σ–π Interaction in some σ-bonded allyl compounds. A MNDO study

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Abstract

The MNDO calculation results for the following allyl compounds $AllXH_n$, $XH_n = CH_3$, SiH_3, GeH_3, SnH_3, PbH_3, HgH and Li are discussed. It is shown that the experimental evidence for the σ,π-conjugation obtained from UV photoelectron and absorbtion spectra arises from the interaction between the two highest occupied $\pi(C=C)$ and $\sigma(X-C, X-H)$ orbitals. It is found that $\sigma-\pi$ interaction energy (ca. 1.1 eV) does not depend on X (X = Si, Ge, Sn, Pb, Hg) and is similar to the $\pi-\pi$ interaction energy between occupied π orbitals of butadiene (ca. 1.2 eV). The stability of the π-complex is also estimated. A decrease in the Slater exponential value of the metal shell orbitals stabilizes the π-complex.

Introduction

The σ,π-conjugation problem in allyl compounds is well known. There is much experimental evidence for this hypothesis. Mostly, it is based on data obtained from UV absorbtion, IR and Raman spectra, but it is not adequate. Application of photoelectron spectroscopy made it possible to obtain information on the energies of occupied MO and gave quantitative information on some aspects of the σ,π-conjugation problem in allyl compounds [1–3]. The shifts in ionization potentials (ca. 1 eV) due to σ,π-conjugation were found. Earlier, qualitative experimental evidence of this effect (the bathochromic shifts of longwave absorbtion bands) was obtained from UV absorbtion spectra [4–6]. However, the analysis and assignment of UV photoelectron and absorbtion spectra and the study of the $\sigma-\pi$ interaction were based on the intuition of the authors, supported by fragment analysis. In the present paper, the MNDO calculation results are used to analyse the experimental data.

Method

The MNDO procedure, developed by Dewar and his collaborators [7], is used in the present paper, as it is known to be effective in predicting the orbital sequence in

large molecules and may be used to study systems containing heavy atoms. The calculation results of the MNDO study on the following compounds are discussed

$$C_\gamma H_2 = C_\beta H \underset{\theta}{\dots} C_\alpha H_2 - XH_n$$
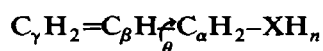
$(XH_n = CH_3, SiH_3, GeH_3, SnH_3, PbH_3, HgH$ and Li)$

Rotation about the C_α–C_β bond is considered. The bond lengths and valence angles were optimized. θ is defined as the dihedral angle, such that $0\,^\circ$ corresponds to a planar *s-cis* structure and $180\,^\circ$ to *s-trans*. The energies and oscillator strengths of electronic transitions were calculated by the CI method, taking into account 16 monoexcited configurations.

Results and discussion

Conformation and atomic charges
(1) Non-planar *gauche* conformation ($\theta = 90$–$100\,^\circ$) corresponds to the lowest energy structure (Fig. 1). It seems to be mainly the result of steric hindrance. The contribution of σ,π-conjugation to *gauche* conformer stabilization seems to be small, as the rotation barrier does not seem to depend on the nature of atom X.
(2) Atomic charges calculated for different conformations are listed in Table 1. It shows that the distribution of electronic density does not seem to depend on θ.

On the basis of both results (1) and (2), we may conclude that the interaction between occupied and unoccupied fragment orbitals is weak, as only this interaction may change the potential energy profiles (Fig. 1) and atomic charges (Table 1).

