

## Crystal and Molecular Structures of N-Toluene-*p*-sulphonyliminodimethylsulphur(IV) and N-Toluene-*p*-sulphonyliminotriphenylphosphorane: Two Sulphonyl-stabilised Ylides

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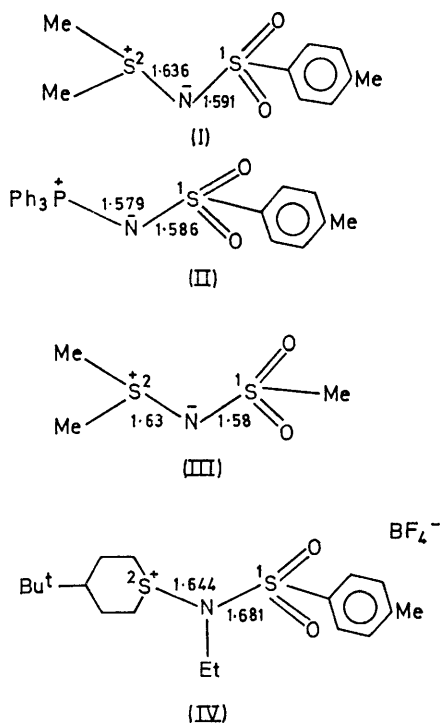
**Summary** Crystal structure analyses of the sulphur(IV) and phosphorane ylides (I) and (II), respectively, suggest  $d_{\pi}-p_{\pi}$  bonding between the 'onium groups and the vicinal atoms, and in addition, allow direct comparison to be made of the dimensions of (I) with those of the related compounds (III) and (IV).

FOR ylides ( $+X-Y^-$ ) in which the 'onium group (X) is a second or higher row element, formal bonding of the  $d_{\pi}-p_{\pi}$  type between the 'onium group and the vicinal atom may occur. In an attempt to rationalise such bonding, we

nitrogen atoms are capable of bonding by  $d_{\pi}-p_{\pi}$  overlap with both adjacent atoms. The choice of compound (I) for study was influenced by the recent analyses of the similar ylide (III)<sup>1</sup> and the *N*-alkylated compound (IV).<sup>2</sup> It has been suggested that apparent anomalies in the N-S(1) distances in (III) and (IV) could be explained by involvement of the sulphonyl-bonded aromatic group in (IV). The presence of the aromatic moiety in (I) was designed to test this hypothesis.

Crystals of (I) are monoclinic, space group  $P2_1/c$ , with four molecules of  $C_9H_{13}NO_2S_2$  in a cell of dimensions  $a = 12.93$ ,  $b = 7.17$ ,  $c = 12.50$  Å,  $\beta = 104.2^\circ$ . The structure was solved by Patterson and Fourier methods using 1082 independent reflexions estimated visually from series of Weissenberg photographs. Refinement of positional and anisotropic thermal parameters by block-diagonal least-squares calculations converged when  $R$  was 0.107. Compound (II) crystallises in the triclinic system, space group  $P\bar{1}$  (confirmed by statistical tests), with two molecules of  $C_{25}H_{22}NO_2PS$  in a cell of dimensions  $a = 11.58$ ,  $b = 9.05$ ,  $c = 13.14$  Å,  $\alpha = 99.9^\circ$ ,  $\beta = 113.3^\circ$ ,  $\gamma = 60.6^\circ$ . Solution of this structure was accomplished by a combination of symbolic addition, Patterson, and Fourier methods using 3276 independent observed reflexions measured on a Hilger and Watts Y290 diffractometer. Hydrogen atoms were located from a difference synthesis, and refinement of positional and anisotropic thermal parameters (isotropic for H atoms) by block-diagonal least-squares calculations has reduced  $R$  to 0.072.

