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SPIROCONJUGATION INVOLVING SULFUR 3p ATOMIC ORBITALS

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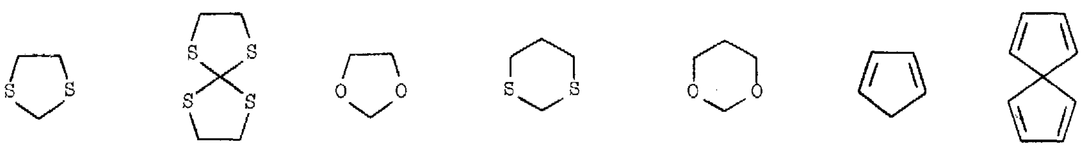
Previous work has shown that photoelectron spectroscopy is a most useful technique for studying *through-bond and through-space interactions*[1-3] and for obtaining information about the related phenomenon of spiroconjugation.[4-9] We report here photoelectron spectroscopic studies and MO calculations on dithiolane (1) and on 1,4,6,9-tetrathiaspiro[4.4]nonane (2) which elucidate the mechanisms whereby the sulfur 3p atomic orbitals mutually interact. Both compounds were made according to previously specified procedures.[10,11]

In most other studies of spiroconjugation, the interacting π systems were of C-C π type; the present study is the first investigation of spiroconjugation involving exclusively hetero-atom orbitals of π symmetry, and is also the first investigation of spiroconjugation in a spiro compound where the rings are not necessarily constrained to a planar geometry. Experimental and calculated ionization potential values are summarized in Table I for 1 and 2, as well as for 1,3-dioxolane (3). Photoelectron spectra for 1 and 2 are shown in Figure 1.



1 2 3 4 5 6 7

We first examined the mechanism by which the S 3p atomic orbitals within the same ring interact. This was possible by comparing the photoelectron spectrum of 1 with those of other heterocycles containing sulfur or oxygen atoms, specifically 3-5.

The ionization potentials shown in Table I reveal that the splitting between the energies of the two highest M.O.'s is greater for 4 in the six-membered ring series, but for 3 in the five-membered ring series. The small splitting seen for compound 1 relative to 3 strongly

TABLE I. Photoelectron Spectroscopic Results and Molecular Orbital Calculations

Compound	HOMO's	Calculated Eigenvalues (eV) CNDO/2	Other	Experimental Vertical I.P.	Splitting between levels of a and b symmetry Expt.	Calc.
2	a_2	11.00	6.10*	8.35		2.01 (CNDO/2)
	e	10.69	6.36	8.80, 9.05	1.10	
	b_1	13.01	7.75	9.45		1.65 (ab initio
1	a	11.53		8.75	0.30	0.36
	b	11.89		9.05		
3	a	14.53		10.1	0.55	0.67
	b	15.20		10.65		
4	a			8.54	0.41	
	b			8.95		
5	a			10.1	0.25	
	b			10.35		

*ab initio SCF STO 3G Calculation

implies that for these two molecules a through-bond rather than a through-space interaction dominates. This agrees with an earlier conclusion made by Turner and Sweigert on the basis of the photoelectron spectra of 3, 4, and 5,[12] as well as with the CNDO/2 calculations given in Table I.

We further investigated the bonding picture in 1 and 3 by carrying out M.O. calculations (see Table).[13] Since the geometries of these two compounds are not known, we based our calculations on a planar geometry; Turner and Sweigert also assumed an almost planar geometry.[12] The S 3p orbitals transform as a and b type M.O.'s. The a M.O. can interact with the highest M.O. localized on the carbon-hydrogen bonds of the same symmetry, thus giving rise to a splitting of the predominantly ''lone pair'' M.O.'s. In fact, the band at lower I.P. is broader, supporting this assignment. Although the CNDO/2 calculations are not in good agreement with the measured ionization potentials, they do generate splittings between the a and b molecular orbitals for compounds 1 and 3 that agree rather well with the experimental splittings, both in a relative and absolute sense (see Table). An earlier CNDO/2 calculation on 1 had assumed a 20° distortion from planarity;[14] this calculation gave only a very small splitting between the two HOMO's. Most probably then the true geometry is closer to planar than assumed by these authors.

