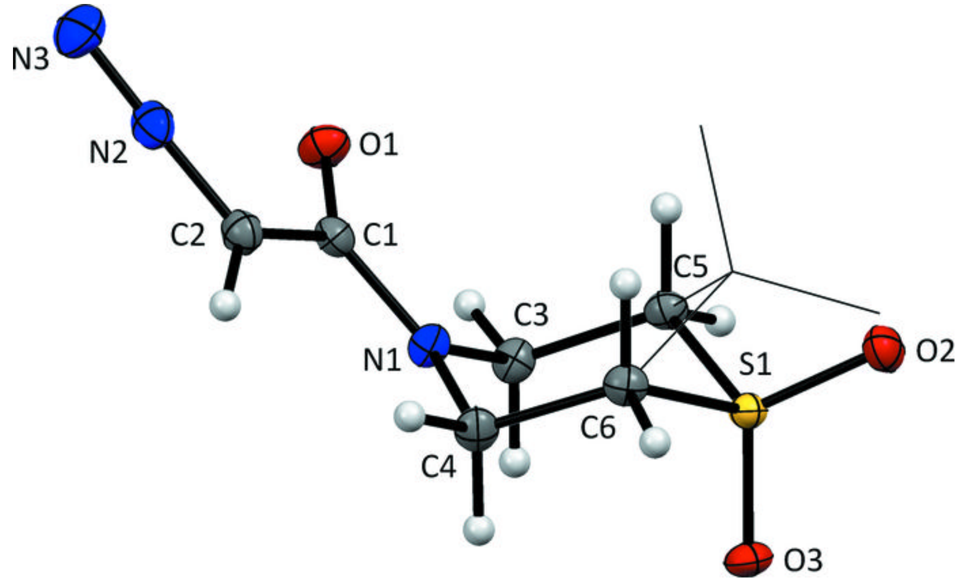


Fig. 2