

involved being intermediate between the covalent and van der Waals values. 1,4-Dioxane molecules, which lie on centres of symmetry displaced by  $b/2$  relative to Hg, bridge the Hg atoms. The structure consists of layers of Hg atoms linked parallel to  $c$  by the trifluoroacetate groups and parallel to  $b$  by the 1,4-dioxane molecules. There are no other close contacts to Hg, the overall coordination thus being six.

Two other structures involving 1,4-dioxane complexed to Hg have been reported: in the 1:1 complex of 1,4-dioxane and mercury(II) chloride (Groth & Hassel, 1964) the dioxane molecules have a bridging role with Hg—O 2.66 Å in a closely similar structure also in space group  $P\bar{1}$  ( $Z = 1$ ). In the case of the 1:2 compound of mercury(II) bromide and 1,4-dioxane (Frey & Monier, 1971) Hg occupies a fourfold special position in a tetragonal structure with four Hg—O contacts of 2.83 Å. The present structure may be compared with the complexes of mercury(II) trifluoroacetate and pyridine (Halfpenny, Small & Thorpe, 1978; Halfpenny & Small, 1978) in which the pyridine molecules are more closely coordinated to Hg than are the trifluoroacetate groups. The close coordination of the trifluoroacetate groups to Hg in the present compound indicates that 1,4-dioxane is a weaker base than trifluoroacetate.

In the trifluoroacetate groups the significantly different C—O distances, C(1)—O(2) 1.21 (2) and

C(1)—O(1) 1.28 (2) Å, reflect the unequal coordination distances of these two O atoms to Hg. In this structure the  $U$  values of the F atoms have fairly normal values; this is in contrast with most other mercury(II) trifluoroacetate complexes where large values of  $U_{ij}$  or  $U$  for these atoms are observed (Halfpenny & Small, 1981).

#### References

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.  
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
 FREY, M. & MONIER, J. C. (1971). *Acta Cryst.* **B27**, 2487–2490.  
 GROTH, P. & HASSEL, O. (1964). *Acta Chem. Scand.* **18**, 1327–1333.  
 HALFPENNY, J. & SMALL, R. W. H. (1978). *Acta Cryst.* **B34**, 3758–3760.  
 HALFPENNY, J. & SMALL, R. W. H. (1981). *Acta Cryst.* **B37**, 2223–2225.  
 HALFPENNY, J., SMALL, R. W. H. & THORPE, F. G. (1978). *Acta Cryst.* **B34**, 3075–3077.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 SHELDRIK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. Cambridge, England.

*Acta Cryst.* (1982). **B38**, 2887–2889

## Tetraphenylarsonium Bis(fluorosulfonyl)amide at 290 and 112 K

BY WILHELM ISENBERG, MATHIAS NOLTEMAYER AND GEORGE M. SHELDRIK

*Anorganisch-Chemisches Institut der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany*

(Received 9 March 1982; accepted 18 May 1982)

**Abstract.**  $C_{24}H_{20}As^+ \cdot N(SO_2F)_2^-$ ,  $M_r = 563.46$ , monoclinic,  $P2_1/n$ ,  $Z = 4$ ,  $a = 17.447$  (5),  $b = 7.325$  (2),  $c = 19.494$  (6) Å,  $\beta = 94.20$  (2)°,  $U = 2484.6$  Å<sup>3</sup>,  $D_x = 1.506$ ,  $D_m = 1.46$  (3) Mg m<sup>-3</sup>,  $\mu(Mo K\alpha) = 1.57$  mm<sup>-1</sup> at 290 (1) K, and  $a = 17.16$  (2),  $b = 7.53$  (1),  $c = 18.40$  (2) Å,  $\beta = 94.2$  (1)°,  $U = 2371.2$  Å<sup>3</sup>,  $D_x = 1.578$  Mg m<sup>-3</sup>,  $\mu(Mo K\alpha) = 1.64$  mm<sup>-1</sup> at 112 (2) K. The structure refined to  $R = 0.076$  for 1946 unique observed data at 290 K and to  $R = 0.047$  for 3332 data at 112 K. The thermal motion of the anion and hence the effect of libration and torsion on the observed dimensions are substantially reduced on cooling. The geometry and thermal motion of the cation are normal at both temperatures. The anion adopts

