The Photoelectron Spectra of Dimethoxysulfane and Dimethoxydisulfane☆

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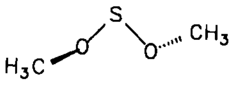
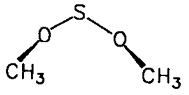
The He(I) photoelectron spectra of dimethoxysulfane (**1**) and dimethoxydisulfane (**2**) have been recorded. The lowest energy ionizations in the PE spectrum of **1** can be explained by assuming C_2 symmetry. They can be described as arising from linear combinations between the 3p lone-pair at sulfur and 2p lone-pairs at the oxygen atoms. A comparison between the calculated MO sequence of **2** for different conformations and the first PE bands shows a good agreement with an OSSO torsional angle near 90°. The highest occupied MOs of **2** can be described as linear combinations between the 3p MOs of the S_2 unit and linear combinations between the 2p AOs of the oxygen atoms.

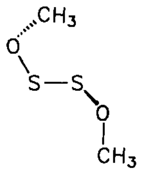
Dimethoxysulfane $(CH_3O)_2S$ (**1**) and dimethoxydisulfane $(CH_3O)_2S_2$ (**2**) are stable methyl esters which are derived from sulfoxylic acid (H_2SO_2) and dihydroxydisulfane ($H_2S_2O_2$), respectively. Since both acids are unknown in the condensed phase[1], their esters may serve as model compounds for a structural characterization. An electron diffraction study of **1** shows that this molecule exhibits C_2 symmetry (**1a**) in the gas phase[2] and this also holds for the solid state[3]. Ab initio MO calculations on **1** predict that the C_s conformer **1b** is less stable by 12 kJ/mol[2].



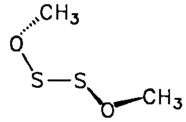
1a



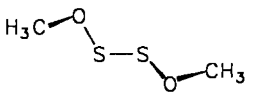
1b



2a



2b



2c

For **2** an electron diffraction study reveals[4] conformation **2b** as the major species in the gas phase, while crystalline **2** consists of helical molecules **2a** only[5]. Molecular orbital calculations on **2a**–**2c** result in rather small energy differences of 5.8 and 12.8 kJ/mol between **2b** and the other conformers, predicting **2b** as the global minimum and **2c** as the least stable structure.

In this paper we report on MO calculations on **1** and **2** and on the He(I) photoelectron (PE) spectra of these compounds. These studies have been undertaken to explore the extent of the interaction between the lone pairs of sulfur and oxygen and to contribute to the gas phase structures of **1** and **2**.

Results

To interprete the PE spectra of **1** and **2** we have assumed the validity of Koopmans' theorem[6] which states that the negative value of the calculated orbital energy ($-\varepsilon_j$) can be set equal to the recorded vertical ionization energy. It has been demonstrated on many sulfur compounds that this approximation is valid at least for the first few PE bands[7]. To calculate the orbital energies we have used either the Hartree Fock self consistent field (HF-SCF) method with 3-21G* basis applying the Gaussian 86 program[8] or the semiempirical MNDO procedure[9]. The geometrical parameters adopted for these calculations were the experimental ones. It should be noted that there are only minor differences between experiment and calculation.

PE Spectrum and MO Sequence of $(CH_3O)_2S$

The PE spectrum of **1** (Figure 1) shows three peaks below 14 eV. The ratio between the area below the peaks amounts to 1:2:2. This suggests that we assign one and two times two ionic states to these peaks. The recorded vertical ionization energies are given in Table 1.

To understand the MO pattern as a function of the C–O–S–O-torsional angle ϑ we have carried out HF/3-21G* calculations on **1** by changing ϑ and leaving all other parameters constant. As starting geometry the geometrical parameters obtained from the electron diffraction studies have been adopted. In Figure 2 the highest occupied MOs of **1** are shown for C_{2v} and C_2 symmetry. While the HOMO (12b, $4b_1$) is clearly separated for both conformations from the other occupied MOs, the latter form two pairs of closely situated levels only for C_2 symmetry. The PE spectrum ex-

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hibits only three peaks below 14 eV which is in agreement with calculations for C_2 symmetry. Since C_2 symmetry is found in the electron diffraction experiment we adopt this structure for our further discussion.

