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ULTRA LONG-RANGE THROUGH-BOND INTERACTIONS IN DITHIASPIRANE DISULFOXIDES AS REVEALED BY PHOTOELECTRON SPECTROSCOPY

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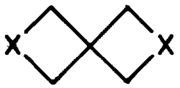
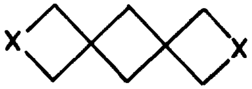
Summary: Ultraviolet photoelectron spectra of the disulfoxides of 2,6-dithiaspiro [3.3.] heptane,2,8-dithiaspiro[3.1.3.1.] decane, and 2,10-dithiaspiro [3.1.1.3.1.1.] tridecane show that there are substantial through-bond interactions of the sulfur lone-pairs, ranging from 0.85 eV for the compound with two rings to 0.25 eV for the compound with four rings.

Through-bond interactions of orbitals[1] can have significant chemical consequences. A recent review, dealing with this issue[2], noted that interactions between basis orbitals separated by up to six bonds have been observed. "The possibility of an electron or positive hole being transmitted through-bonds over large distances within a molecule is intriguing." (quote from ref. 2).

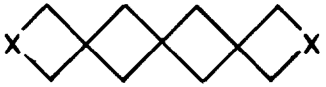
Since the mechanism of electron transfer between redox sites in proteins is not well understood, we have for some time[3,4] been investigating, as simple models, small binuclear complexes. One of the most interesting results to emerge from these studies has been the observation of an intra-valence charge transfer (IT) band in the near infra-red spectra of Ru^{2+}/Ru^{3+} complexes of the type $(NH_3)_5Ru(II)\text{-}L\text{-}Ru(III)(NH_3)_5{}^{5+}$ where L is one of the bridging ligands 1 - 3.



1. X=S
4. X=S-O



2. X=S
5. X=S-O



3. X=S
6. X=S-O

These results imply that electron delocalization involving the two metal sites occurs. This is surprising because the ligands are fully saturated and the metal atoms are far apart (more than 10-Å). However the ability of cyclobutane Walsh orbitals to function as conjugation relays has been noted.[11] Thus we have now examined the photoelectron spectra of the bridging ligands, and of their disulfoxides 4 - 6 to seek evidence for unusual orbital properties that might be useful in understanding the charge-transfer properties of the mixed-valence binuclear complexes. The metal complexes are naturally much too involatile for photoelectron spectroscopic study, so the disulfoxides provide an appealing set of relatively volatile compounds that model complexation of the sulfur atoms.

The disulfoxides were prepared by oxidation of the parent ligands with two equivalents of hydrogen peroxide in acetic acid[5]. NMR spectra confirmed that the desired disulfoxides had formed.

Photoelectron spectroscopy[2,6] has played a useful role in quantitating both through-bond and through-space interactions; the extent of interaction is revealed by the energy gap between the photoelectron bands corresponding to the symmetric and anti-symmetric combinations of the basis interacting orbitals. In the present case, then, interaction of the remote sulfur lone-pairs is revealed by the presence of two sulfur lone-pair peaks.

The photoelectron spectrum of thiacyclobutane 7 needed for comparison purposes has already been reported[7,8] and we have obtained the spectrum of thiacyclobutane sulfoxide 8 as part of the present study.

7 X = S; 8 X = S-O

The partial photoelectron spectra of 8 and of the disulfoxides 4,5 and 6 are shown in the figure. The first two bands in the spectrum of 8 are interpreted as "sulfur lone-pair" (n_S) and "sulfoxide π-orbital" (π_{SO}). Other simple sulfoxides, with the exception of thiacyclopropane sulfoxide[9], have similar spectra, and identical interpretations have been given[10]. On comparing the spectra of 4 and 8, a significant difference is seen in the low i.p. region — the n_S band of 8 has split into two peaks in compound 4 with $\Delta E = 0.85$ eV. Photoelectron spectra of 5 and 6 are qualitatively similar to that of 4 in the low i.p. region except that the splitting ΔE between the two n_S peaks is smaller (see Table). In no case was there any clear splitting of the n_S bands in the parent dithiaspirocyclobutanes 1 - 3.

TABLE

Photoelectron Spectroscopic Data for Thiacyclobutanes and Their Sulfoxides

Compound	Ionization Potentials Below 11.0 eV
2,6-Dithiaspiro [3.3] heptane (1)	8.71(n_S);10.04
2,8-Dithiaspiro [3.1.3.1.] decane (2)	8.75(n_S); 9.55
2,10-Dithiaspiro [3.1.1.3.1.1] tridecane (3)	8.75(n_S), 9.45
2,6-Dithiaspiro [3.3] heptane disulfoxide (4)	8.75(n_S); 9.60(n_S);10.45(π_{SO})
2,8-Dithiaspiro [3.1.3.1.] decane sulfoxide (5)[5]	8.78(n_S), 9.16(n_S),10.10(π_{SO})

(Table continued on next page)

TABLE (cont'd)

