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N-Bromo-*S*-(4-nitrophenyl)-*S*-phenylsulfimide

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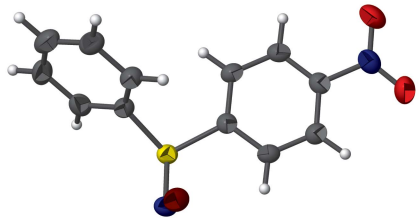
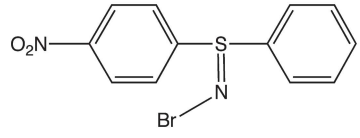
The title compound, $C_{12}H_9BrN_2O_2S$, the first crystal structure of an *N*-halosulfimide, adopts a *syn* conformation about the S=N bond, with a Br—N—S—C(phenyl) torsion angle of −54.64 (17)°. The dihedral angle between between the phenyl and 4-nitrophenyl rings is 65.04 (14)°. In the crystal, molecules are linked by C—H···Br, C—H···N and C—H···O interactions, forming a tape structure along the *c* axis.

3D view



Chemical scheme



Structure description

The chemistry of *N*-halosulfimides (R,R'S=NX) has attracted much attention due to their unique structures and reactivities (Oae & Furukawa, 1983; Yoshimura *et al.*, 1977; Kumar & Shreeve, 1981; Aucott *et al.*, 2004). Previously, we have synthesized diaryl(fluoro)-λ^6-sulfanenitriles by the reaction of *S*,*S*-diaryl-*N*-bromosulfimides with tetrabutylammonium fluoride (Yoshimura *et al.*, 1992) and also by the reaction of *S*,*S*-diarylsulfimides using Selectfluor™, an electrophilic fluorinating reagent, where the reaction proceeds *via* *S*,*S*-diaryl-*N*-fluorosulfimides as intermediates which undergo 1,2-migration of the F atom (Fujii *et al.*, 2003). We have also performed DFT calculations using a model compound, *S*,*S*-dimethyl-*N*-fluorosulfimide, which showed that the *syn* conformer of *N*-fluorosulfimide is more stable than the *anti* one. In order to elucidate the mechanism of this 1,2-migration (retention or inversion), it is important to examine the structures of *N*-halosulfimides. However, the corresponding *N*-fluorosulfimides could not be isolated, and similar compounds of *N*-chlorosulfimides are also unstable for X-ray analysis. The crystal structure of the title compound, *N*-bromo-*S*-(4-nitrophenyl)-*S*-phenylsulfimide, has now been successfully resolved.

The molecular structure of the title compound was found to have a *syn* conformation, consistent with the prediction of the DFT calculation, as illustrated in Fig. 1. In the

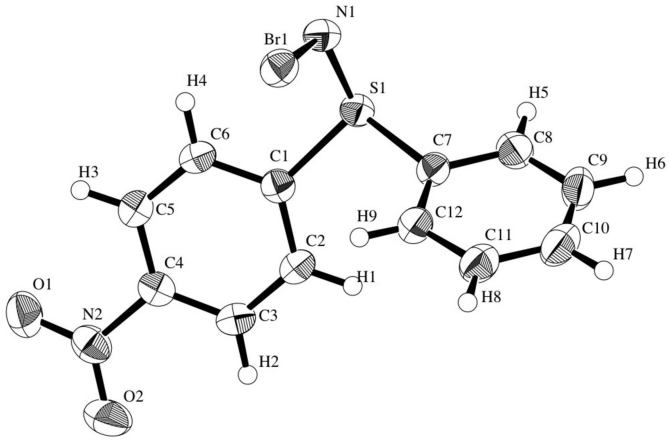


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.

crystal, the molecules are linked through weak C3—H2···(N═Br) and C5—H3···O1 hydrogen bonds, forming a tape along the *c* axis (Table 1 and Fig. 2).