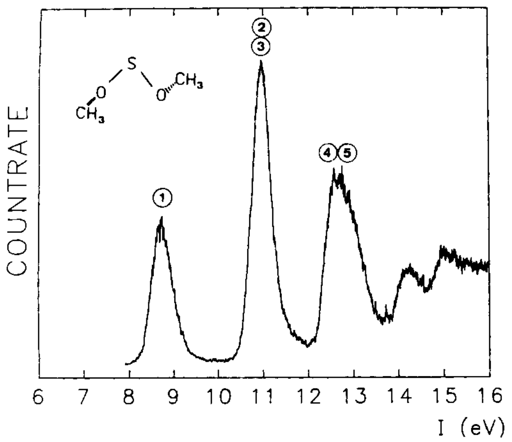

Figure 1. PE spectrum of **1**

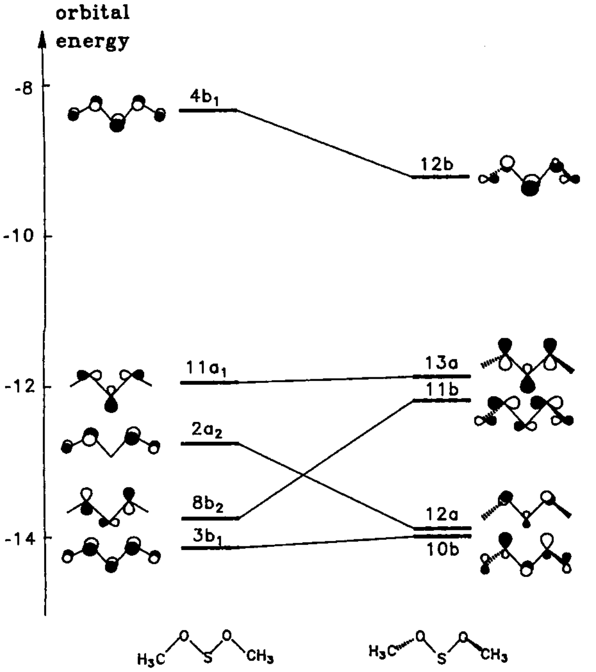

Figure 2. Correlation diagram between the highest MOs of **1** assuming C_{2v} and C_2 symmetry. The energies are based on HF/3-21G* calculations

In Table 1 the recorded ionization energies of **1** and the orbital energies calculated by using the 3-21G* basis set and the MNDO method are compared. In Figure 2 the wave functions of the first MOs for C_{2v} symmetry are shown schematically.

The highest occupied MO can be described as the 3p AO of the sulfur atom, whereas the following four MO's are linear combinations between the sulfur and oxygen lone-pairs.

Table 1. Comparison between recorded vertical ionization energies $I_{v,j}$ and calculated orbital energies, ε_j of **1** and **2**. All values in eV

Compound	Band	$I_{v,j}$	Assignment	$-\varepsilon$ (3-21G*)[a]	$-\varepsilon$ (MNDO)[a]
1	1	8.80	12b	9.20	9.80
	2	11.0	13a	11.90	11.60
	3		11b	12.20	12.00
	4	12.6	12a	13.80	13.00
	5	12.8	10b	13.80	13.20
2	1	9.5	12a″[b]	10.20	10.40
	2	9.6	13a′	10.40	10.50
	3	10.2	12a′	11.30	11.30
	4	11.3	11a″	13.00	12.50
	5	12.4	10a″	13.60	13.10
	6	12.55	11a″	13.80	13.10
	7	13.1	10a′	14.30	13.60

[a] For **1** and **2** the experimentally determined geometrical parameters were adopted. — [b] The assignment is based on C_s symmetry (see Figure 4, left side) and the numbering of orbitals applies to the hydrogen compound shown in Figure 4.

Photoelectron Spectrum and MO sequence of $(CH_3O)_2S_2$

In Figure 3 the PE spectrum of **2** is shown. It exhibits five peaks below 14 eV, the ratio of the area below the peaks amounts to 2:1:1:2:1, suggesting two ionic states each for the first and fourth peak. The recorded vertical ionization energies are listed in Table 1. Ab initio (3-21G* basis) and semiempirical (MNDO) MO calculations predict for **2** three minima (**2a**–**2c**) on the potential surface. A value of about 83–95° for the O^1–S^1–S^2–O^2 torsional angle ϑ is common to all three structures. Such values are to be expected if one recalls the torsional angles of S_2F_2 (88°)[10], S_2Cl_2 (85°)[11], and $(CH_3)_2S_2$ (85°)[12]. The main difference between the three minima is due to the orientation of the methyl groups. This can be described by the torsional angles C^1–O^1–S^1–S^2 (α) and C^2–O^2–S^2–S^1 (β).The three structures discussed above show the following values for ϑ, α and β, **2a**: 83.1°, 76.1°, 76.1°; **2b**: 83.5°, 81.3°, −75.5°; **2c**: 95.1°, −98.1, −98.1°.