Ionization potentials and absorbtion spectra
The calculated energies of the two highest occupied and the two lowest unoccupied MO for *trans* and *gauche* conformers (XH_n = HgH, PbH$_3$ and SnH$_3$) are
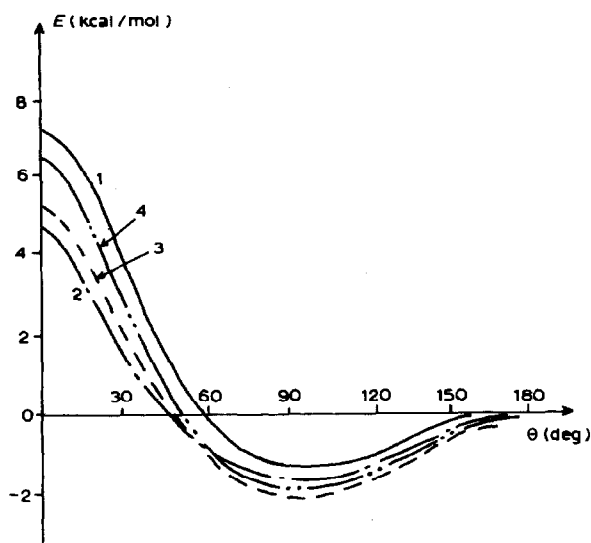

Fig. 1. Potential energy profile for the rotation about the C_α–C_β bond: 1, X = C; 2, X = Si and Ge; 3, X = Sn; 4, X = Pb. The energy of the *trans* conformer is supposed to be equal to zero.
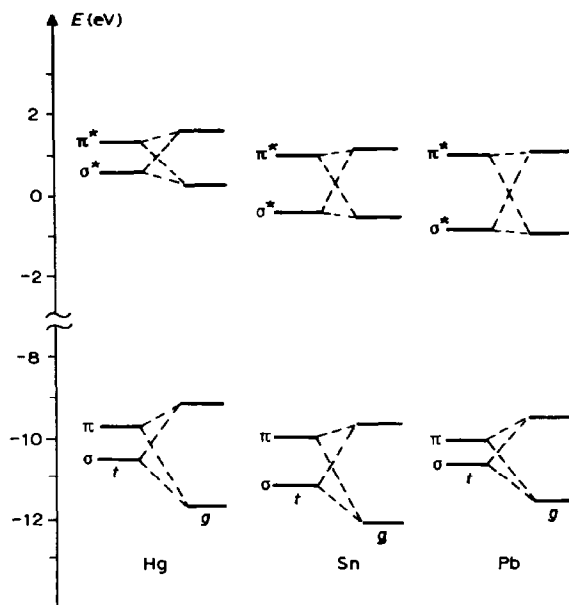
Fig. 2. Correlation diagram for allyl compounds: t = *trans* conformer, g = *gauche* conformer, X = Hg, Sn and Pb.

Table 1

Charges on atoms and groups of allylmercury

Conformation	Hg	HgH	C_α	C_β	C_γ	Allylic fragment	
						π-bond	σ-bonds
cis	0.39	0.18	-0.14	-0.08	-0.07	0.011	0.16
trans	0.39	0.18	-0.14	-0.09	-0.07	0.007	0.17
gauche	0.39	0.18	-0.13	-0.08	-0.08	0.021	0.16

shown in Fig. 2. If the allyl compound has a planar structure, then the π(C=C) and σ(X–C, X–H) orbitals do not interact because of different symmetries. Interaction between these orbitals in non-planar conformations results in an increase in the π–σ separation energy. A similar result was obtained for the σ^*(X–C, X–H) and π^*(C=C) orbitals. Interaction between the σ and π orbitals increases the HOMO energy and results in a decrease in the first ionization potential. Interaction between both pairs of orbitals π–σ and σ^*–π^* decreases the energy separation between HOMO and LUMO * and results in a decrease in the longwave electronic transition energy (Table 2).

σ–π-interaction energy

The most interesting question of the σ,π-conjugation problem is the estimation of the interaction energy between the π(C=C) and σ(X–C, X–H) orbitals. The energy

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* π – σ interaction gives the main contribution.

