Synthesis and *X*-Ray Structure of Bistetraphenylphosphonium Tris(phenylsulphonylimino)sulphite

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Summary An aza-analogue of sulphite, the structure of which was determined by *X*-ray diffraction, is prepared from sodium amide and a sulphur di-imide in liquid ammonia.

SULPHITE, SO_3^{2-}, and its derivatives are well established. In contrast, the aza-analogues of sulphite are rare.[1,2] We now report the first synthesis of the dianion $(PhSO_2N)_3S^{2-}$, which is obtained by the reaction of $PhSO_2{-}N{=}S{=}N{-}SO_2Ph$ with $NaNH_2$ in liquid ammonia. From the reaction of sulphur di-imides with alkoxides,[2] we know that the first step of this reaction is the nucleophilic attack of the R^2O^- group at the central sulphur atom. Anions of the composition $[(R^1SO_2N)_2SOR^2]^-$ could be isolated.[2] In the present case we also suggest a nucleophilic attack of NH_2^- at the sulphur followed by a rearrangement to yield the triaza-analogue of sulphite. By-products of the reaction are $PhSO_2NH_2$ and $Na^+RSO_2NSN^-$. The sodium salt of composition $2Na^+(PhSO_2N)_3S^{2-}$ was converted by use of $Ph_4P^+Cl^-$ in acetonitrile into the salt (**1**), which was isolated as colourless crystals (yield 35%) by cooling to −20 °C. The salt (**1**) was purified by recrystallisation from acetonitrile.

$$[Ph_4P^+]_2[(PhSO_2N)_3S]^{2-}$$

(**1**)

The ^{1}H n.m.r. spectrum of (**1**) exhibits as expected two multiplets for the protons of the different phenyl groups [δ(PhSO$_2$) 7·44; δ(PhP) 7·76], and the salt (**1**) was characterised by *X*-ray structural analysis.† The dianion (Figure) does not display threefold symmetry. A pyramidal configuration of the central sulphur atom, S(4), analogous to that of SO_3^{2-}, is observed with bond angles N(3)–S(4)–N(1) 98·7(6), N(3)–S(4)–N(2) 104·9(5), and N(2)–S(4)–N(1) 106·1(5)° and bond lengths N(1)–S(4) 1·62(1), N(2)–S(4) 1·64(1), and N(3)–S(4) 1·60(1) Å. It is interesting to note that the adjacent N–S(O$_2$) bonds do not correlate with one another; *i.e.* a short S–N distance from S(4) is not accompanied by a long N–S(O$_2$) distance and *vice versa* [N(1)–S(1) 1·51(1), N(2)–S(2) 1·58(1), and N(3)–S(3) 1·59(1) Å]. We must, therefore, conclude that the negative charges of the dianion are partially delocalised over the S(NSO$_2$)$_3$-skeleton.

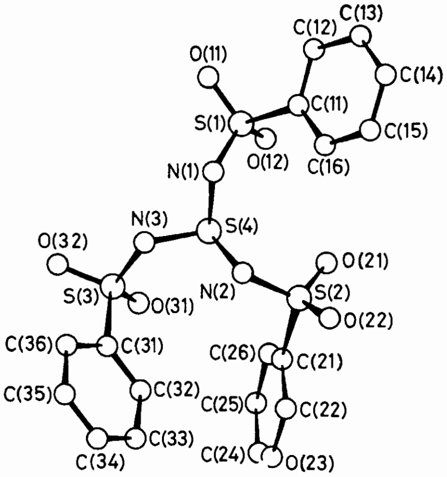

FIGURE 1. Perspective view of the dianion S(NSO$_2$Ph)$_3^{2-}$ illustrating the atom numbering scheme.

We expect that variations of this reaction will be of use for the preparation of a wide variety of other aza-analogues of known sulphur–oxygen derivatives.

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† *Crystal data:* monoclinic; space group $P2_1/n$; a = 35·526(8), b = 12·203(6), c = 12·430(6) Å, β = 97·56(4)°; Z = 4; D_c = 1·35 g cm^{-3}. The structure was solved by direct methods (SHELX-76; G. M. Sheldrick) and refined to R = 0·083, R_w = 0·078 for 4111 unique absorption-corrected reflections ($2\theta \leqslant 130°$, $F^2 \geqslant 2{\cdot}5\sigma(F^2)$, Cu-$K_\alpha$, μ = 23·4 cm^{-1}) collected on a Syntex P2$_1$ diffractometer.

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] A. Gieren and P. Narayanan, *Acta Crystallogr., Sect. A*, 1975, **31**, 120.
[2] H. W. Roesky, W. Schmieder, W. Isenberg, and G. M. Sheldrick, *Angew. Chem.*, in the press.