a staggered conformation of approximately 2 ( $C_2$ ) symmetry at 112 K, with S—N—S 121.4 (2)°, S—N (mean) 1.568 (4), S—O (mean) 1.415 (7), S—F (mean) 1.574 (3) Å. The apparently quite different geometry observed for the anion at 290 K may be accounted for by two superimposed conformers subject to considerable thermal smearing; an attempt to determine the structure by room-temperature measurements alone would have led to chemically fallacious results.

**Introduction.**  $Ph_4As^+ \cdot N(SO_2F)_2^-$  was prepared for us by Professor R. Mews by the reaction of  $Ph_4As^+ \cdot Cl^-$  with  $HN(SO_2F)_2$ . Physical and spectroscopic measurements agreed with those reported by Roesky & Babb

(1969) for a sample obtained by a different route. The structure was determined to investigate the effect of the strongly electron-withdrawing fluorosulfonyl groups on the N–S bond lengths and SNS angle. Room-temperature data yielded an entirely normal cation geometry and thermal motion, but a puzzling structure and extensive thermal motion for the anion. Low-temperature measurements proved very revealing.

All data were obtained with graphite-monochromated Mo  $K\alpha$  radiation and a Stoe two-circle diffractometer, in the  $\omega$ -scan mode with variable reflexion widths and counting times. A modified Nonius attachment was used to cool the crystals by means of coaxial cold and warm dry-nitrogen streams. One crystal (dimensions 0.7 × 0.3 × 0.2 mm) was employed for the room-temperature measurements and the first half of the low-temperature measurements; it was then lost as a result of a malfunction of the low-temperature device, and the data collection was completed with a second crystal (0.5 × 0.3 × 0.3 mm). Both crystals were mounted in Lindemann-glass

Table 1. *Atom coordinates* ( $\times 10^4$ ) *and equivalent isotropic thermal parameters* ( $\text{\AA}^2 \times 10^3$ ) at 290 K

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}^*$
S(1)	−7339 (2)	3846 (7)	−408 (2)	96 (2)
N	−7687 (11)	3156 (34)	187 (7)	258 (13)
S(2)	−7780 (2)	1111 (7)	411 (2)	97 (2)
F(1)	−7181 (10)	291 (26)	−4551 (9)	347 (12)
O(11)	−8359 (6)	−741 (28)	−4689 (8)	256 (11)
O(12)	−7520 (11)	−1891 (26)	−3971 (7)	288 (12)
O(21)	−7758 (17)	−132 (28)	−13 (10)	374 (17)
F(2)	−6484 (10)	−3831 (30)	−5596 (13)	398 (16)
O(22)	−7622 (11)	−4047 (30)	−5961 (9)	310 (13)
As	−9993 (1)	3733 (2)	2569 (1)	59 (1)
C(1)	−10901 (5)	2119 (18)	2417 (6)	65 (4)
C(2)	−11341 (5)	2356 (18)	1811 (5)	69 (5)
C(3)	−11989 (7)	1148 (20)	1720 (6)	96 (6)
C(4)	−12081 (6)	−186 (19)	2185 (6)	79 (5)
C(5)	−11595 (7)	−390 (21)	2766 (7)	101 (6)
C(6)	−10988 (6)	790 (18)	2891 (6)	73 (5)
C(11)	−10160 (6)	5278 (17)	3359 (5)	69 (5)
C(12)	−10719 (6)	5022 (19)	3771 (5)	79 (5)
C(13)	−10814 (8)	6072 (24)	4324 (6)	108 (7)
C(14)	−10259 (8)	7465 (25)	4467 (6)	107 (7)
C(15)	−9679 (8)	7785 (18)	4067 (6)	98 (6)
C(16)	−9566 (7)	6681 (19)	3497 (6)	96 (6)
C(21)	−9902 (5)	5242 (17)	1781 (5)	54 (4)
C(22)	−9323 (6)	4925 (19)	1333 (6)	76 (5)
C(23)	−9305 (8)	6123 (23)	752 (6)	103 (7)
C(24)	−9795 (8)	7511 (21)	661 (6)	100 (7)
C(25)	−10347 (7)	7750 (22)	1106 (6)	96 (6)
C(26)	−10368 (6)	6701 (16)	1658 (5)	69 (5)
C(31)	−9140 (5)	2204 (16)	2744 (5)	56 (4)
C(32)	−8608 (6)	2377 (20)	3318 (6)	85 (5)
C(33)	−8026 (6)	1198 (21)	3422 (7)	115 (7)
C(34)	−7906 (8)	−150 (23)	2956 (7)	124 (8)
C(35)	−8380 (8)	−371 (21)	2372 (7)	104 (6)
C(36)	−9018 (7)	837 (18)	2284 (7)	89 (6)

