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Intramolecular Interaction of Remote Sulfur Lone-pairs through Homoconjugation

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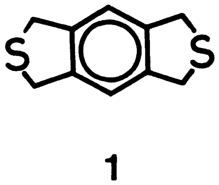
The intramolecular interactions between the lone-pair electrons of remote sulfur atoms in tetrahydrobenzodithiophenes were revealed by means of the He (I) photoelectron spectroscopy and ab initio calculations.

Photoelectron (PE) spectroscopy provides a useful role in detecting both through-space and through-bond interactions;1) the extent of interaction is revealed by the energy gap between the PE bands corresponding to the symmetric and antisymmetric combinations of the basis interacting orbitals. In this context, the interactions of the lone-pairs on the equivalent sulfur atoms in a variety of sulfur heterocycles, such as 1,4-dithiane,2) 1,4-dithiete,3) S-terathianes,4) and dithiaspiranes,5) have been investigated by the PE spectroscopy. We now wish to demonstrate the novel tetrakis-homoconjugative interaction between the two sulfur atoms in isomeric tetrahydrobenzodithiophenes **1** and **2**.

To interprete the PE spectra of **1** and **2** it is instructive to consider first the spectrum of dihydrobenzothiophene **3**, shown in Fig. 1. We can empilically assign the bands, comparing the spectrum of **3** with those of related compounds. The first band at 8.46 eV corresponds to the ionization of the sulfur lone-pair electrons in dihydrothiophene.6) The second and the third bands can be assigned to π-MO's based on the data for o-xylene7) and trimethylene-fused benzene.8) For confirmation of the orbital assignments we have performed ab initio calculations using 4-31G basis set and made use of Koopman's theorem. Since a geometrical



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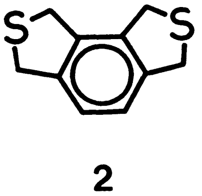

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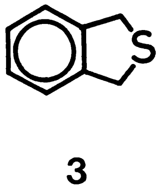

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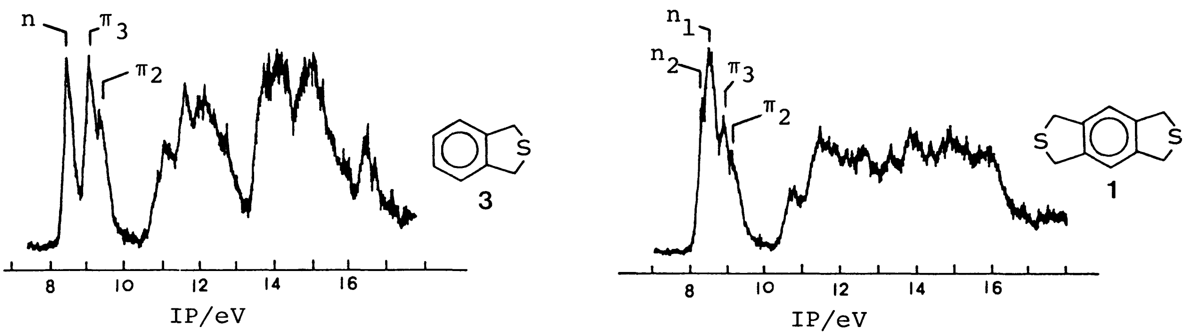


Fig. 1. The He (I) PE spectra of dihydrobenzothiophene **3** and tetrahydrobenzodithiophene **1**.

optimization at the 4-31G level was not undertaken,[9] the results would remain qualitative in character. Nevertheless the comparison between calculated and experimental values for **1** shows a good agreement for the first three bands, as summarized in Table 1.

Figure 1 presents the PE spectrum of compound **1**. In the region below 10 eV, we find four peaks, of which the first and the second bands are due to the ionization of the sulfur lone-pairs, as the ionization energies correspond to that observed in compound **3**. Thus, the lone pair splitting of 0.20 eV is clearly displayed for compound **1**. The characteristic feature in the spectrum of **1** is a considerably intense peak for the second band, as compared with other bands. As non-bonding electron orbitals often lead to more intense peaks than that of π-energy levels, the second band at 8.49 eV is ascribable to the n-orbital which is strongly localized in the sulfur atom. On the other hand, the first peak at 8.29 eV is due to the n-orbital significantly mixed with π-orbitals on the benzene ring.

Table 1. Vertical ionization energies (I) of **1**, **2**, and **3** together with calculated orbital energies (E)

Compd.	MO	Assignment	I/eV	-E/eV	Compd.	MO	Assignment	I/eV	-E/eV
1	n_2	$4b_{1g}$	8.29	8.62	**2**	n_2	$5a_2$	8.34	8.70
	n_1	$4a_{2u}$	8.49	9.17		n_1	$7b_1$	8.52	9.02
	π_3	$2b_{2g}$	8.90	9.32		π_3	$6b_1$	8.97	9.45
	π_2	$3b_{1g}$	9.15	9.56		π_2	$4a_2$	9.17	9.54
3	n	$5b_1$	8.46	8.70					
	π_3	$2a_2$	9.09	9.19					
	π_2	$4b_1$	9.32	9.37					

To analyze the orbital mixing we can use the concept of orbital interaction. Figure 2 shows the qualitative interaction diagram between the basis orbitals of a benzene fragment and two dimethyl sulfide fragments to yield the valence MO's of **1**. The sulfide pairs are represented by the H-C hyperconjugative π-MO's and are formally subdivided into the through space combinations n_s^+ and n_s^-. For reasons of symmetry only n_s^- possesses correct symmetry to interact with the benzene fragment; the antibonding interaction should raise n_s^- up to the HOMO of **1**. Thus, the HOMO is mixed with the π-orbital of benzene, whereas the next HOMO is the almost pure n-orbital of dimethyl sulfide.

