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STUDY OF d_π—p_π INTERACTION IN VINYL- AND ALKYLSILICON-CONTAINING COMPOUNDS BY PHOTOELECTRON SPECTROSCOPY

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Summary

Based on photoelectron spectra of a series of vinyl compounds of silicon, it is shown that d_π—p_π interaction increases by the small value of ~0.1 eV as one goes from monosilanes to disilanes; σ—π conjugation is practically absent. Interaction between π-electrons of the double bond in divinyldichlorosilane, corresponding to 0.2 eV, has been established. In a series of 1,1-disubstituted derivatives of silacyclopentene a relationship has been found between the electron-donating and -accepting properties of the substituent and the ionization potentials: the ionization potential increases with an increase of the electron-accepting tendency of the substituent.

Introduction

The problem of the participation of vacant atomic *d* orbitals in molecular bonds is still controversial. In particular, the extent of d_π—p_π conjugation in various organosilicon compounds has not been determined. Further research in this direction has been undertaken by us.

In the present work an attempt has been made, with the aid of photoelectron spectroscopy, to establish the presence of d_π—p_π conjugation in vinyl compounds of silicon containing a silicon—silicon bond, and also in the series of 1,1-silacyclopentenes with electron-donor and -acceptor substituents. The presence of such interaction was established in previous works on the photoelectron spectra of a series of vinylsilanes [1,2]. Photoelectron spectra of disilanes are investigated for the first time. In the UV spectra of vinyldisilanes a strong bathochromic shift in the order of 40 nm, as compared with vinylsilanes, was noted [3]. The authors explained such a shift by the interaction of the π-electrons of the double bond with the σ-electrons of the Si—Si bond. Interaction of such a kind should also be seen in the photoelectron spectra of these compounds. In ref. 4 it was shown

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that in 1,1-dimethylsilacyclopentene d_π—p_π interaction through the ring is absent, but that σ—π conjugation takes place (interaction of the orbitals of Si—R bonds, where R is a substituent at the silicon, with p-orbitals of the double bond), which leads to destabilization of the upper occupied molecular orbital (UOMO). In the present work photoelectron spectra of 1,1-silacyclopentene derivatives with electron-donor and -acceptor substituents have been obtained with a view to investigating the influence of the substituents on the effectiveness of the σ—π interaction.

Results and discussion

In Fig. 1 are shown the vertical ionization potentials (IP) of vinyltrimethylsilane (I), vinylpentamethyl- (II) and divinyltetramethyldisilanes (III), hexamethyldisilane (IV), tetramethylsilane (V) and hexachlorodisilane (VI). The data for compounds IV and V were obtained from the literature [5,6]. For compounds II and III the ionization potentials were calculated by the CNDO/2 method.

The first IP of compounds II, III and IV is assigned to the ionization of the σ-electrons of the Si—Si bond. The constant value of the first IP in the series II—IV indicates the absence of an interaction of the π-MO orbitals of the double bond with the orbital localized mainly on the Si—Si bond. The second and third bands of the spectrum in II and III are poorly resolved, but, by comparison with

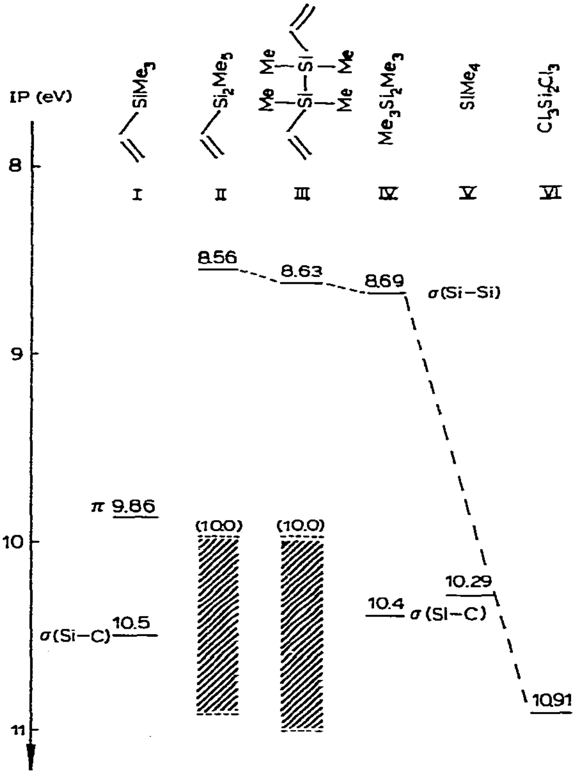


Fig. 1. Vertical IP's of compounds I—VI.

the spectrum of vinyltrimethylsilane (I), the IP in the region of 10 eV for II and III may be assigned to the ionization of the π-MO of the double bond. (Calculation by CNDO/2 gives a large contribution from the Si—C σ-bonds to this band) The 0.1 eV increase of the IP of the π-MO in II and III as compared to compound I may be explained by an increase of the d_π—p_π interaction in vinyldisilanes as compared to vinylmonosilanes. This is also indicated by stabilization of the orbitals of the Si—C bond in compound IV as compared with compound V.

