

# UPS Study of Spirosilane

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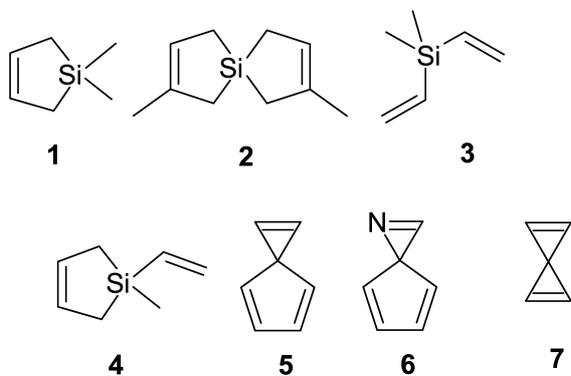
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The electronic structure of 2,7-dimethyl-5-silaspiro[4,4]nona-2,7-diene has been investigated by UV photoelectron spectroscopy (UPS). The analysis of the spectra has been performed by DFT and ROVGF calculations and comparison with the UPS spectra of related compounds. An unusual  $\pi$ -orbital degeneracy in this molecule of  $C_2$ -symmetry was observed. The spiroconjugation is quenched, and the reasons are discussed.

**Key words:** Spiroconjugation; Photoelectron Spectroscopy.

## 1. Introduction

The intramolecular interaction between nonconjugated  $\pi$  orbitals is of considerable interest and was studied by UV photoelectron spectroscopy (UPS) in many molecules [1]. The presence of interaction is indicated by the splitting of  $\pi$  bands when compared with  $\pi$  ionizations in the fragment molecules. One special case of such non-conjugated  $\pi$  interactions is "spiroconjugation". The work related to molecules which may exhibit spiroconjugation has been reviewed in [2] and the research concerning spiroconjugation has recently been extended to aza compounds [3]. The molecules **1–7** are of special interest in this respect.



One of the conclusions regarding spiroconjugation was that it is negligible in molecules like **5** which have lower than  $D_{2d}$  symmetry [2]. The exception occurs when  $\pi$  orbitals can interact with non- $\pi$  orbitals, e. g. a nitrogen lone pair [3] as shown in **6**. However, even in

the molecule dimethyldivinylsilane, which has low  $C_{2v}$  symmetry,  $\pi$  band splitting of 0.2 eV was observed and attributed to spiroconjugation [4]. It was further commented that a saturated silicon atom between two  $\pi$  systems can not perform an isolating function [4].

In this work we report the UPS of the low symmetry molecule **2** ( $C_2$  point group) and compare the role of spiroconjugation in several related organosilicon compounds.

## 2. Experimental

The HeI spectrum of **2** was recorded on the Vacuum Generators UV-G3 photoelectron spectrometer with a spectral resolution of 25 meV when measured as the full width at half maximum (FWHM) of the  $Ar^{+} 2P_{3/2}$  calibration line. The sample inlet temperatures required to generate sufficient sample vapour pressures were 25–30 °C.

The electronic structure calculation was performed with the Gaussian 98 program package [5]. The calculation included full geometry optimization using the density functional method (DFT) with B3PW91 functional and TZ2P basis set. In order to improve the agreement with the measured ionization energies, a single point calculation at B3PW91 optimized geometry was performed by the ROVGF method, which uses many-body perturbation theory and was used previously for the quantitative assignment of photoelectron spectra of such molecules [6].

The sample was purchased from Aldrich, and its identity / purity was checked by melting point determination and mass spectrometry.

