

X-Ray Photoelectron Spectroscopic Study of the S–N Bonding Character of Carbonyl-stabilized Sulphilimines

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X-Ray photoelectron spectra of carbonyl-stabilized sulphilimines and their salts were measured and a strong interaction through the σ bond between S^+ and N^- was found.

Much of the physical data on sulphur ylides has been interpreted as supporting the existence of π bonding between the 3d-orbital of sulphur and the p-orbital of the anionic atom.¹ However, MO calculations and X-ray crystal structure analyses have implied that the stabilization of the anionic atom is due to factors other than the participation of sulphur d-orbitals,² and so the exact nature of the bonding in sulphur ylides remains uncertain. We have already reported a new stabilizing effect, which we termed the electron displacement effect,³ in the N^+-N^- bonding of aminimides which do not have d-orbitals available. Hence, if sulphilimines do not have a strong $d\pi-p\pi$ interaction between S^+ and N^- , the electron displacement effect will be a major stabilizing factor. In order to investigate this, X-ray photoelectron spectra of sulphilimines and their salts have been measured.

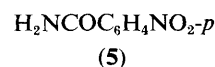
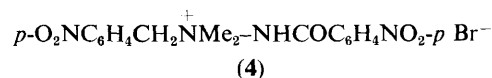
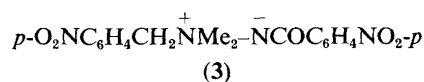
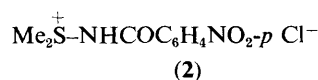
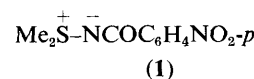
The sulphilimines and their salts were prepared by the published methods.^{4,5} X-Ray photoelectron spectra were determined using a JASCO ESCA-1 spectrometer, with $Mg-K_{\alpha}$ radiation. The samples were examined as fine powders mounted on double-side sticky tape. The C 1s line was taken as 284 eV.

The formal charge on the sulphur atom of a sulphilimine is the same as that for the corresponding salt. Thus, the same S 2p binding energy would be expected for both compounds. However, we found a striking difference between two values as shown in Table 1; the S 2p binding energy of the salt (2) is 1.1 eV higher than that of the sulphilimine (1). Since this difference could arise from the lattice energy and the reorganization energy, we measured the N 1s spectra of both compounds.³ If these effects contribute to the S 2p values, there should be a difference between the N 1s values for the nitro-group of (1) and (2). However, a difference was not found (405.0 and 404.9 eV, respectively), suggesting that the S 2p binding energies are not affected by the lattice energy and the reorganization energy.

Another factor could be the coulombic potential due to the anionic nitrogen, but, the negative charge on the anionic nitrogen in sulphilimines is delocalized into the carbonyl

Table 1. X-Ray photoelectron (N 1s and S 2p binding energies) and i.r. data for various ylides and the amide (5).

	Binding energy/eV				$\nu(C=O)/$ cm^{-1}
	NO_2	NH or NH_2	N^-	S^+	
(1)	405.0	—	397.2	164.8	1570
(2)	404.9	399.5	—	165.9	1700
(3)	405.0	—	397.6	—	1580
(4)	405.0	400	—	—	1690
(5)	405.0	398.7	—	—	1680



group by amide resonance.⁶ In the sulphilimine salts, the charge on the anionic ion (Cl^-) is localized. For the aminimides the effect of coulombic potential is not large; there is a considerable difference between the N 1s binding energy for the N^+ in hydrazone salts and in metal complexes of aminimides.⁷ The differences (0.8 and 1.3 eV) between the N 1s binding energies for NH of the salts (2) and (4) and that for

NH₂ of the amide (5) also indicate that the coulombic potential due to the positive atom is not important. From these results, we believe that the difference observed in S 2p binding energies is real. The lower S 2p binding energy indicates that the electron density on the sulphur atom of the sulphilimine (1) is higher than that of the salt (2).

We suggest that there are two main reasons for this. The first is d-orbital participation in S-N bonding,¹ and the second is the electron displacement effect; the electron cloud of the σ bond between S⁺ and N⁻ lies closer to the sulphur atom. If there is a strong π interaction between S⁺ and N⁻ in sulphilimines, we would expect a higher binding energy for the anionic nitrogen of the sulphilimine (1) compared with the aminimide (3), whereas the opposite is in fact found (Table 1).³ In addition, the difference (2.4 eV) between the N 1s binding energy for NH of the salt (4) and that for N⁻ of the aminimide (3) is almost the same as that (2.3 eV) between the salt (2) and the sulphilimine (1). These results suggest that the $d\pi$ - $p\pi$ interaction in sulphilimines is not important.⁸ Hence, we may conclude that one of the reasons for the high electron

density on S⁺ of carbonyl-stabilized sulphilimines is the electron displacement effect and this is a stabilizing factor.

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