Acta Cryst. (1978). B**34**, 1034–1035

N-Methyl-*S*,*S*-difluorosulphoximine–Arsenic Pentafluoride

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(*Received* 8 *November* 1977; *accepted* 25 *November* 1977)

Abstract. $AsF_5N(CH_3)SOF_2$, monoclinic, $P2_1/n$, a = 8·795 (8), b = 13·46 (2), c = 6·521 (6) Å, β = 108·75 (3)°, U = 731·0 Å^3, Z = 4, D_x = 2·589 g cm^{-3}, μ(Mo $K\alpha$) = 48·43 cm^{-1}. The structure was refined to an R of 0·083 for 997 unique diffractometer data measured at −40 °C. The molecule adopts a staggered conformation, with an approximate mirror plane through F(axial), As, N, S, O but not CH_3. Mean bond lengths are: As–F, 1·695 (10); As–N, 1·985 (16); C–N, 1·515 (19); S–N, 1·498 (15); S–F, 1·514 (9); S–O, 1·383 (12) Å.

Introduction. The structure of the AsF_5 adduct of *N*-methyl-*S*,*S*-difluorosulphoximine has been determined by single-crystal X-ray diffraction to confirm the spectroscopic evidence (Mews & Braeuer, 1978) that the N rather than the O atom is coordinated by As, and to establish the molecular conformation. The crystals are extremely moisture sensitive and sublime easily at room temperature, so data were collected at low temperature.

A crystal was mounted in a Lindemann-glass capillary tube in an argon atmosphere (Raithby, 1976). 2104 reflexions were measured (*h*0–9*l*) with an automated Stoe STADI-2 two-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, and a low-temperature attachment in which the nitrogen-gas stream is cooled by recirculating refrigerated methanol (Bellard & Sheldrick, 1978). After Lp corrections, equivalent reflexions were averaged to give 997 unique reflexions with $F > 5\sigma(F)$ based on counting statistics. No absorption corrections were applied because of problems caused by crystal sublimation; this probably accounts for the relatively high final R. Cell dimensions were determined from diffractometer measurements at the same temperature (−40 ± 2 °C).

The structure was solved by multisolution Σ_2 sign expansion and refined by full-matrix least squares with complex neutral-atom scattering factors and weights $w = 1/[\sigma^2(F) + 0{\cdot}000726|F|^2]$. The three H atoms were located from a difference synthesis, and refined with C–H and H···H distances constrained to idealized values (C–H = 1·00 Å); a common isotropic temperature factor was employed for H, with the remaining atoms anisotropic. The assignment of the O atom was based on the appreciable differences in S=O and S–F distances and in the angles at S, and confirmed by the reasonable values of the temperature factors. The refinement converged to $R' = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|$ = 0·0786 and R = 0·0827. Positional parameters are given in Table 1, bond lengths and angles in Tables 2 and 3. A perspective view of the molecule showing the atomic labelling is given in Fig. 1.*

Table 1. *Atom coordinates* (× 10^4)

	x	y	z
As	2350 (2)	3440 (1)	4630 (2)
F(1)	1763 (11)	3596 (7)	1884 (12)
F(2)	2928 (13)	3208 (7)	7324 (12)
F(3)	413 (10)	3183 (7)	4436 (14)
F(4)	4283 (10)	3579 (8)	4740 (14)
F(5)	2125 (14)	4658 (11)	5006 (15)
N	2641 (15)	2015 (10)	4070 (18)
C	3504 (20)	1745 (13)	2476 (23)
H(1)	4679	1855	3033
H(2)	3230	1043	2033
H(3)	2977	2203	1246
S	2130 (5)	1178 (4)	5214 (6)
F(6)	1144 (11)	449 (8)	3533 (14)
F(7)	3514 (11)	468 (7)	6094 (14)
O	1376 (15)	1351 (9)	6742 (18)

Discussion. Ignoring the methyl group, the molecule possesses a good approximation to a mirror plane through F(axial), As, N, S and O (r.m.s. deviation 0·004 Å). The positions of the methyl H atoms, which

Table 2. *Bond lengths* (Å)

F(1)–As	1·710 (9)	F(2)–As	1·694 (9)
F(3)–As	1·703 (10)	F(4)–As	1·688 (11)
F(5)–As	1·678 (17)	N–As	1·985 (16)
C–N	1·515 (19)	S–N	1·498 (15)
F(6)–S	1·518 (12)	F(7)–S	1·509 (12)
O–S	1·383 (12)		

