

***N*-Iodoimidosulfinyl Difluoride,\* INSO<sub>F</sub><sub>2</sub>**

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(Received 15 September 1983; accepted 1 November 1983)

**Abstract.**  $M_r = 226.97$ , monoclinic,  $P2_1/c$ ,  $a = 4.866(5)$ ,  $b = 18.77(1)$ ,  $c = 11.22(1)$  Å,  $\beta = 97.3(1)^\circ$ ,  $V = 1016.5$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 2.97$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 65.4$  cm<sup>-1</sup>,  $F(000) = 816$ , room temperature, final  $R = 0.033$  for 1640 reflections. The molecules are connected by intermolecular N–I bonds forming chains in the [201] direction. The N–I–N groups are almost linear, but not symmetric.

**Introduction.** *N*-Iodo compounds show a marked tendency to form strong intermolecular I–X bonds to atoms with free electron pairs, preferably to N atoms (Jander, 1976). In all known structures of *N*-iodo compounds the N–I–X group is almost linear. The length of the N–I bond varies from 2.03 to 2.30 Å depending on the strength of the intermolecular interaction. In *N*-iodo amides, where the free electron pair of the N atom takes part in the  $\pi$ -bonding of the amide group, it cannot form an intermolecular N–I bond. The molecules are held together by intermolecular I–O bonds. In *N*-iodoimidosulfinyl difluoride the N atom has another free electron pair, which is not involved in the  $\pi$ -bonding.

**Experimental.** Synthesis and properties have been reported by Seppelt & Sundermeyer (1971). As the yellow crystals are easily hydrolyzed, they must be handled in a dry box. All the X-ray measurements had to be done with crystals sealed in glass capillaries. In contrast to other *N*-iodo compounds *N*-iodoimidosulfinyl difluoride is volatile and can be sublimed.

Cell parameters from precession films calibrated with Pb(NO<sub>3</sub>)<sub>2</sub>. 1775 unique reflections measured with a Stoe–Weissenberg diffractometer (Mo  $K\alpha$  radiation, graphite monochromator,  $\omega$  scan),  $3^\circ \leq \theta \leq 25^\circ$ , layers  $\pm hk0$  to  $\pm hk13$ , absorption correction (crystal dimensions  $0.50 \times 0.12 \times 1.00$  mm,  $c$  rotation axis,  $0.08 \leq T \leq 0.46$ ), 135 reflections considered unobserved [ $I \leq \sigma(I)$ ]. Heavy-atom method, full-matrix least-squares refinement on  $F$  (all atoms anisotropic, 13 individual scale factors, 121 parameters refined),  $R = 0.033$ ,  $R_w = 0.042$  [ $w = \sigma(F)^{-2}$ ] for 1640 observed reflections,  $R = 0.036$  for all 1775 reflections,  $(\Delta/\sigma)_{\text{max}}$

in final refinement cycle  $< 0.15$ , all maxima in the last  $\Delta\rho$  map  $< 0.6$  e Å<sup>-3</sup>, scattering factors from Cromer & Mann (1968),  $f'$  and  $f''$  for iodine included (*International Tables for X-ray Crystallography*, 1974), program system *SHELX76* (Sheldrick, 1976) used.

**Discussion.** Fig. 1 shows the two molecules with the atomic labelling, Fig. 2 a projection along [100]. Atomic parameters are given in Table 1, distances and angles in Table 2.†

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39000 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

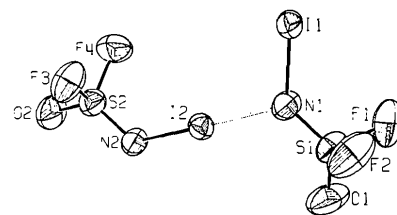


Fig. 1. ORTEP plot of the two crystallographically independent molecules of *N*-iodoimidosulfinyl difluoride with 40% probability thermal ellipsoids.

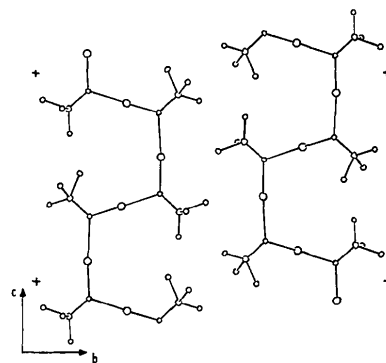


Fig. 2. Projection of the structure along [100].

\* *S,S*-Difluoro-*N*-iodosulphoximine.