Synthesis and crystallization

The title compound was prepared by the method previously reported (Yoshimura *et al.*, 1977) using *S*-(4-nitrophenyl)-*S*-phenylsulfimide mono hydrate and *N*-bromosuccinimide and crystallized from a benzene-hexane (1:1) solution (yield: 95%; m.p. 425–426 K).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H2···Br1^{i}	0.95	2.86	3.598 (3)	135
C3—H2···N1^{i}	0.95	2.44	3.286 (3)	149
C5—H3···O1^{ii}	0.95	2.54	3.435 (3)	158

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_9BrN_2O_2S$
M_r	325.18
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, *b*, *c* (Å)	9.12236 (10), 18.7734 (3), 7.70271 (10)
β (°)	108.576 (1)
V (Å^3)	1250.42 (3)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	6.02
Crystal size (mm)	0.52 × 0.27 × 0.20
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan (*ABSCOR*; Higashi, 1995)
T_{min}, T_{max}	0.226, 0.300
No. of measured, independent and observed [$F^2 > 2.0\sigma(F^2)$] reflections	14491, 2279, 2124
R_{int}	0.077
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.101, 1.08
No. of reflections	2279
No. of parameters	163
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.83, −0.40

Computer programs: *RAPID-AUTO* (Rigaku, 2001), *SIR92* (Altomare *et al.*, 1994), *SHELXL97* (Sheldrick, 2008), *CrystalStructure* (Rigaku, 2010).

Acknowledgements

The authors are grateful to the Department of Applied Chemistry, Faculty of Engineering, University of Toyama, for the provision of laboratory facilities. They also acknowledge the University of Toyama for providing funds for single-crystal X-ray analyses.

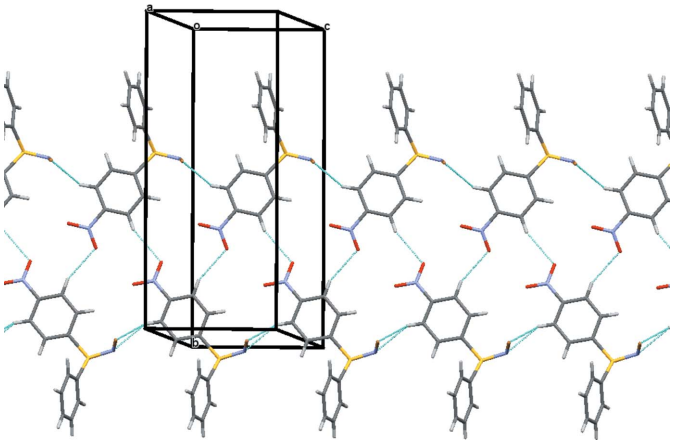


Figure 2
A partial packing diagram for the title compound with C—H···(N═Br) and C—H···O hydrogen bonds shown as blue dashed lines.

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full crystallographic data

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Crystal data

$C_{12}H_9BrN_2O_2S$
M_r = 325.18
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 9.12236 (10) Å
b = 18.7734 (3) Å
c = 7.70271 (10) Å
β = 108.576 (1)°
V = 1250.42 (3) Å^3
Z = 4
$F(000)$ = 648.00
D_x = 1.727 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54187 Å
Cell parameters from 13002 reflections
θ = 4.7–68.3°
μ = 6.02 mm^{-1}
T = 173 K
Block, yellow
0.52 × 0.27 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.226, T_{max} = 0.300
14491 measured reflections
2279 independent reflections
2124 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.077
θ_{max} = 68.2°
h = −10→10
k = −21→22
l = −9→9

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.101
S = 1.08
2279 reflections
163 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.2679P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.83 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Special details