Should  $d_{\pi}-p_{\pi}$  overlap occur in compounds of which (I) and (II) are representative, one result would be shortening of the bonds involving the nitrogen atom compared with the respective single-bond values. In (I) the pertinent lengths are N-S(1) = 1.591(8) Å, and N-S(2) = 1.636(8) Å, whilst in (II) the corresponding dimensions of N-S(1) = 1.586(4) Å and N-P = 1.579(4) Å are found. Comparison of these values with reported single-bond values for N-S bonds [1.74 Å from Pauling's covalent radii and 1.76(2) Å in sulphamic acid<sup>3</sup>] and N-P bonds [1.80 Å from Pauling's covalent radii and 1.77(2) Å in sodium phosphoramidate<sup>4</sup>], not only indicates appreciable shortening of all four bonds, but also reveals that the present values are



have determined the crystal structures of the sulphonyl-stabilised ylides (I) and (II), in which the respective

consistent with significant  $d_{\pi-p_{\pi}}$  overlap. That the compounds (I) and (II) have similar opportunities for  $d_{\pi-p_{\pi}}$  overlap with the respective sulphonyl moieties is borne out by the virtual duplication of the N-S(1) bond lengths in each molecule. However, the N-P bond in (II) is relatively more shortened than the corresponding N-S(2) bond in (I), and this may reflect a more effective participation of the phosphonium grouping in the possible  $d_{\pi-p_{\pi}}$  overlap.

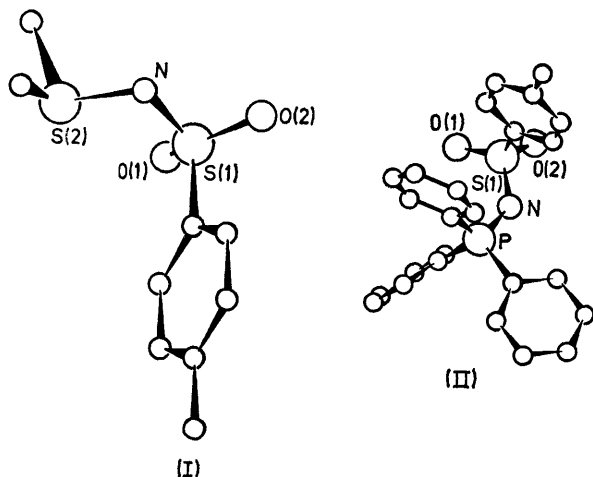


FIGURE. Views of the molecules (I) and (II), showing the solid-state conformations, and the numbering of the relevant atoms.

The dimensions of (I) agree well with those of the imino-sulphurane (III),<sup>1</sup> in which the corresponding N-S(1) and N-S(2) bonds have lengths of 1.58 and 1.63 Å, respectively. It would seem, therefore, that the presence of the aromatic ring in (I) has played a negligible role in the electron

delocalisation throughout the S-N-S system. Also, since the N-S(2) bonds of both (I) and (III) are identically longer than the N-S(1) bonds, we may infer that the nitrogen atom of each molecule is bonded more efficiently with S(1) of the sulphonyl groups. Alkylation of iminosulphuranes has been shown to occur on the nitrogen atom, and the analysis of one such alkylated derivative (IV)<sup>2</sup> reveals the corresponding N-S(1) and N-S(2) lengths of 1.681 and 1.644 Å, respectively. Thus *N*-alkylation has resulted in a lengthening of the N-S(1) (sulphonyl) bond in comparison with the values found in both (I) and (III). A possible interpretation of these results is therefore, that not only is the nitrogen atom bonded more efficiently to the sulphonyl groupings in (I) and (III), and that this bonding is not influenced by the presence or absence of a sulphonyl-bonded aromatic group, but also that it is the electron delocalisation throughout the *N*-sulphonyl system which is more readily affected by *N*-alkylation. The average S(1)-O distances of 1.411 Å in (IV), and 1.432 Å in (I), are in keeping with this suggestion, the latter value being taken to indicate a  $\pi$ -bond order of ca. 0.66 for S-O bonds.<sup>5</sup>

We have previously shown that in *N*-ammonio-amidates,<sup>6</sup> the quaternary nitrogen atom and the heteroenolate moieties are coplanar, and that this conformation is associated with a maximising of electrostatic interactions and a minimising of non-bonded interactions. Not only are the conformations of (I) and (II) very similar, but it appears that the electron delocalisation achieved by  $d_{\pi-p_{\pi}}$  overlap has lessened the requirement for *syn*-planarity. This is reflected in the values of 36.8° and 37.6° for the dihedral angles S(2)-N-S(1)-O(1) and P-N-S(1)-O(1) in (I) and (II) respectively, [in both (I) and (II), S(1) is tetrahedral], both these values being slightly smaller than the interpolated value of 52° for the corresponding angle in (IV).

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