Table 1. Atomic coordinates for INSOF<sub>2</sub>

$$U_{eq} = (24\pi^2)^{-1} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
I(1)	0.86640 (8)	0.35427 (2)	0.59569 (3)	0.058
I(2)	0.36590 (8)	0.24219 (2)	0.35646 (3)	0.054
S(1)	0.7105 (4)	0.40789 (11)	0.32996 (14)	0.063
S(2)	0.0842 (3)	0.09519 (11)	0.39747 (12)	0.060
F(1)	0.6372 (12)	0.4810 (3)	0.3746 (6)	0.138
F(2)	1.0140 (10)	0.4264 (4)	0.3321 (5)	0.072
F(3)	0.3633 (9)	0.0678 (3)	0.4562 (4)	0.075
F(4)	0.0102 (11)	0.1249 (3)	0.5160 (4)	0.122
O(1)	0.5891 (13)	0.4042 (4)	0.2111 (4)	0.124
O(2)	-0.0858 (12)	0.0364 (3)	0.3672 (4)	0.104
N(1)	0.6667 (11)	0.3513 (3)	0.4165 (4)	0.071
N(2)	0.1162 (12)	0.1520 (3)	0.3099 (4)	0.070

Table 2. Distances (Å) and angles (°) for INSOF<sub>2</sub>

I(1)—N(1)	2.120 (5)	S(1)—F(1)	1.518 (6)
I(1)—N(2)	2.554 (5)	S(1)—F(2)	1.515 (5)
I(2)—N(1)	2.558 (5)	S(2)—F(3)	1.521 (4)
I(2)—N(2)	2.110 (5)	S(2)—F(4)	1.527 (5)
S(1)—O(1)	1.390 (5)	S(2)—O(2)	1.395 (5)
S(1)—N(1)	1.472 (5)	S(2)—N(2)	1.472 (5)
N(2')—I(1)—N(1)	175.7 (2)	O(2)—S(2)—F(4)	107.6 (3)
N(2)—I(2)—N(1)	179.1 (1)	N(2)—S(2)—F(3)	111.7 (3)
F(2)—S(1)—F(1)	93.2 (3)	N(2)—S(2)—F(4)	111.9 (3)
O(1)—S(1)—F(1)	105.8 (3)	N(2)—S(2)—O(2)	121.4 (3)
O(1)—S(1)—F(2)	108.8 (3)	I(2)—N(1)—I(1)	116.6 (2)
N(1)—S(1)—F(1)	112.0 (3)	S(1)—N(1)—I(1)	121.3 (3)
N(1)—S(1)—F(2)	112.2 (3)	S(1)—N(1)—I(2)	122.0 (2)
N(1)—S(1)—O(1)	121.1 (3)	I(2)—N(2)—I(1'')	117.4 (2)
F(4)—S(2)—F(3)	92.4 (2)	S(2)—N(2)—I(1'')	121.1 (2)
O(2)—S(2)—F(3)	107.9 (3)	S(2)—N(2)—I(2)	121.5 (2)

Symmetry operations: (')  $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (")  $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$ .

The structure contains two crystallographically independent molecules which are almost identical. The molecules are connected by intermolecular N—I bonds forming chains in the [201] direction (Fig. 2).

The two molecules possess approximate mirror planes through I, N, S and O (r.m.s. deviation 0.018 and 0.009 Å respectively). The two F atoms of each molecule are approximately symmetry-related by this plane. Each N atom is bound to a S and two I atoms and has a trigonal planar coordination. The distances and angles of INSOF<sub>2</sub> are in agreement with those of other imidosulfinyl fluorides XNSOF<sub>2</sub> [Bellard, Rivera & Sheldrick (1978): X = methyl; Oberhammer, Glemser & Klüver (1974): X = Cl; Cassoux, Kuczowski & Creswell (1977): X = H; Buss & Altena (1978), Buss,

Altena, Mews & Glemser (1975) (in Mews, 1976) and Buss, Altena, Mews & Glemser (1978): NSOF<sub>2</sub><sup>-</sup> as ligand in transition-metal complexes]. In the metal complexes the S—N and S—O distances are, however, respectively shorter and longer than in the uncomplexed molecules.

In N-iodo compounds the molecules are connected by intermolecular bonds between the N—I group, which acts an acceptor, and an electron-pair donor. This type of interaction can be compared with the triiodides or complexes of donors with iodine and can be rationalized by a  $3c-4e$  bond. The group X—I—Y is linear and the distances X—I and I—Y correlate with each other. The intermolecular interaction lengthens the intramolecular and shortens the intermolecular bond. Sometimes the interaction is so strong that the N—I—N group becomes symmetric and a differentiation between intra- and intermolecular bond is no longer possible (Hartl, Bärnighausen & Jander, 1968; Hagedorn, Pritzkow & Jander, 1977). In INSOF<sub>2</sub> the N—I—N group is linear, but has two different distances. The N—I distances are in good agreement with those in the asymmetric N—I—N groups in NI<sub>3</sub>.NH<sub>3</sub> (Hartl, Bärnighausen & Jander, 1968) and NI<sub>3</sub>.C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>.I<sub>2</sub> (Pritzkow, 1974). The formation of an intermolecular N—I bond (and not O—I or F—I) confirms that nitrogen is a better donor for iodine than oxygen or fluorine.

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