\*  $U_{eq} = \frac{1}{3}$  trace of the orthogonalized  $U_{ij}$  tensor.

Table 2. *Atom coordinates* ( $\times 10^5$ ) *and equivalent isotropic thermal parameters* ( $\text{\AA}^2 \times 10^4$ ) at 112 K

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}^*$
S(1)	−74418 (4)	40772 (16)	−3553 (4)	211 (3)
F(1)	−77317 (11)	31951 (31)	−11002 (9)	346 (7)
O(12)	−66476 (12)	35342 (35)	−2464 (12)	339 (9)
O(11)	−76083 (14)	59004 (38)	−4591 (12)	308 (10)
N	−80174 (14)	33005 (42)	1915 (13)	188 (10)
S(2)	−79587 (5)	13280 (15)	4526 (4)	250 (3)
O(21)	−86505 (15)	8976 (37)	7939 (13)	396 (10)
O(22)	−76607 (17)	1144 (37)	−361 (12)	468 (11)
F(2)	−73146 (12)	14187 (30)	11079 (10)	411 (8)
As	−100442 (2)	38261 (5)	26503 (1)	161 (1)
C(1)	−109006 (16)	22189 (48)	24804 (14)	169 (11)
C(2)	−110107 (17)	9319 (47)	30016 (15)	186 (12)
C(3)	−116219 (17)	−2515 (50)	28876 (15)	196 (12)
C(4)	−121121 (16)	−1517 (51)	22538 (15)	212 (12)
C(5)	−119996 (16)	11211 (48)	17346 (15)	202 (12)
C(6)	−113935 (16)	23253 (48)	18416 (15)	171 (22)
C(11)	−102062 (16)	53471 (50)	34559 (14)	190 (12)
C(12)	−97068 (17)	67752 (53)	35706 (16)	243 (12)
C(13)	−98013 (19)	79140 (55)	41494 (17)	296 (13)
C(14)	−104053 (20)	76192 (55)	45970 (17)	321 (14)
C(15)	−109085 (19)	62030 (53)	44766 (16)	294 (14)
C(16)	−108128 (17)	50415 (52)	39087 (14)	209 (12)
C(21)	−99528 (16)	53202 (49)	18208 (14)	170 (11)
C(22)	−104423 (17)	67768 (52)	17472 (16)	248 (12)
C(23)	−104042 (18)	78869 (53)	11443 (16)	241 (12)
C(24)	−98717 (18)	75168 (51)	6330 (16)	254 (13)
C(25)	−93875 (18)	60598 (51)	7075 (16)	258 (13)
C(26)	−94226 (17)	49420 (52)	13002 (15)	225 (12)
C(31)	−91247 (16)	24231 (49)	28656 (15)	189 (12)
C(32)	−90018 (18)	9772 (50)	24207 (16)	237 (13)
C(33)	−83364 (18)	−431 (53)	25661 (17)	274 (13)
C(34)	−78158 (19)	3516 (55)	31567 (17)	326 (14)
C(35)	−79447 (18)	17763 (55)	35995 (17)	306 (13)
C(36)	−86011 (17)	28274 (53)	34590 (15)	249 (13)

