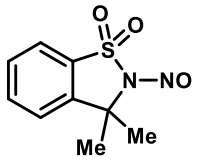
5 February, 2021



NO-1

3,3-dimethyl-2-nitroso-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (NO-1)

A yellow block with approximate orthogonal dimensions 0.060 x 0.154 x 0.338mm^3 was placed and optically centered on the Bruker Duo[1] APEXII CCD system at –183°C(90K). Indexing of the unit cell used a random set of reflections collected from three series of 0.5° wide ω-scans, 10 seconds per frame, and 30 frames per series that were well distributed in reciprocal space. Five ω-scan data frame series were collected [MoK$_\alpha$] with 0.3° wide scans, 15 seconds per frame and 606 frames collected per series at varying φ angles (φ=0°, 72°, 144°, 216°, 288°). The crystal to detector distance was 5.15cm, thus providing a complete sphere of data to $2\theta_{max}$=61.01°.

Structural determination and Refinement:

All crystallographic calculations were performed on an Intel Xeon E5-1620v2 at 3.70GHz an eight core processor and 16GB of extended memory. Data collected were corrected for Lorentz and polarization effects with Saint[1] and absorption using Blessing's method and merged as incorporated with the program Sadabs[2,3]. The SHELXTL[4] program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences and intensity statistics indicated the centrosymmetric monoclinic space group $P2_1/n$ (no. 14). The structure was determined by direct methods with the non-hydrogen atoms being located directly for the molecule using the program XT[5]. The structure was refined with XL[6]. The 20407 data collected were merged, based upon identical indices to 11861 data, then for least squares refinement to 3091 unique data [R(int)=0.0224]. All non-hydrogen atoms were refined anisotropically. A disorder was modeled for the terminal N-O, group with the final ratio 0.87:0.13. Hydrogen atoms were idealized initially and then allowed to refine freely throughout the final refinement stage. The final structure was refined to convergence with R(F)=3.63%, wR(F^2)=8.27%, GOF=1.065 for all 3091 unique reflections [R(F)=3.08, wR(F^2)=7.87% for those 2706 data with Fo > 4σ(Fo)]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete.

Table 1. Crystal data and structure refinement for [$C_9H_{10}N_2O_3S$].

Identification code	JF2913FMI (JDGR2)
Empirical formula	C9 H10 N2 O3 S
Formula weight	226.25
Temperature	90(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.7236(7) Å	α= 90°.
	b = 9.8965(9) Å	β= 94.6681(13)°.
	c = 13.3301(12) Å	γ = 90°.
Volume	1015.53(16) $Å^3$	
Z	4	
Density (calculated)	1.480 Mg/m^3	
Absorption coefficient	0.307 mm^{-1}	
F(000)	472	
Crystal size	0.338 x 0.154 x 0.060 mm^3	
Crystal color and habit	Yellow Block	
Diffractometer	Bruker APEX-II CCD	
Theta range for data collection	2.566 to 30.509°.	
Index ranges	-11<=h<=11, -14<=k<=14, -19<=l<=19	
Reflections collected	11861	
Independent reflections	3091 [R(int) = 0.0224]	
Observed reflections (I > 2sigma(I))	2706	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9575 and 0.8766	
Solution method	SHELXT (Sheldrick, 2014)	
Refinement method	SHELXL-2018/3 (Sheldrick, 2018) Full-matrix least-squares on F^2	
Data / restraints / parameters	3091 / 14 / 194	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0308, wR2 = 0.0787	
R indices (all data)	R1 = 0.0363, wR2 = 0.0827	
Largest diff. peak and hole	0.470 and -0.392 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for JF2913FMI. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	4763(1)	2078(1)	2767(1)	15(1)
O(1)	3101(1)	1688(1)	3080(1)	27(1)
O(2)	4988(1)	2114(1)	1712(1)	26(1)
N(1)	6354(1)	1119(1)	3387(1)	14(1)
N(2)	6463(5)	-229(2)	3272(2)	20(1)
O(3)	5421(1)	-686(1)	2611(1)	25(1)
N(2B)	6240(30)	-193(10)	3105(16)	19(2)
O(3B)	7244(9)	-925(7)	3622(6)	26(1)
C(1)	7391(1)	1780(1)	4250(1)	12(1)
C(2)	6875(1)	3255(1)	4121(1)	13(1)
C(3)	5548(1)	3530(1)	3384(1)	14(1)
C(4)	6827(2)	1211(1)	5241(1)	16(1)
C(5)	9330(1)	1573(1)	4149(1)	18(1)
C(6)	4931(2)	4826(1)	3157(1)	20(1)
C(7)	5712(2)	5886(1)	3705(1)	24(1)
C(8)	7030(2)	5636(1)	4460(1)	23(1)
C(9)	7620(2)	4329(1)	4680(1)	18(1)

Table 3. Bond lengths [Å] and angles [°] for JF2913FMI.