Geometry. ENTER SPECIAL DETAILS OF THE MOLECULAR GEOMETRY

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2. R-factor (gt) are based on F. The threshold expression of F^2 > 2.0 sigma(F^2) is used only for calculating R-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.91904 (3)	0.032258 (15)	0.74644 (3)	0.04051 (15)
S1	0.64227 (7)	0.07351 (3)	0.43986 (8)	0.03335 (18)
O1	0.6655 (3)	−0.22788 (11)	0.0004 (3)	0.0550 (6)
O2	0.7188 (3)	−0.15518 (13)	−0.1882 (3)	0.0597 (6)
N1	0.7002 (3)	0.05179 (12)	0.6514 (3)	0.0377 (5)
N2	0.6924 (3)	−0.16817 (13)	−0.0455 (3)	0.0410 (6)
C1	0.6804 (3)	0.00334 (13)	0.2999 (4)	0.0312 (5)
C2	0.6876 (3)	0.01676 (14)	0.1252 (4)	0.0344 (6)
C3	0.6935 (3)	−0.03971 (13)	0.0125 (4)	0.0349 (6)
C4	0.6913 (3)	−0.10794 (14)	0.0781 (4)	0.0336 (6)
C5	0.6850 (3)	−0.12264 (14)	0.2515 (4)	0.0365 (6)
C6	0.6798 (3)	−0.06594 (14)	0.3630 (4)	0.0344 (6)
C7	0.7462 (3)	0.14683 (13)	0.3886 (3)	0.0342 (6)
C8	0.6725 (4)	0.21283 (15)	0.3750 (4)	0.0409 (6)
C9	0.7501 (4)	0.27343 (15)	0.3495 (4)	0.0479 (7)
C10	0.8984 (4)	0.26804 (16)	0.3384 (4)	0.0514 (8)
C11	0.9707 (4)	0.20242 (15)	0.3515 (4)	0.0445 (7)
C12	0.8943 (3)	0.14113 (15)	0.3777 (4)	0.0386 (6)
H1	0.6884	0.0644	0.0837	0.0413*
H2	0.6989	−0.0317	−0.1071	0.0418*
H3	0.6842	−0.1703	0.2924	0.0438*
H4	0.6758	−0.0742	0.4831	0.0413*
H5	0.5709	0.2161	0.3831	0.0490*
H6	0.7016	0.3187	0.3396	0.0575*
H7	0.9511	0.3098	0.3217	0.0617*
H8	1.0720	0.1993	0.3426	0.0534*
H9	0.9433	0.0959	0.3879	0.0464*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0399 (3)	0.0421 (3)	0.0385 (2)	0.00127 (10)	0.01095 (15)	0.00459 (10)
S1	0.0334 (4)	0.0342 (4)	0.0354 (4)	0.0022 (3)	0.0151 (3)	0.0019 (3)
O1	0.0734 (15)	0.0357 (12)	0.0560 (13)	0.0016 (10)	0.0207 (11)	−0.0056 (10)
O2	0.0776 (16)	0.0631 (15)	0.0474 (12)	−0.0027 (12)	0.0324 (11)	−0.0130 (11)
N1	0.0408 (12)	0.0407 (12)	0.0363 (11)	0.0022 (10)	0.0188 (10)	0.0024 (10)
N2	0.0373 (12)	0.0461 (15)	0.0375 (12)	0.0036 (10)	0.0089 (10)	−0.0066 (10)
C1	0.0275 (12)	0.0327 (14)	0.0335 (12)	−0.0007 (10)	0.0098 (10)	−0.0004 (10)
C2	0.0346 (14)	0.0356 (13)	0.0336 (13)	−0.0014 (11)	0.0115 (11)	0.0063 (11)
C3	0.0318 (14)	0.0434 (16)	0.0305 (13)	−0.0026 (10)	0.0115 (11)	0.0019 (11)
C4	0.0286 (12)	0.0382 (14)	0.0331 (12)	−0.0013 (10)	0.0088 (10)	−0.0041 (11)
C5	0.0382 (14)	0.0343 (14)	0.0368 (13)	−0.0001 (11)	0.0118 (11)	0.0034 (11)
C6	0.0356 (13)	0.0381 (14)	0.0315 (12)	−0.0011 (11)	0.0134 (10)	0.0042 (10)
C7	0.0413 (14)	0.0311 (13)	0.0305 (12)	−0.0003 (11)	0.0118 (11)	0.0015 (10)
C8	0.0477 (15)	0.0413 (16)	0.0317 (13)	0.0083 (12)	0.0099 (11)	0.0017 (11)

C9	0.071 (2)	0.0304 (15)	0.0371 (14)	0.0057 (14)	0.0106 (13)	0.0035 (12)
C10	0.070 (2)	0.0410 (17)	0.0407 (15)	−0.0135 (15)	0.0141 (14)	0.0054 (13)
C11	0.0498 (16)	0.0425 (17)	0.0418 (15)	−0.0083 (13)	0.0153 (12)	0.0024 (12)
C12	0.0436 (15)	0.0349 (15)	0.0384 (14)	−0.0010 (11)	0.0145 (12)	0.0032 (11)

Geometric parameters (Å, º)