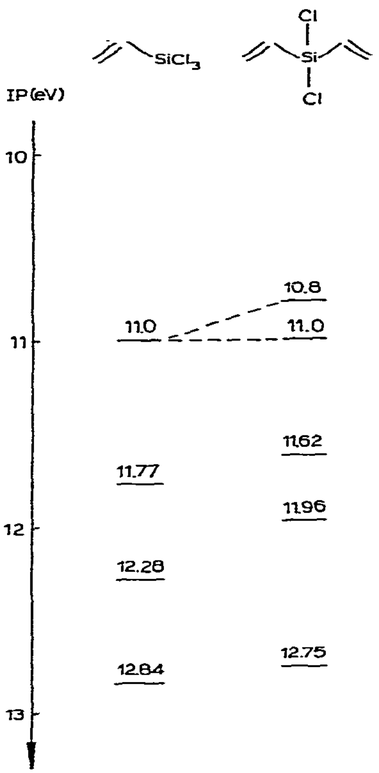
In the UV spectra a strong bathochromic shift is noted as one goes from monosilanes to disilanes, which may be explained by strong interaction of the σ^*-MO of the Si—Si bond with the π^*-MO of the double bond, possibly with a change of geometry of the disilanes in the excited state. Naturally, in this case there will be no significant shift of the level of the occupied MO.

Two alternative explanations are given in the literature for the observed bathochromic shifts. Sakurai [7] and Gilman [8] explain this phenomenon by d_π—p_π conjugation with the d-orbitals of the second silicon atom, by so-called "conducting" p_π—d_π—d_π—p_π conjugation. Mironov [3] explains it by conjugation of the Si—Si bond with the π-MO of the double bond, i.e. by σ—π conjugation, implying conjugation of occupied MO. However, consideration of the electron spectroscopy data in combination with the photoelectron spectroscopy data shows that there is no conducting conjugation and there is no strong interaction of the π-MO of the double bond with the σ-MO of the Si—Si bond either, since the energy level of the σ-MO of the Si—Si bond practically does not change upon introduction of vinyl groups into the disilane molecule.

The presence of two vinyl groups at the silicon atom raises the possibility of conjugation between the double bonds through the silicon atom. The possibility of such a conjugation was mentioned in ref. 9. Splitting of the first band in the spectrum of divinyldimethylsilane, caused by this interaction, was 0.2 eV. From the spectrum we obtained of divinyldichlorosilane the interaction of the π-MO of the double bonds was found to be 0.2 eV. For comparison a refined spectrum of vinyltrichlorosilane [2] is presented in Fig. 2.

Structural features of the silacyclopentene ring might, with certain substituents at the silicon atom, contribute to the d_π—p_π interaction in these systems, although in 1,1-dimethylsilacyclopentene there is no contribution [4]. We have obtained photoelectron spectra of 1,1-silacyclopentene derivatives with electron-donor and -acceptor substituents at the silicon atom in order to investigate such influence. Since the presence of an interaction of the C—Si σ-bonds with the π-system had been established, it was of interest to investigate the influence of the substituents at the silicon atom on this interaction. The first IP's of 1,1-silacyclopentene derivatives are presented in Fig. 3 as a diagram of levels.

As is known, the possibility and the value of the interaction of the orbitals requires the presence of at least two factors: the necessary symmetry for such interaction and close energies of the interacting orbitals. Analysis of the data presented in Fig. 3 shows that the first condition for the interaction of the substituent at the Si—R σ-bond and of the p_π double bond is fulfilled for all substituents. The energy of the Si—R molecular orbital is mainly conditioned by the inductive influence of the substituent, i.e. by its accepting or donating properties. Comparison of tne first IP's of 1,1-substituted silacyclopentenes (R = CH_3; C_2H_5; $OSi(CH_3)_3$; OC_2H_5; OCH_3 and Cl) with the first IP of *cis*-butene (9.33 eV),



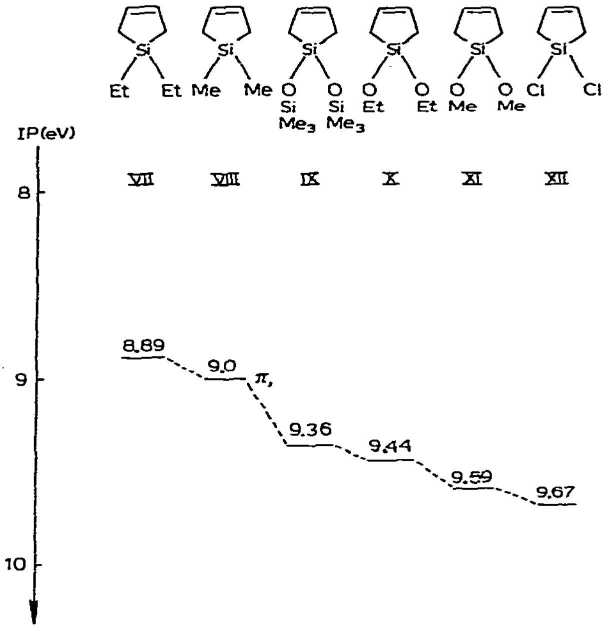


Fig. 2. Observed IP's of vinyltrichlorosilane and divinyldichlorosilane.

Fig. 3. IP's of the upper occupied MO of 1,1-silacyclopentene derivatives.

carried out in the same manner as for 1,1-dimethylsilacyclopentene [4], shows that in diethylsilacyclopentene (VII) the first ionization potential is 8.89 eV, whereas for the dimethyl derivative VIII it increases by 0.11 eV to 9.0 eV. Substitution of the electron-donor substituents by the electron-acceptor ones (compounds IX—XII) leads to further increase of the IP. Such a change in IP is indicative of weakening of the σ—π conjugation and excludes interaction of the π-electrons with the electrons of the unshared pair of the substituent. However d_π—p_π conjugation is not excluded for 1,1-dimethoxy- (XI) and 1,1-dichlorosilacyclopentenes (XII). The data obtained make it clear that the reactivity of the double bond depends on the type of substituent at the silicon.

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