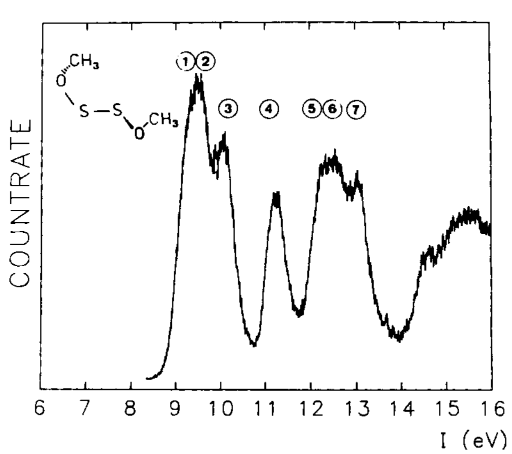

Figure 3. PE spectrum of **2**

To understand the electronic structure of **2** we have correlated in Figure 4 the highest occupied MOs of dihydroxydisulfane **3** with the experimental values of α and β of **2** and setting ϑ equal to 0°, 90° and 180°. The orbital energies have been derived from HF/3-21G* calculations on **3**[13]. By increasing ϑ from 0° to 90° the MO 12a″ (the antibonding linear combination of the 3pπ-MOs) is losing its antibonding character and is stabilized. The reverse holds for 12a′, the bonding linear combination of the 3pπ-MOs. A similar change is observed for 10a″ and 11a′. The MO sequence shown for **3b** ($\vartheta = 90°$, $\alpha = 74.1°$, $\beta = -74.1°$) is the same as that of **2b** and remains unchanged if one goes to **2a** (90°, 74.1°, 74.1°). In the case of **2c** (90°, −74.1°, −74.1°), however, the calculated MO sequence predicts, two ionic states for peak 1 and 5 in disagreement with experimental evidence. A comparison between the PE data and the results of the MO calculations shows clearly that only for **2a** and **2b** with $\vartheta = 90°$ experiment and calculations agree.

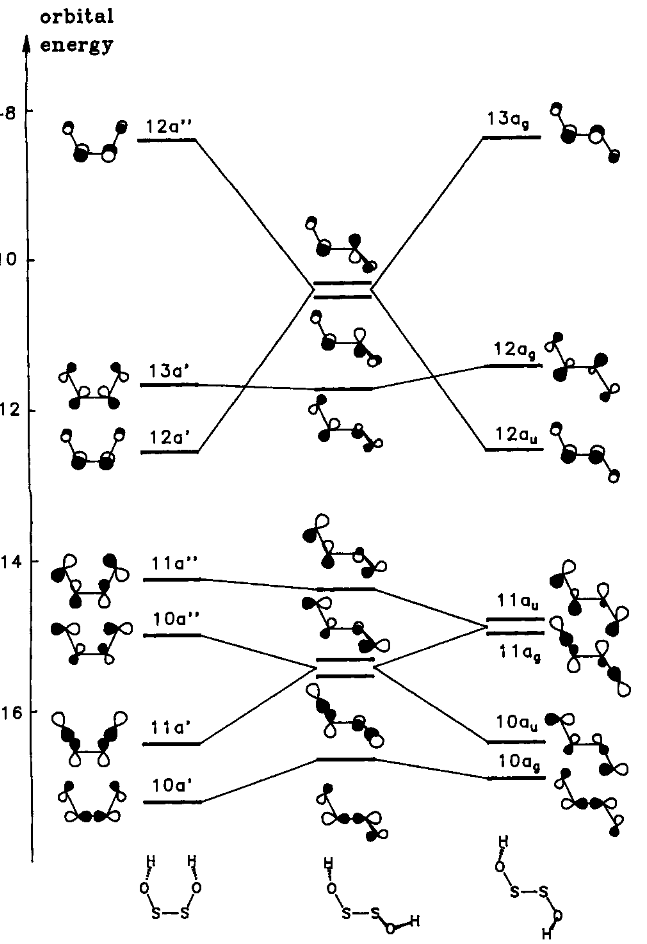

Figure 4. Correlation diagram between the highest occupied MOs of $(HO)_2S_2$ assuming OSSO torsional angles of 0° (left), 90° (center) and 180°. The energies are based on HF/3-21G* calculations

Conclusions

The PE investigation yields the sequence of the highest occupied MOs of **1** and **2**. Within the limitations of PE spectroscopy[14] it was possible to deduce C_2 symmetry for **1** and to support an OSSO torsional angle around 90° for **2a** and **2b**. Surprizingly, the ionization energy of **1** is considerably smaller than that of **2**. Therefore, **1** should be a better ligand than **2** in transition metal complexes. In fact, palladium(II) and platinum(II) complexes with diisopropoxysulfane as a ligand have been prepared[15], while complexes with dialkoxydisulfane ligands are unknown to our knowledge.

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Experimental

1 was prepared from methanol and di[imidazolyl-(1)] sulfide as described in ref.[2]. **2** was synthesized from methanol and dichlorodisulfane according to Thompson et al.[16]. The PE spectra of **1** and **2** were recorded on a PS 18 photoelectron spectrometer (Perkin-Elmer Ltd., Beaconsfield) at room temperature. The spectra were calibrated with Ar (15.76 eV, 15.94 eV) and Xe (12.13 eV, 13.44 eV). A resolution of 20 meV on the Ar line $^2p_{3/2}$ was obtained.

☆ Dedicated to Professor *Otto J. Scherer* on the occasion of his 60th birthday.

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