Table 2

Longwave electronic transitions in allyltin

θ (deg)	Energy (eV) (oscillator strengths)	
	First electronic band	Second electronic band [a]
0	5.1 (0)	5.7–5.9 (0.71)
30	4.5 (0.08)	5.8–5.9 (0.70)
60	4.3 (0.18)	5.7–5.8 (0.57)
90	4.2 (0.30)	5.7–5.8 (0.58)
120	4.4 (0.40)	5.7–5.8 (0.57)
150	4.9 (0.35)	5.7–5.8 (0.53)
180	5.2 (0.03)	5.6–5.8 (0.61)

[a] Consists of two electronic transitions.

separation within the two-level model (ΔE) may be calculated as:

$$\Delta E = \left((\Delta E_0)^2 + 4\beta^2 \right)^{1/2}$$

where ΔE_0 is the energy separation of the non-interacting levels, and β is the interaction energy between π and σ orbitals. It follows that:

$$\beta(\sigma - \pi) = \left[\left((\Delta E)^2 - (\Delta E_0)^2 \right)/4 \right]^{1/2}$$

We used ΔE and ΔE_0 values obtained from the MNDO calculations: ΔE was assumed to be equal to the energy separation between the $\pi(C=C)$ and $\sigma(X-C, X-H)$ orbitals for the *gauche* conformer, and ΔE_0 the energy separation for the *trans* conformer. β was also calculated using the data of photoelectron spectroscopy [1–3]. ΔE was assumed to be equal to the energy separation of the first and the second ionization bands of the allyl compound, and ΔE_0 the difference in the first ionization potentials of the molecules, which may be considered as the fragments of the allyl compound. The results are listed in Table 3. They show that the interaction energy between the $\pi(C=C)$ and $\sigma(X-C, X-H)$ orbitals is ca. 1.1 eV and does not depend on the nature of heavy atom X. This result shows that the differences in the properties of the allyl compounds, which are attributed to σ,π-conjugation, arises from the differences in ΔE_0.
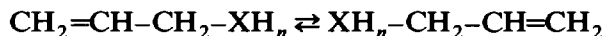
Table 3

Interaction energy ($\beta(\sigma-\pi)$) between highest occupied π and σ MO in allyl compounds $CH_2=CH-CH_2-XH_n$

Calculation		Experiment	
XH_n	β	XH_n	β
CH_3	$\ll 1$	–	–
SiH_3	1.04	SiH_3, $SiMe_3$	1.15 ± 0.07
GeH_3	1.09	$GeMe_3$	1.15 ± 0.07
SnH_3	0.99	$SnMe_3$	1.15 ± 0.07
			1.08
PbH_3	0.88	–	–
HgH	1.18	HgCl	1.13
HgI	1.14	HgBr	1.11

We also estimated the interaction energy between the two occupied π orbitals of butadiene (IP 9.08 and 11.47 eV [8]) and found that it is ca. 1.2 eV. Thus, we see that the interaction energies between the $\pi(C=C)$ and $\sigma(X-C, X-H)$ orbitals of allyl compounds and between the $\pi(C=C)$ orbitals of butadiene have the same value.

π-complex stability

In the present paper, the properties of the σ-bonded allyl compounds are considered. For such molecules, the π-complex may be considered as the transition state for the following reaction (1,3-shift of the XH_n group):

$$CH_2=CH-CH_2-XH_n \rightleftarrows XH_n-CH_2-CH=CH_2$$

Furthermore, for many allyl compounds the π-complex is the most stable structure. Therefore, it is interesting to consider the influence of the different parameters of atom X on π-complex stability. The calculations were performed for allyllithium. The π-complex is the most stable structure for this compound. We varied the Li atomic parameters widely and found that π-complex stability depends on the Slater exponential value ξ for the $2s$ and $2p$ orbitals of Li. If $\xi = 0.702$ a.u., then the π-complex is the most stable structure. If $\xi = 1.0$ a.u., then the σ-bonded structure is the most stable. This result shows that π-complex stability depends on the properties of the metal valance shell orbitals. The π-complex will be the most stable structure if the mentioned orbitals are diffuse functions and overlap with all three $2p_z$ orbitals of the carbon atoms, which form the π-orbitals of the allyl fragment.

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