Compound	Ionization Potentials Below 11.0 eV
2,10-Dithiaspiro [3.1.1.3.1.1] tridecane disulfoxide (6)	8.75(n_S), 9.00(n_S),10.15(π_{SO})
Thiacyclobutane (7)	8.65(n_S);10.7
Thiacyclobutane sulfoxide (8)	8.90(n_S);10.1(π_{SO})

Thus it appears that photoelectron spectroscopy is providing clear proof for through-bond interactions of the sulfur lone pairs in the disulfoxides. In the case of the 4-ring compound, this interaction is occurring over eight bonds, making it the longest range interaction of its type known at this time. Earlier work[2] had indicated that, in general, an interaction over eight bonds would be of the order 0.2eV, as found in this present case. The ΔE (IP_2-IP_1) values are 0.85 and 0.38 eV for the 2-ring and 3-ring sulfoxides where the interactions take place over four and six bonds respectively. Interestingly there is a correlation between the ΔE values and the relative intensities of the IT bands in the RuII/RuIII binuclear complexes formed by the parent ligands (ϵ= 43±2, 9±1 and 2.3±7 for the 2-, 3- and 4-ring compounds[3]).

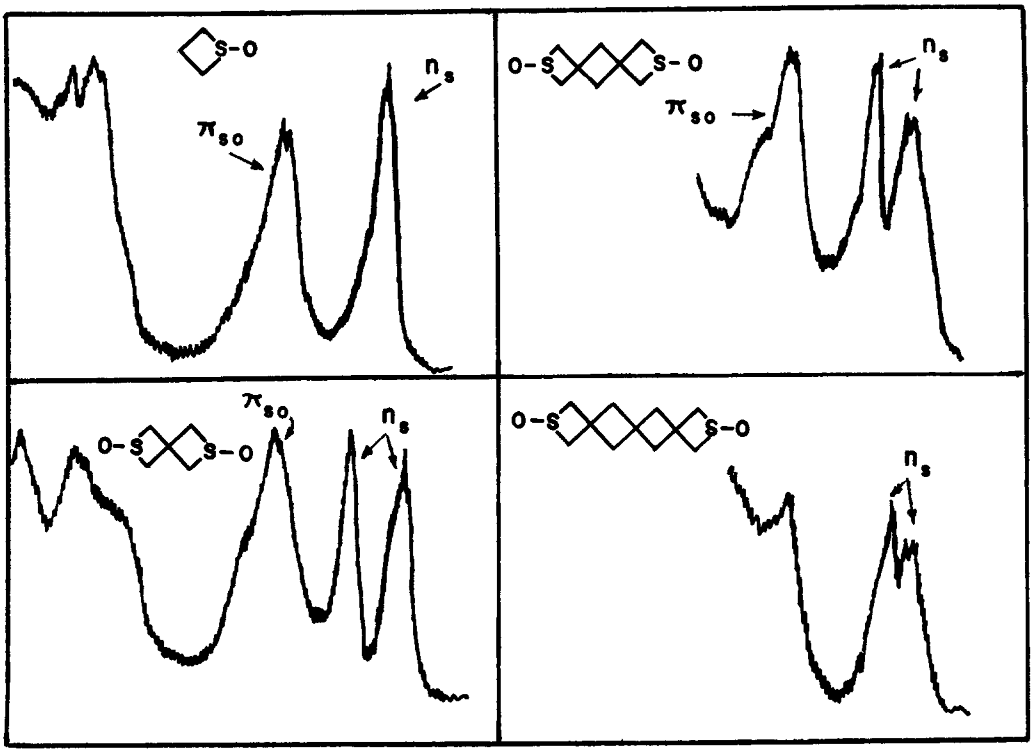


Figure Photoelectron spectra in the 8-13 eV region for the sulfoxides. Vertical i.p. values measured from these spectra are given in the table above.

The assignment of the first two bands in the spectra of the multiple-ring disulfoxides to orbitals of predominently sulfur lone-pair type is thought to be reasonably certain since no other interpretation is in accord with all our observations. For example, there appears to be no problem of confusing S=O (π) bands and n_S (π) bands since all the multiple ring disulfoxides give a band in approximately the same position, and with approximately the same shape as the S=O (π) band in thiacyclobutane sulfoxide. Also it is unlikely that the second band (σ_{cc}) in the spectra of the unoxidized compounds has a counterpart in the "sulfur lone pair region" of the disulfoxides, since the spectrum of thiacyclobutane sulfoxide contains no such band, and furthermore CNDO calculations[4] show that the orbital in question moves to much lower energy (higher i.p.) on complexation.

The reason that the disulfoxides show large through-bond interactions in photoelectron spectroscopy while the parent ligands do not, cannot yet be answered. The disulfoxides are certainly expected to have lower symmetries and lowering of symmetry often results in breaking of degeneracies. In the present case, though, the nature of the σ-relay orbitals which might be responsible for lifting the degeneracy of the n_S levels is unknown. M.O. calculations and further experiments are in progress to address these important questions.

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