S(1)-O(2)	1.4308(9)	N(1)-S(1)-C(3)	91.20(5)
S(1)-O(1)	1.4346(9)	N(2)-N(1)-C(1)	119.06(11)
S(1)-N(1)	1.7109(9)	N(2B)-N(1)-C(1)	130.6(6)
S(1)-C(3)	1.7400(11)	N(2)-N(1)-S(1)	122.93(11)
N(1)-N(2)	1.3461(18)	N(2B)-N(1)-S(1)	111.8(6)
N(1)-N(2B)	1.352(9)	C(1)-N(1)-S(1)	116.55(7)
N(1)-C(1)	1.4976(13)	O(3)-N(2)-N(1)	113.74(15)
N(2)-O(3)	1.230(2)	O(3B)-N(2B)-N(1)	112.8(11)
N(2B)-O(3B)	1.229(10)	N(1)-C(1)-C(2)	102.34(8)
C(1)-C(2)	1.5196(14)	N(1)-C(1)-C(5)	109.90(9)
C(1)-C(5)	1.5283(15)	C(2)-C(1)-C(5)	111.63(9)
C(1)-C(4)	1.5324(15)	N(1)-C(1)-C(4)	109.30(8)
C(2)-C(3)	1.3877(15)	C(2)-C(1)-C(4)	111.10(9)
C(2)-C(9)	1.3955(15)	C(5)-C(1)-C(4)	112.11(9)
C(3)-C(6)	1.3931(15)	C(3)-C(2)-C(9)	118.54(10)
C(4)-H(4A)	0.976(15)	C(3)-C(2)-C(1)	116.11(9)
C(4)-H(4B)	0.969(16)	C(9)-C(2)-C(1)	125.35(10)
C(4)-H(4C)	0.964(17)	C(2)-C(3)-C(6)	123.65(10)
C(5)-H(5A)	0.986(17)	C(2)-C(3)-S(1)	112.43(8)
C(5)-H(5B)	0.938(18)	C(6)-C(3)-S(1)	123.91(9)
C(5)-H(5C)	0.968(17)	C(1)-C(4)-H(4A)	110.8(9)
C(6)-C(7)	1.3877(18)	C(1)-C(4)-H(4B)	109.1(9)
C(6)-H(6)	0.956(16)	H(4A)-C(4)-H(4B)	109.6(13)
C(7)-C(8)	1.394(2)	C(1)-C(4)-H(4C)	109.7(9)
C(7)-H(7)	0.924(19)	H(4A)-C(4)-H(4C)	108.2(13)
C(8)-C(9)	1.3939(17)	H(4B)-C(4)-H(4C)	109.4(13)
C(8)-H(8)	0.926(18)	C(1)-C(5)-H(5A)	108.7(10)
C(9)-H(9)	0.959(15)	C(1)-C(5)-H(5B)	109.6(11)
		H(5A)-C(5)-H(5B)	109.8(14)
O(2)-S(1)-O(1)	118.40(6)	C(1)-C(5)-H(5C)	112.1(10)
O(2)-S(1)-N(1)	110.40(5)	H(5A)-C(5)-H(5C)	108.9(14)
O(1)-S(1)-N(1)	109.57(5)	H(5B)-C(5)-H(5C)	107.7(14)
O(2)-S(1)-C(3)	112.20(6)	C(7)-C(6)-C(3)	117.06(11)
O(1)-S(1)-C(3)	111.73(5)	C(7)-C(6)-H(6)	122.9(10)

