

Analysis of 1,2-Dithiolium Salt Structures Using X-Ray Photoelectron Spectroscopy

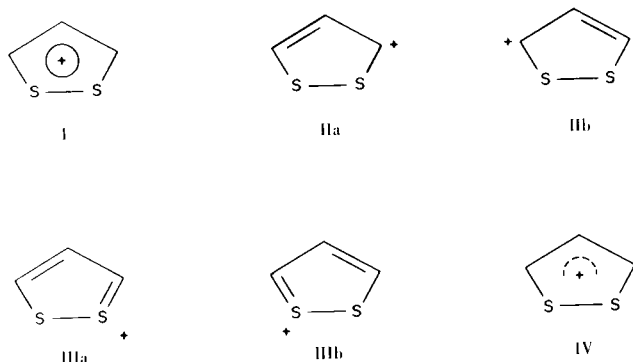
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Sir:

Molecular orbital calculations (1), thermochemical (2), and X-ray crystallographic studies (3) suggest that the structure of 1,2-dithiolium salts (4) is best represented by I, which is aromatic and π -isoelectronic with the tropylium ion, rather than the localized forms (IIa and IIb; IIIa and IIIb) or the allylic form IV. However, uncertainty (4) still exists as to the actual involvement of sulfur atomic orbitals in the electronic framework of such salts.



It has been demonstrated (5) that X-ray photoelectron spectroscopy (XPS) can detect chemical shifts in S(2p) binding energies for sulfur atoms with differing chemical environments. This technique has recently been employed (6) to provide structural information about the thiathio-*phthenes* (V). These studies (5,6) indicate that XPS analysis of I would provide further insight into the structure of the 1,2-dithiolium salt.



The S(2p) binding energies were measured for VI (7), VII (7), and VIII using a McPherson ESCA 36 Photoelectron Spectrometer equipped with an aluminum excitation source. The S(2p_{1/2}, 2p_{3/2}) spin orbit splitting is not large enough to enable resolution under normal cir-

stances. Therefore, the reported data are taken from the centroid of the unresolved doublet. The S(2p) binding energies and the full-width-half-maxima (FWHM) of the photoelectron lines are reported in the Table. The binding energies are reproducible to ± 0.2 eV. The samples were run as powders pressed into an etched aluminum sheet. To compensate for sample charging, the binding energies were calibrated using a C(1s) binding energy of 285.0 eV.

TABLE

Compound	S(2p) binding energy (eV)	FWHM (eV)
VI	164.8	2.5
VII	165.5	2.4
VIII	165.5	2.5

In each case, only a single S(2p) photoelectron line is observed with a FWHM of *ca.* 2.5 eV. Since the nominal FWHM of a S(2p) line obtained for a single form of sulfur is *ca.* 2.5 eV under identical experimental conditions, the data indicates that the charge distribution about the two sulfur atoms in the 1,2-dithiolium salts are essentially identical. This eliminates IIIa and IIIb as possible structures since the charge distribution on the two sulfur atoms would be drastically different, giving rise to at least extensive broadening of the S(2p) line (5). In addition, only one C(1s) photoelectron line (FWHM *ca.* 2.0 eV) is observed in the XPS spectra. These data indicate that all of the carbon atoms present must bear comparable charges. Therefore, structures IIa, IIb, and IV are also unlikely since their C(1s) spectra would contain two well resolved C(1s) lines due to the localized positive charge (8). As a consequence, it must be concluded that the delocalized form (I) best represents the structure of the 1,2-dithiolium salts.

Compound VIII (violet needles; m.p. 235°) was prepared in 25% yield via a procedure similar to that for VI and VII (7). However all attempts to purify VIII from warm methanol or acetic acid appeared to result in a reaction, probably from a solvent involved nucleophilic

attack on the dithiolium ring (4). As a consequence, VIII was treated with perchloric acid in ethanol (9) and conveniently characterized as its perchlorate salt (10).

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