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33214 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

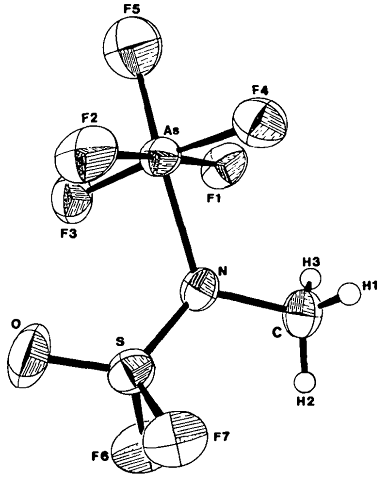

Fig. 1. *ORTEP* diagram of *N*-methyl-*S*,*S*-difluorosulphoximine–arsenic pentafluoride, showing 50% probability ellipsoids for the anisotropic atoms.

Table 3. *Bond angles* (°)

F(2)–As–F(1)	176·4 (5)	F(4)–As–F(3)	174·3 (5)
F(3)–As–F(1)	89·4 (5)	F(3)–As–F(2)	89·9 (6)
F(4)–As–F(1)	89·6 (5)	F(4)–As–F(2)	90·8 (6)
F(5)–As–F(1)	91·4 (6)	F(5)–As–F(2)	92·2 (6)
F(5)–As–F(3)	92·7 (6)	F(5)–As–F(4)	92·9 (7)
N–As–F(1)	86·5 (5)	N–As–F(2)	89·9 (6)
N–As–F(3)	88·6 (6)	N–As–F(4)	85·8 (6)
N–As–F(5)	177·5 (5)	C–N–As	118·7 (11)
S–N–As	124·0 (8)	S–N–C	117·2 (12)
H(1)–C–N	114·0	H(2)–C–N	107·4
H(2)–C–H(1)	112·0	H(3)–C–N	101·4
H(3)–C–H(1)	111·3	H(3)–C–H(2)	110·3
F(6)–S–N	108·7 (7)	F(7)–S–N	109·4 (3)
O–S–N	121·5 (9)	F(7)–S–F(6)	93·9 (7)
O–S–F(6)	109·5 (8)	O–S–F(7)	110·3 (3)

appear to be determined by the various F···H interactions, are not consistent with this mirror plane, and the methyl C atom lies 0·048 Å out of the plane. The C and O are staggered with respect to the F atoms [O···F(As), 2·81 and 2·87; C···F(As), 2·84 and 2·88; C···F(S), 2·92 and 2·96 Å]; the relatively wide As–N–S angle of 124·0 (8)° serves to equate the O···F(As) and C···F(As) repulsions. The S–O and S–F lengths are consistent with those found by Lau, Lynton, Passmore & Siew (1973) for OSF_3^+ [1·35 (1) and 1·45 (1) Å, possibly shortened by libration]. The geometry of the $NSOF_2$ group is analogous to that found by Buss, Altena, Mews & Glemser (1975) in $(OC)_5ReNSOF_2$ [N–S, 1·443 (20); S–O, 1·435 (20); S–F, 1·540 (20) and 1·514 (20) Å; F–S–F, 90·8°] if allowance is made for the higher N–S bond order and corresponding lower S–O and S–F bond orders in the Re derivative. Although the As–N bond is relatively long, it is shorter than the very weak interaction in $Cl_3As–NMe_3$ [2·286 (23) Å; Webster & Keats, 1971]; the mean N–As–F angle of 87·7 is less than 90°, although the smallest valence angles are usually found between the most electronegative single-bonded ligands, so there is some evidence for assigning a fractional As–N bond order. The As–F distances do not differ significantly; the mean of 1·695 (10) is a little shorter than the 1·719 (3) Å found by Gafner & Kruger (1974) in $KAsF_6$, which is also consistent with a fractional negative charge on the F_5As– moiety.

We are grateful to the Science Research Council for providing the diffractometer, to Churchill College and the University of Los Andes, Venezuela, for financial support to SB and AVR, respectively, and to Dr R. Mews and Mr H. H. Braeuer for suggesting the project and providing the crystals. Calculations were performed on the Cambridge University IBM 370/165 computer with the program *SHELX* written by GMS.

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