X-Ray Crystal Structure of $[AsPh_4]^+[NSF_2NSO_2F]^-$: Three Different Types of S–N Bonds in the Anion

By B. BUSS,* D. ALTENA, R. HÖFER, and O. GLEMSER

(*Anorganisch-Chemisches Institut der Universität Gottingen, Tammammstr.* 4, D 3400 *Göttingen, Germany*)

Summary X-Ray crystal structure determination of $[AsPh_4]^+[NSF_2NSO_2F]^-$ has revealed that the anion $[NSF_2NSO_2F]^-$ has three different types of S–N bonds with triple, double, and single bond character.

THE compounds NSF_2NSF_2[1] and NSF_2NSOF_2,[2] which have been prepared recently, have three different types of S–N bonds, which can be formally ascribed as having triple-, double-, and single-bond character. Partial hydrolysis of NSF_2NSOF_2 leads to the anion $NSF_2NSO_2F^-$, which is isoelectronic with NSF_2NSOF_2 and can be crystallized as its tetraphenylarsonium salt.

Crystal data: tetragonal, space group $P\bar{4}$-S_4^1 (No. 81), $a = b = 18{\cdot}437(5)$, $c = 7{\cdot}067(3)$ Å (at 20 °C), $Z = 4$, $D_c = 1{\cdot}56$ g cm^{-3}. A total of 2753 unique intensities were recorded on a computer-controlled four-circle diffractometer. The structure was solved by Patterson, Fourier, and least-squares techniques. The final R-value (taking anisotropic vibration into account) is 6·4%.

The structure consists of the cations $[As(Ph)_4]^+$ and the anions $NSF_2NSO_2F^-$ which Van der Waals contacts between them. There are three crystallographically independent $[As(Ph)_4]^+$ cations which have nearly-tetrahedral symmetry consistent with structures of other similar molecules.[3] The anion consists of two corner-sharing tetrahedra, where the corner is occupied by a nitrogen atom and the two centres of the tetrahedra by sulphur atoms. The overall structure of the anions is very similar to that of isoelectronic species, *e.g.* the imido-disulphate anion $[NH(SO_3)_2]^{2-}$,[4] and especially the inorganic pyroanions $X_2O_7^{y-}$.[5] The structure of the anion $[NSF_2NSO_2F]^-$ is shown in the Figure.†

The anion has as expected, three different S–N bond lengths which can be ascribed bond orders of 2·5, 1·35, and 1·9 for S(1)–N(1), S(1)–N(2), and S(2)–N(2), respectively.[6]

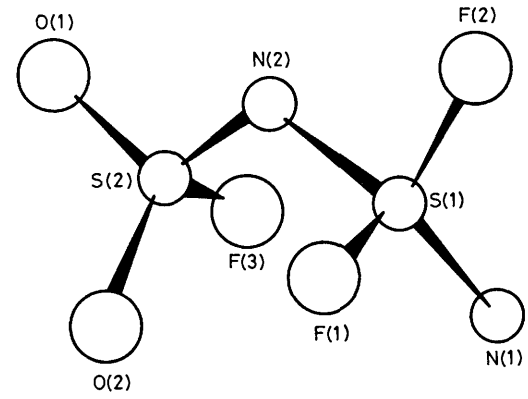

FIGURE. The structure of the anion $[NSF_2NSO_2F]^-$. Bond lengths (Å) and bond angles (°) are: S(1)–N(1), 1·439(10); S(1)–N(2), 1·587(9); S(2)–N(2), 1·517(9); S–F (av), 1·514(9); S(2)–O(1), 1·391(10); S(2)–O(2), 1·368(10); and S(1) · · · S(2), 2·686(7); ∠S(1)–N(2)–S(2), 119·9(9); ∠F(3)–S(2)–O(2), 105·6(9); ∠F(1)–S(1)–F(2), 98·5(9); ∠N(1)–S(1)–N(2), 128·9(9); ∠O(1)–S(2)–O(2), 115·4(9); ∠N(1)–S(1)–F(1), 113·9(9); ∠F(3)–S(2)–O(1), 102·3(9); and ∠N(1)–S(1)–F(2), 115·6(9).

The S–F and S–O bonds are short compared to those in other similar molecules, *e.g.* in the NSO_2F group.[7] However, the F–S–F angle is relatively large (98·5°) compared to that in the NSO_2F group (90·6°).[7] It is interesting to note that the F–S–F angle (102·0°) in OSF_3^+ is much larger while the cation has much shorter S–F bonds.[8] In the anion $[NSF_2NSO_2F]^-$ the S · · · S contact is very short which is similar to those in cyclic sulphur compounds, *e.g.* S_4N_4.[9]

This work was supported by Deutsche Forschungsgemeinschaft.

(*Received, 26th September* 1977; *Com.* 999.)

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] O. Glemser and R. Höfer, *Angew. Chem.*, 1971, **83**, 890.
[2] O. Glemser and R. Höfer, *Z. Naturforsch.*, 1974, **29b**, 121.
[3] P. H. Collins and M. Webster, *J.C.S. Dalton*, 1974, 1545 and literature cited there.
[4] D. W. J. Cruickshank and D. W. Jones, *Acta Cryst.*, 1963, **16**, 877.
[5] G. M. Clark and R. Morley, *Chem. Soc. Rev.*, 1976, **5**, 269.
[6] O. Glemser, A. Müller, D. Böhler, and B. Krebs, *Z. anorg. Chem.*, 1968, **357**, 184.
[7] B. Buss and D. Altena, *Z. anorg. Chem.*, in the press.
[8] C. Lau, H. Lynton, J. Passmore, and P. Y. Siew, *J.C.S. Dalton*, 1973, 2535.
[9] B. D. Sharma and J. Donohue, *Acta Cryst.*, 1963, **16**, 891.