C(3)-C(6)-H(6)	120.0(10)	C(9)-C(8)-H(8)	119.6(11)
C(6)-C(7)-C(8)	120.44(11)	C(7)-C(8)-H(8)	118.8(11)
C(6)-C(7)-H(7)	119.5(11)	C(8)-C(9)-C(2)	118.70(11)
C(8)-C(7)-H(7)	120.1(11)	C(8)-C(9)-H(9)	121.4(9)
C(9)-C(8)-C(7)	121.59(11)	C(2)-C(9)-H(9)	119.9(9)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for JF2913FMI. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	13(1)	19(1)	14(1)	-2(1)	-2(1)	2(1)
O(1)	14(1)	29(1)	38(1)	-8(1)	1(1)	-4(1)
O(2)	33(1)	32(1)	12(1)	-2(1)	-4(1)	9(1)
N(1)	16(1)	12(1)	14(1)	-1(1)	-1(1)	1(1)
N(2)	27(1)	14(1)	19(1)	-2(1)	5(1)	-1(1)
O(3)	32(1)	21(1)	23(1)	-9(1)	4(1)	-8(1)
N(2B)	25(3)	14(3)	20(3)	2(2)	9(3)	2(2)
O(3B)	27(3)	20(3)	31(3)	-1(3)	4(3)	3(3)
C(1)	12(1)	13(1)	12(1)	0(1)	-1(1)	0(1)
C(2)	14(1)	13(1)	13(1)	0(1)	4(1)	-1(1)
C(3)	14(1)	14(1)	14(1)	0(1)	3(1)	1(1)
C(4)	19(1)	17(1)	14(1)	2(1)	1(1)	-3(1)
C(5)	13(1)	21(1)	21(1)	2(1)	1(1)	2(1)
C(6)	23(1)	19(1)	18(1)	5(1)	6(1)	7(1)
C(7)	33(1)	13(1)	27(1)	3(1)	15(1)	4(1)
C(8)	29(1)	14(1)	26(1)	-4(1)	12(1)	-7(1)
C(9)	19(1)	17(1)	18(1)	-2(1)	4(1)	-5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for JF2913FMI.

	x	y	z	U(eq)
H(4A)	5570(20)	1298(16)	5272(11)	20(4)
H(4B)	7420(20)	1698(16)	5798(12)	22(4)
H(4C)	7120(20)	266(17)	5294(12)	25(4)
H(5A)	9560(20)	596(17)	4100(12)	27(4)
H(5B)	9970(20)	1934(17)	4714(13)	31(4)
H(5C)	9710(20)	2018(17)	3558(13)	27(4)
H(6)	4010(20)	4955(16)	2645(12)	23(4)
H(7)	5330(20)	6759(19)	3577(13)	33(5)
H(8)	7520(20)	6358(18)	4823(13)	31(4)
H(9)	8530(20)	4161(15)	5198(12)	19(4)

Table 6. Torsion angles [°] for JF2913FMI.

O(2)-S(1)-N(1)-N(2)	-68.4(2)	N(1)-S(1)-C(3)-C(2)	-6.36(8)
O(1)-S(1)-N(1)-N(2)	63.8(2)	O(2)-S(1)-C(3)-C(6)	60.31(11)
C(3)-S(1)-N(1)-N(2)	177.4(2)	O(1)-S(1)-C(3)-C(6)	-75.39(11)
O(2)-S(1)-N(1)-N(2B)	-65.0(14)	N(1)-S(1)-C(3)-C(6)	172.96(10)
O(1)-S(1)-N(1)-N(2B)	67.1(14)	C(2)-C(3)-C(6)-C(7)	0.36(16)
C(3)-S(1)-N(1)-N(2B)	-179.3(14)	S(1)-C(3)-C(6)-C(7)	-178.89(9)
O(2)-S(1)-N(1)-C(1)	125.60(8)	C(3)-C(6)-C(7)-C(8)	-1.28(17)
O(1)-S(1)-N(1)-C(1)	-102.28(8)	C(6)-C(7)-C(8)-C(9)	0.83(18)
C(3)-S(1)-N(1)-C(1)	11.33(8)	C(7)-C(8)-C(9)-C(2)	0.61(17)
C(1)-N(1)-N(2)-O(3)	172.4(2)	C(3)-C(2)-C(9)-C(8)	-1.50(15)
S(1)-N(1)-N(2)-O(3)	6.7(4)	C(1)-C(2)-C(9)-C(8)	178.68(10)
C(1)-N(1)-N(2B)-O(3B)	-5(3)		
S(1)-N(1)-N(2B)-O(3B)	-172.2(17)		
N(2)-N(1)-C(1)-C(2)	-178.7(2)		
N(2B)-N(1)-C(1)-C(2)	-179.1(17)		
S(1)-N(1)-C(1)-C(2)	-12.12(10)		
N(2)-N(1)-C(1)-C(5)	62.6(2)		
N(2B)-N(1)-C(1)-C(5)	62.2(17)		
S(1)-N(1)-C(1)-C(5)	-130.84(8)		
N(2)-N(1)-C(1)-C(4)	-60.9(2)		
N(2B)-N(1)-C(1)-C(4)	-61.2(17)		
S(1)-N(1)-C(1)-C(4)	105.72(9)		
N(1)-C(1)-C(2)-C(3)	7.11(12)		
C(5)-C(1)-C(2)-C(3)	124.60(10)		
C(4)-C(1)-C(2)-C(3)	-109.45(10)		
N(1)-C(1)-C(2)-C(9)	-173.06(10)		
C(5)-C(1)-C(2)-C(9)	-55.57(14)		
C(4)-C(1)-C(2)-C(9)	70.38(13)		
C(9)-C(2)-C(3)-C(6)	1.05(16)		
C(1)-C(2)-C(3)-C(6)	-179.11(10)		
C(9)-C(2)-C(3)-S(1)	-179.63(8)		
C(1)-C(2)-C(3)-S(1)	0.21(12)		
O(2)-S(1)-C(3)-C(2)	-119.01(8)		
O(1)-S(1)-C(3)-C(2)	105.30(9)		

