

## Photoelectron Spectra of Dithiapropepanes

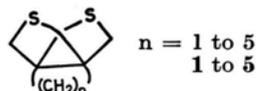
Michio Kobayashi and Rolf Gleiter  
 Institut für Organische Chemie  
 der Technischen Hochschule Darmstadt

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Spatial Interaction, Sulfur Lone Pairs,  
 PE Spectra

The photoelectron spectra of the dithiapropepanes **1** to **5** have been recorded. The first bands have been assigned by comparison with the PE spectra of cyclic thioethers. The resonance integral between the 3p orbitals of the sulfur centers in **1** to **5** is found to be  $-0.15$  to  $-0.25$  eV.

In connection with studies concerning the interaction between 3p sulfur lone pairs in sulfides [1] we have investigated the He(I) photoelectron (PE) spectra of the dithiapropepanes **1** to **5** prepared recently [2].



In Fig. 1 we show the PE spectrum of **2** as a representative. All PE spectra exhibit two sharp peaks in the region between 8 and 9 eV well separated from strongly overlapping bands below 10 eV. In Fig. 2 the first peaks are correlated. The dots indicate the center of gravity of the first two bands.

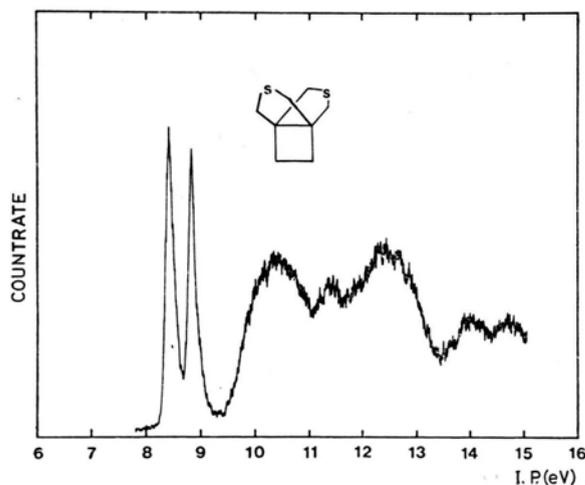


Fig. 1. Photoelectron spectrum of **2**.

Requests for reprints should be sent to Prof. Dr. R. Gleiter, Institut für Organische Chemie der Technischen Hochschule, Petersenstraße 22, D-6100 Darmstadt.

To interpret the PE spectroscopic results we compare them with the PE data of thioethers. This procedure is possible since the interaction between the two thioether units in **1**–**5** relatively small due to their spatial separation.

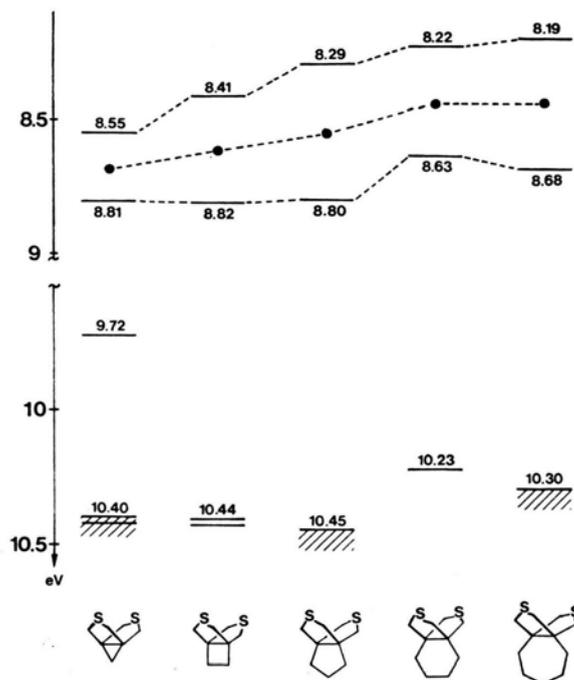


Fig. 2. Comparison between the first bands of the photoelectron spectra of **1** to **5**. The center of gravity of the first two bands is indicated by a ●.

Thioethers exhibit a sharp band between 8 and 9 eV which has been assigned [3] to the ionization from a 3p orbital on sulfur. Based on the results, which assume the validity of Koopmans' theorem ( $-\epsilon_J = I_{V,J}$ ) [4], the data shown in Fig. 2 can be rationalized by assuming two effects: i) a spatial interaction between the 3p lone pairs on the sulfur center and ii) an increase of the inductive effect on the basis orbital energies with increasing  $n$ .

From Dreiding models we deduce a larger distance between the sulfur centers in **1** (ca. 4.9 Å) compared to that in **3** to **5** (4.6 Å). This amounts to an increase in the overlap between the 3p orbitals in **3** to **5** compared with **1**. From this spatial interaction we obtain the split between the two linear combinations  $n_+$  and  $n_-$  defined in Fig. 3. The energy difference between both niveaus amounts to  $2\beta$  in a simple ZDO model. For  $\beta$  the following values are obtained:

$$\begin{aligned} 1: \beta &= -0.13 \text{ eV}; 2: \beta = -0.20 \text{ eV}; 3: \beta = \\ &= -0.26 \text{ eV}; 4: \beta = -0.21 \text{ eV} \text{ and } 5: \beta = \\ &= -0.24 \text{ eV}. \end{aligned}$$

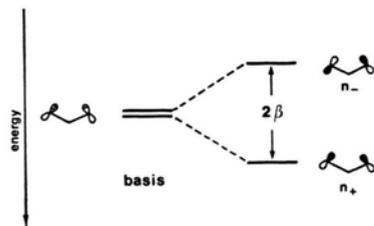


Fig. 3. Qualitative interaction scheme for the 3p orbitals in **1** to **5**.

The increasing number of methylene groups in the series **1** to **5** shifts the basis orbital energies of the 3p orbitals towards lower values as exemplified in the cyclic olefins [5]. This leads to a shift of the center of gravity in the beginning of our series (see

Fig. 2). At higher members ( $n > 4$ ) the increase is minute.

The consideration of both effects leads to a consistent rationalization of the observed data.

#### Experimental

The preparation of the compounds **1** to **5** has been described in [2]. All compounds used were analytically pure. The PE spectra were recorded on a PS 18 photoelectron spectrometer (Perkin Elmer Ltd. Beaconsfield, England). The recording temperature was 25–40 °C.

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