\*  $U_{eq} = \frac{1}{3}$  trace of the orthogonalized  $U_{ij}$  tensor.

capillaries with [010] parallel to the diffractometer oscillation axis. Cell dimensions were obtained by least-squares fit to diffractometer  $\omega$ -angle measurements. 4592 data ( $3 \leq 2\theta \leq 30^\circ$ ) at 290 (1) K were merged to give 1946 unique reflexions with  $F > 5\sigma(F)$ ; 4383 measurements ( $3 \leq 2\theta \leq 54^\circ$ ) at 112 (2) K were merged to give 3332 unique reflexions with  $F > 4\sigma(F)$ ; these observed data were employed for structure solution and refinement. No corrections were made for absorption. The structure was solved by direct and Fourier methods using the 290 K data; the low-temperature anion coordinates were found by a difference electron-density synthesis based on the room-temperature cation structure. For both 290 K and 112 K data, the structure was refined with anisotropic non-H atoms, riding H atoms [ $C-H$  0.96 Å, on CCC external bisectors,  $U = 1.2U_{eq}(C)$ ], complex neutral-atom scattering factors and weights [ $\sigma^2(F) + gF^2$ ] $^{-1}$  [ $g = 5.2 \times 10^{-4}$  (290 K) and  $5 \times 10^{-4}$  (112 K)]. The least-squares refinements converged to  $R(w) = 0.0811$ ,  $R = 0.0763$  (290 K), and  $R(w) =$

Table 3. Selected bond lengths (Å) and angles (°)

	290 K	112 K
S(1)—F(1)	1.349 (19)	1.571 (2)
S(1)—O(11)	1.255 (12)	1.412 (3)
S(1)—O(12)	1.332 (15)	1.423 (3)
S(1)—N	1.439 (18)	1.573 (3)
S(2)—N	1.572 (24)	1.562 (4)
S(2)—F(2)	1.360 (20)	1.577 (3)
S(2)—O(21)	1.232 (21)	1.421 (3)
S(2)—O(22)	1.242 (18)	1.404 (3)
As—C(average)	1.929 (10)	1.912 (4)
F(1)—S(1)—O(11)	114.3 (13)	104.2 (1)
F(1)—S(1)—O(12)	101.0 (11)	103.9 (1)
O(11)—S(1)—O(12)	110.3 (11)	118.7 (2)
O(11)—S(1)—N	115.2 (10)	108.5 (2)
O(12)—S(1)—N	121.9 (12)	116.3 (2)
F(1)—S(1)—N	91.5 (12)	103.1 (1)
S(1)—N—S(2)	128.1 (15)	121.4 (2)
F(2)—S(2)—O(21)	106.1 (17)	103.5 (1)
F(2)—S(2)—O(22)	105.0 (14)	104.5 (2)
O(21)—S(2)—O(22)	117.8 (15)	119.3 (2)
O(21)—S(2)—N	120.6 (11)	108.4 (2)
O(22)—S(2)—N	105.4 (12)	116.1 (2)
F(2)—S(2)—N	99.3 (12)	102.7 (1)

0.0395,  $R = 0.0469$  (112 K). Final atomic coordinates and selected molecular dimensions are presented in Tables 1–3.\*