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for JF2913FMI [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(4)-H(4B)...O(2)#1	0.969(16)	2.530(16)	3.4309(14)	154.8(13)
C(4)-H(4C)...O(3B^b)	0.964(17)	2.531(18)	3.058(7)	114.4(12)
C(5)-H(5A)...O(3B^b)	0.986(17)	2.385(18)	3.003(7)	120.0(12)
C(6)-H(6)...O(1)#2	0.956(16)	2.503(16)	3.3121(15)	142.4(13)

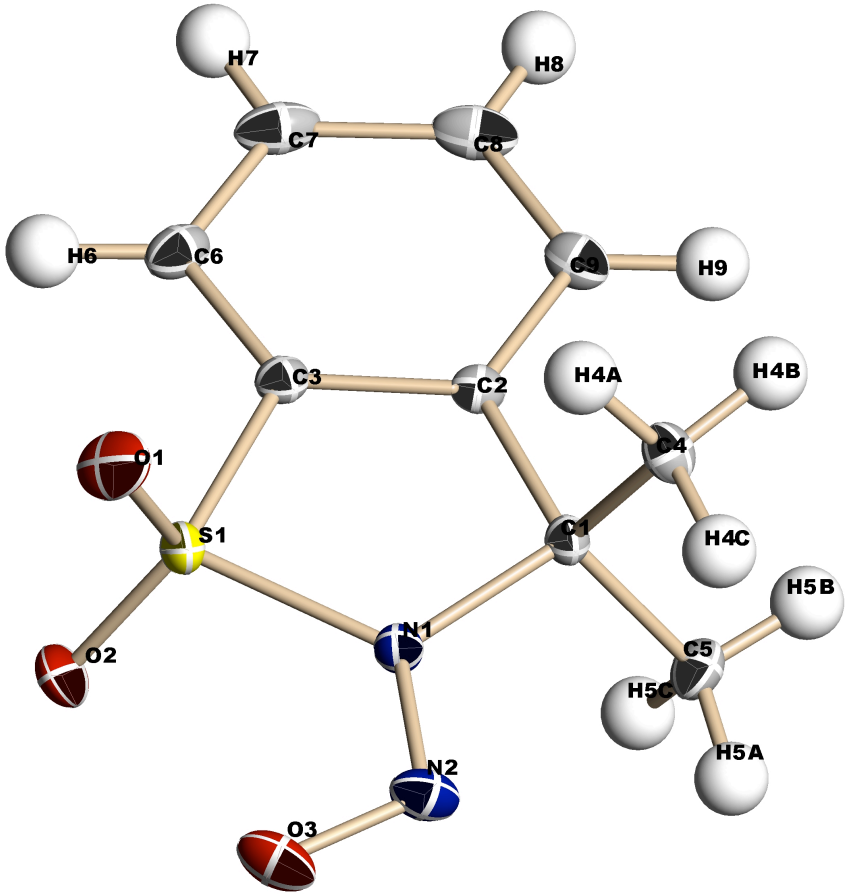
Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,z+1/2 #2 -x+1/2,y+1/2,-z+1/2

References:

1. Bruker (2014) APEX2 (Version 2014.9) and (2016) SAINT (Version 8.37a). Bruker AXS Inc., Madison, Wisconsin, USA.
2. An Empirical Correction for Absorption Anisotropy, Blessing, R. H. (1995). Acta Cryst., A51, 33-38.
3. Sheldrick, G.M., SADABS (2016) Version 2016/2, 'Siemens Area Detector Absorption Correction' Universität Göttingen: Göttingen, Germany.
4. Sheldrick, G.M., (2002). SHELXTL. Version 6.1. Bruker AXS Inc., Madison, Wisconsin, USA.
5. Sheldrick, G. M., (2014) SHELXT, Universität Göttingen: Göttingen, Germany. Structure determination program. Private communication.
6. Sheldrick, G. M., (2017). SHELXL2017/1. Universität Göttingen: Göttingen, Germany.

Acknowledgment: We thank the National Science Foundation (Grant CHE-0840444) for the Dual Source X-ray diffractometer.


H7
H8
C7
C8
H6
C6
C9
H9
C3
C2
H4A
H4B
C4
O1
S1
C1
H4C
H5B
N1
O2
C5
H5C
H5A
N2
O3