Br1—N1	1.930 (3)	C7—C12	1.384 (4)
S1—N1	1.597 (3)	C8—C9	1.387 (5)
S1—C1	1.805 (3)	C9—C10	1.386 (6)
S1—C7	1.786 (3)	C10—C11	1.386 (5)
O1—N2	1.223 (4)	C11—C12	1.393 (5)
O2—N2	1.223 (4)	C2—H1	0.950
N2—C4	1.480 (4)	C3—H2	0.950
C1—C2	1.391 (4)	C5—H3	0.950
C1—C6	1.389 (4)	C6—H4	0.950
C2—C3	1.382 (4)	C8—H5	0.950
C3—C4	1.379 (4)	C9—H6	0.950
C4—C5	1.383 (4)	C10—H7	0.950
C5—C6	1.378 (4)	C11—H8	0.950
C7—C8	1.398 (4)	C12—H9	0.950
N1—S1—C1	111.02 (12)	C9—C10—C11	120.8 (3)
N1—S1—C7	113.30 (11)	C10—C11—C12	119.8 (3)
C1—S1—C7	102.33 (13)	C7—C12—C11	119.2 (3)
Br1—N1—S1	113.69 (15)	C1—C2—H1	120.259
O1—N2—O2	123.9 (3)	C3—C2—H1	120.266
O1—N2—C4	118.1 (3)	C2—C3—H2	120.842
O2—N2—C4	118.0 (3)	C4—C3—H2	120.860
S1—C1—C2	121.54 (19)	C4—C5—H3	121.040
S1—C1—C6	116.8 (2)	C6—C5—H3	121.047
C2—C1—C6	121.0 (3)	C1—C6—H4	119.985
C1—C2—C3	119.5 (3)	C5—C6—H4	119.995
C2—C3—C4	118.3 (3)	C7—C8—H5	120.583
N2—C4—C3	118.0 (3)	C9—C8—H5	120.577
N2—C4—C5	118.7 (3)	C8—C9—H6	119.954
C3—C4—C5	123.3 (3)	C10—C9—H6	119.951
C4—C5—C6	117.9 (3)	C9—C10—H7	119.609
C1—C6—C5	120.0 (3)	C11—C10—H7	119.611
S1—C7—C8	115.0 (3)	C10—C11—H8	120.124
S1—C7—C12	123.5 (2)	C12—C11—H8	120.123
C8—C7—C12	121.3 (3)	C7—C12—H9	120.388
C7—C8—C9	118.8 (3)	C11—C12—H9	120.396
C8—C9—C10	120.1 (3)		
N1—S1—C1—C2	−159.09 (16)	C2—C1—C6—C5	−0.6 (4)
N1—S1—C1—C6	30.08 (19)	C6—C1—C2—C3	0.3 (4)
C1—S1—N1—Br1	59.86 (16)	C1—C2—C3—C4	0.3 (4)

N1—S1—C7—C8	−99.02 (16)	C2—C3—C4—N2	178.03 (19)
N1—S1—C7—C12	75.8 (2)	C2—C3—C4—C5	−0.6 (4)
C7—S1—N1—Br1	−54.64 (17)	N2—C4—C5—C6	−178.29 (18)
C1—S1—C7—C8	141.38 (14)	C3—C4—C5—C6	0.4 (4)
C1—S1—C7—C12	−43.80 (19)	C4—C5—C6—C1	0.2 (4)
C7—S1—C1—C2	−37.90 (19)	S1—C7—C8—C9	175.13 (14)
C7—S1—C1—C6	151.26 (15)	S1—C7—C12—C11	−174.89 (15)
O1—N2—C4—C3	−168.46 (19)	C8—C7—C12—C11	−0.4 (4)
O1—N2—C4—C5	10.3 (3)	C12—C7—C8—C9	0.2 (4)
O2—N2—C4—C3	10.9 (3)	C7—C8—C9—C10	−0.2 (4)
O2—N2—C4—C5	−170.3 (2)	C8—C9—C10—C11	0.4 (4)
S1—C1—C2—C3	−170.17 (15)	C9—C10—C11—C12	−0.6 (4)
S1—C1—C6—C5	170.33 (15)	C10—C11—C12—C7	0.6 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H2···Br1^{i}	0.95	2.86	3.598 (3)	135
C3—H2···N1^{i}	0.95	2.44	3.286 (3)	149
C5—H3···O1^{ii}	0.95	2.54	3.435 (3)	158

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