The peak assignment is verified by the ab initio calculation (Table 1). It is quite of interest to see the electron density maps based on the ab initio calculation (Fig. 3), which clearly revealed the remote interaction of the n-orbitals through homocongugation prevailing in the HOMO of **1**.

Two lone pair bands were also observed for compound **2**. There are no considerable differences in the position of the four first bands between **1** and **2** (Table 1), indicating that the n-orbital splitting is little dependent on the mode of fusion of the sulfur bridge. However, in contrast to **1**, the intensities of the first and the second band in **2** showed no much difference. This is rationalized in terms of the interaction diagram illustrated in Fig. 4, wherein both n_s^+ and n_s^- can enter into symmetry-allowed interaction with the benzene π-orbitals. Electron density maps again revealed the HOMO as well as the next HOMO being spread over the benzene ring by the remote interaction through tetrakis-homoconjugation.

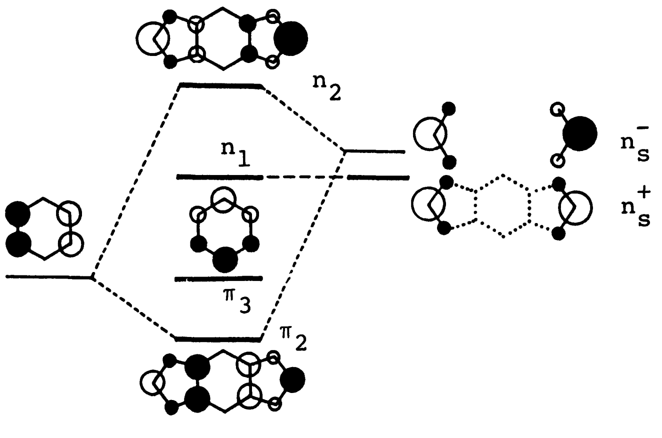
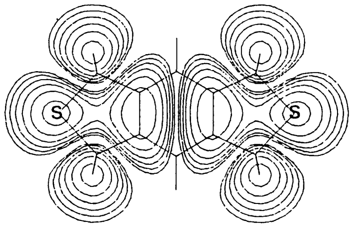
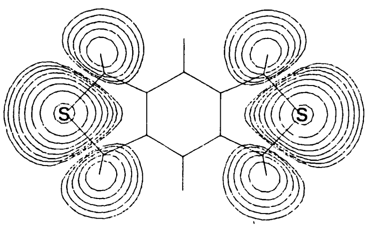


Fig. 2. Qualitative MO interaction diagram between the HOMO of benzene and that of two dimethyl sulfides (n_s^-).



HOMO (n_2)



next HOMO (n_1)

Fig. 3. Electron density maps for the HOMO and the next HOMO of compound **1**.

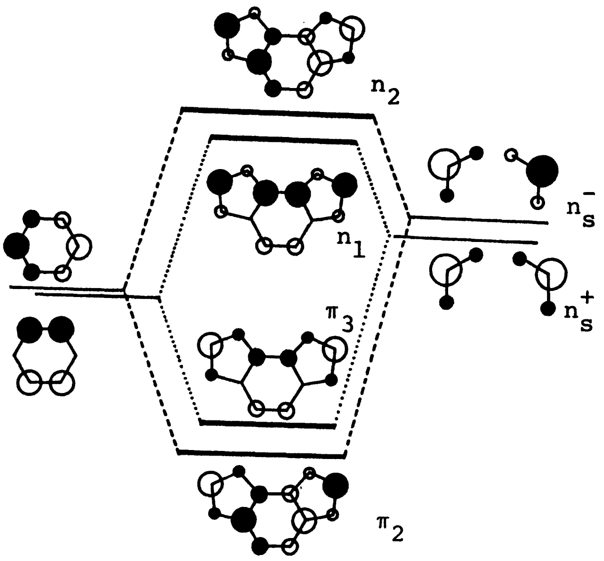


Fig. 4. Qualitative MO interaction diagram between the HOMO's of benzene and those of two dimethyl sulfides.

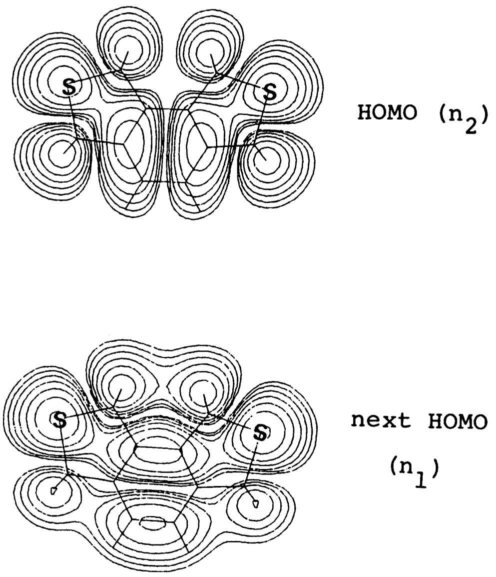


Fig. 5. Electron density maps for the HOMO and the next HOMO of compound 2.

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