Table 1. Vertical ionization energies ( $E_i$ /eV), orbital energies obtained from ROVGF calculations ( $\epsilon_i$ /eV) and UPS assignments for **2**<sup>a</sup>

$E_i$	$\epsilon_i^a$	Assignment (Symmetry)
8.53	8.51, 8.51	$\pi(a)$ , $\pi(b)$
9.95	9.81, 9.81, 9.90	$\sigma(b)$ , $\sigma(a)$ , $\sigma(b)$
11.8	11.81, 11.82	$\sigma(b)$ , $\sigma(b)$

<sup>a</sup> the values were obtained from non-Koopmans ROVGF calculations using DFT optimized geometry

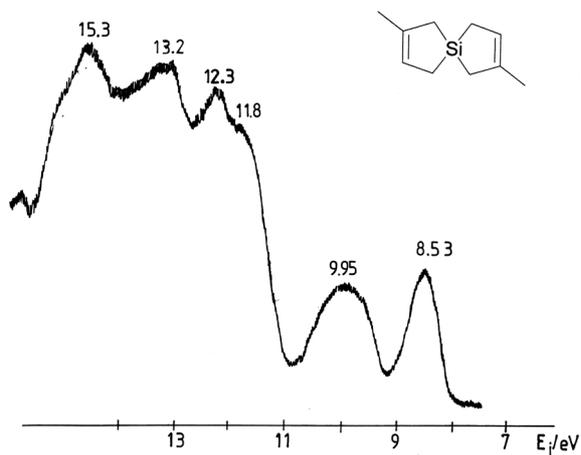


Fig. 1. HeI spectrum of **2**.

### 3. Results and Discussion

The results are summarized in Table 1 and Figures 1–2. The spectrum of **2** shows two broad bands at 8.53 and 9.95 eV whose intensity ratio is 2 : 3 (Fig. 1). These bands can be assigned to ionizations from two ring  $\pi$ -orbitals and three  $\sigma$  orbitals, respectively. The  $\sigma$ -orbitals are strongly delocalized over the central silicon atom. This assignment was based on ROVGF calculation, measured band intensities and comparison with the spectra [7] of the related compounds **1** and **3** (Fig. 2).

The first important conclusion is that the ring  $\pi$  orbitals are accidentally degenerate. This is unusual for a molecule of low  $C_2$  symmetry but agrees with the predictions mentioned earlier [2,3]. The  $\pi$ -orbital degeneracy in **7** can be expected on the basis of the molecule's  $D_{2d}$  symmetry; therefore the  $\pi$ -orbitals belong to e representation. However, such a symmetry related degeneracy is not possible in **2**, which has much lower  $C_2$  symmetry. It must also be borne in mind that

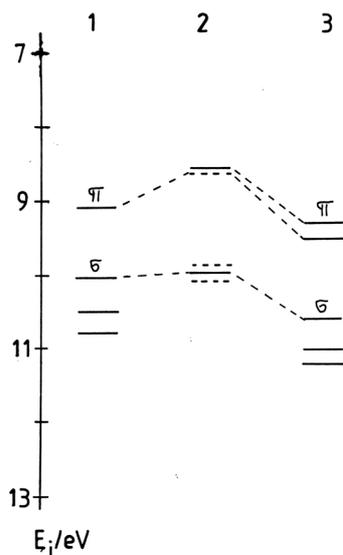
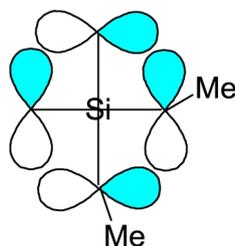


Fig. 2. Energy level diagram of **1**–**3**.



Scheme.

the interaction between two occupied bonding orbitals is always repulsive, destabilizing.

The Newman projection diagram depicting the two bonding, occupied  $\pi$ -orbitals in **2** shows that the degeneracy occurs and hence spiroconjugation is not detected, because of the same amounts of positive and negative  $\pi$ -orbital overlaps / interactions between them. Furthermore, our result suggests that a saturated silicon atom can act isolating between two  $\pi$ -systems.

Another interesting observation comes from the inspection of Figure 2. Comparison of the  $\pi$ -levels in **1** and **2** shows that methyl groups destabilize  $\pi$ -orbitals, leaving  $\sigma$ -orbitals mostly unaffected.

There is a need for further UPS studies of molecules which may exhibit spiroconjugation, especially those containing only a single  $\pi$ -bond per ring. To date only theoretical calculations for such molecules have been reported [6].

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