Photoelectron Spectra of Dithiapropellanes

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The photoelectron spectra of the dithiapropellanes 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.

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 (−\(\epsilon_I = \epsilon_V\)) [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.

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 .

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.

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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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