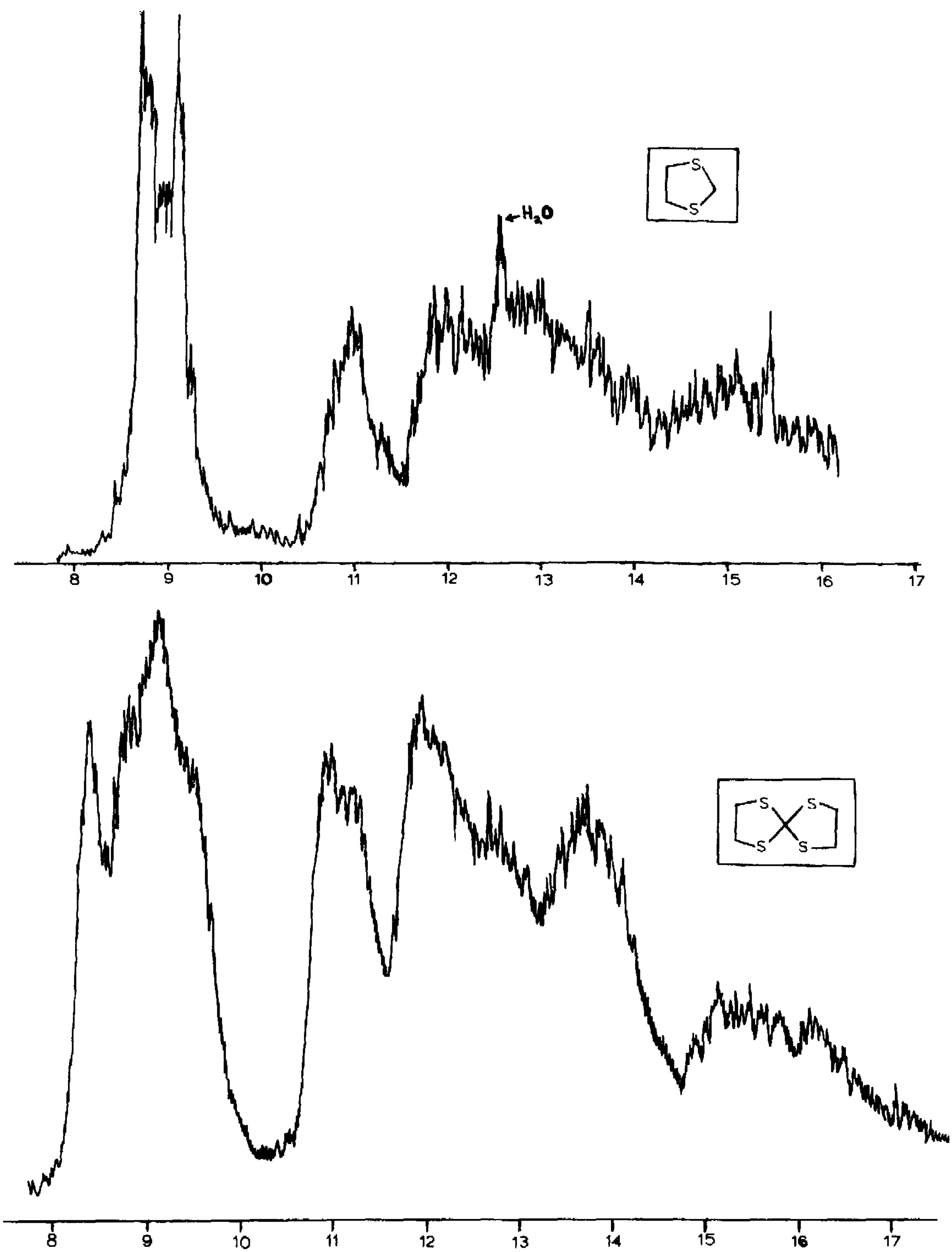


Figure 1. Photoelectron spectra of dithiolane (1) and 1,4,6,9-tetrathiaspiro[4.4]nonane (2). Spectra were obtained on a Perkin-Elmer PS-18 photoelectron spectrometer using the He I excitation line.

Turning now to the spectrum of 2, we note that it bears the same qualitative relationship to the spectrum of 1 as does the spectrum of 7 to that of 6.[9] In the D_{2d} symmetry of 7, through-space spirointeraction of the predominantly C-C π type M.O.'s of the different rings results in there being four π M.O.'s. One of these is of a_2 symmetry, one is of b_1 symmetry, and two (a degenerate pair) are of e symmetry. The photoelectron spectrum of 7 has been adequately interpreted in terms of these orbital levels.[9] In 2 the S 3p orbitals give rise to essentially the same type of spirointeractions, the only difference being the non-interacting e orbitals are predicted to be between the a_2 and b_1 orbitals, rather than below them as in 7. The e orbital should give rise to a Jahn-Teller distortion, as is evident in the second and third bands of the spectrum of 2. While this assignment is in complete agreement with our *ab initio* calculations (see Table) as well as with the magnitude of the a_2-b_1 splitting observed for 7 (1.2 eV),[9] the incomplete resolution of the e and b_1 bands coupled with the lack of experimental geometry for 2, makes a totally unambiguous assignment impossible.

FOOTNOTES AND REFERENCES

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