**Discussion.** The low-temperature anion dimensions are in good agreement with those reported for  $-\text{NSO}_2\text{F}$  groups anchored by incorporation in larger molecules (Tesky, Mews, Krebs & Ramakrishna Udupa, 1978; Krebs, Henkel, Pohl & Roesky, 1980). The valence angle at N and relatively short S–N bonds indicate  $sp^2$  hybridization of the N atom and significant S–N multiple bonding. The wide OSO, intermediate NSO and small FSN and FSO angles are also consistent with this model; it is, however, necessary to invoke non-bonded repulsions [ $\text{O}(22)\cdots\text{S}(1)$  3.069,  $\text{O}(12)\cdots\text{S}(2)$  3.147 Å] to account for the difference between the N–S(1)–O(12) and N–S(2)–O(22) angles (116.3, 116.1°) and the N–S(1)–O(11) and N–S(2)–O(21) angles (108.5, 108.4°). At 112 K the anion possesses non-crystallographic 2 ( $C_2$ ) symmetry and the conformation (Fig. 1) clearly minimizes  $\text{O}\cdots\text{O}$  and  $\text{O}\cdots\text{F}$  repulsions.

At 290 K the anion appears to adopt a sterically unfavorable conformation (Fig. 2), with unreasonably short bonds (Table 3). A librational analysis indicated that large but uncertain corrections should be made to the bond lengths; the O and F atoms appear to move at right angles to the bonds. One can also describe the 290

\* Lists of structure factors, anisotropic temperature factors, H-atom coordinates and a complete list of bond distances and angles (at 112 K) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36947 (88 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

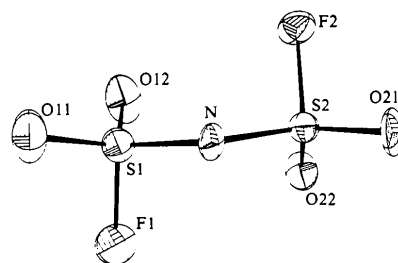


Fig. 1. The  $\text{N}(\text{SO}_2\text{F})_2^-$  anion at 112 K, showing atom labelling and 50% probability thermal ellipsoids.

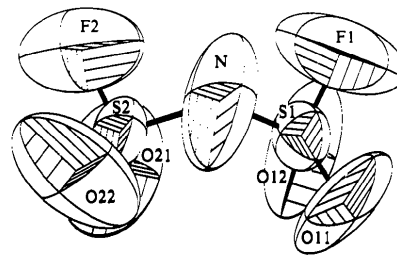


Fig. 2. The  $\text{N}(\text{SO}_2\text{F})_2^-$  anion at 290 K, showing atom labelling and 50% probability thermal ellipsoids.

K structure as a thermally smeared superposition of two staggered (112 K) conformations. Without the benefit of the low-temperature data it is very unlikely that this chemically acceptable interpretation of the room-temperature data could be made. Although the thermal motion is substantially reduced on cooling, a riding model (Johnson, 1970) indicates that a significant correction (in the range 0.014 to 0.024 Å) is still required for libration and internal torsion.

In contrast to the problems with the anion, the cation dimensions and thermal motion are normal at both temperatures. No especially short interionic interactions were observed.

We are grateful to Professor R. Mews for preparing the compound, Drs W. Clegg and P. G. Jones for discussions, and to the Verband der Chemischen Industrie for financial support. All calculations were performed on a DG Eclipse mini-computer using programs written by GMS.

## References

- JOHNSON, C. K. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 220–226. Copenhagen: Munksgaard.
- KREBS, B., HENKEL, G., POHL, S. & ROESKY, H. W. (1980). *Chem. Ber.* **113**, 226–232.
- ROESKY, H. W. & BABB, D. P. (1969). *Inorg. Chem.* **8**, 1733–1735.
- TESKY, F. M., MEWS, R., KREBS, B. & RAMAKRISHNA UDUPA, M. (1978). *Angew. Chem.* **90**, 722–723.