Valence state of a heteroatom and the conjugation problem

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Calculations of the electronic structure and geometry of *s-cis-*, *s-trans-* and *gauche*-conformers of $AllPH_4$ (**1**) molecule ($All = CH_2CHCH_2$) were carried out by the quantum chemical *ab initio* SCF MO LCAO method with the 3-21G* basis. The results obtained were compared to those found earlier for $AllPH_2$ (**2**) and $AllPF_4$ (**3**). The increase in stability of the *gauche*-conformer relative to the *trans*-conformer on going from **2** to **1** is due to the significant contribution of vacant d-orbitals of the P atom in the LUMO, to the increase in interactions of frontier MOs through space, and (to a lesser degree) through bond interaction with the CH_2 bridging group, as well as to transfer of electron density from an allyl fragment. The conjugation in allylphosphines is determined by localization of the HOMO, which correlates with the lone electron pair of the P atom in **2** and with σ-MO in **1**; it should be enhanced in allylphosphines containing the axial P—C bond.

Key words: RHF/3-21G* *ab initio* method; conjugation in allylphosphines; effects of ligand and heteroatom valence state.

Conjugation in compounds of group V elements has been studied both experimentally and theoretically. However, the data available concern mainly compounds of these elements in the trivalent state. According to photoelectron spectroscopy data, in the simplest compounds, hydrides XH_3, the HOMO (corresponding to its lone pair) brings in a small contribution to the X—H bonding, while the contribution of the lone pair orbital to the bonding σ-MO increases in the $SbH_3 \rightarrow AsH_3 \rightarrow PH_3 \rightarrow NH_3$ series. Interpretation of the photoelectron spectra (PES) and UV-absorption spectra of vinyl and phenyl compounds of trivalent N, P, As and Sb is possible only with account for n,π-conjugation,[1] whose contribution decreases significantly on going to heavier heteroatoms. In allyl, benzyl, and similar molecules with trivalent heteroatom, the effects of conjugation (σ,π-conjugation) should increase in the N, P, As, Sb, Bi series (see the MO scheme in Ref. 2).

According to the PES of vinyl-, allyl-, phenyl- and benzylphosphines,[3] the shifts of ionization potentials observed in these molecules, compared to the values for their fragments, are attributed to mixing π-MO and σ-MO of the P—C and C—H bonds [in $VinPBu_2$ and $AllPBu_2$ the π-MO and σ-MO of the P—C bond (vinyl, allyl) correspond to the almost degenerated levels]; however, from these data the mixing of the π-MO with the n- and d-AO of the trivalent phosphorus atom is small. The case is somewhat different in pentavalent phosphorus compounds. In this case it is necessary to include the d-AO into the quantum-chemical calculations to reproduce correctly ionization potentials, dipole moments, and heats of formation.[4]

Previously, the influence of the valence state of the heteroatom on the MO systems and on the properties of some known allyl compounds (AC) of bivalent and hexavalent sulfur (S^{II} and S^{VI}), and trivalent and pentavalent phosphorus (P^{III} and P^{V}) has been investigated by quantum-chemical methods.[5] The geometry and electronic structure of AC conformers has been calculated, including those of P^{V} AC with the equatorial and axial P—C bond, and the role of the d-AO of P^{V} and S^{VI} in conjugation effects has been revealed. It is known that S and P atoms in their highest valence states behave as strong electron donors, easily forming fairly polar bonds with atoms of electronegative elements, such as halogens and oxygen. At the same time, a transfer of electron density to the d-AO of P^{V} and S^{VI} atoms results in the stabilization of the HOMO.

Mixing of the n-orbital of the heteroatom with the π-orbital of the C=C bond in the AC of elements of groups V—VII (S^{II}, P^{V}, N^{V}, O^{II}) is small; however, in the case of heavy elements there is some evidence for σ,π-conjugation. The spectral characteristics of conjugation in the AC of hypervalent element ($X = P^{V}$, S^{VI}) are determined by the closeness of the HOMO energies in comparison with the HOMO energies of P^{III} and S^{II} AC, which in a nonplanar conformer is accompanied by their significant mixing*, and also by a decrease in the first ionization potential and the bathochromic shift of the long-wave band in the electronic absorption spectra.

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* "Mixing" orbitals display a rather simple way of description and comparison of modified electronic structures of molecules (within the framework of the MO LCAO method).

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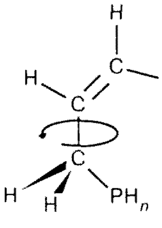
Calculations show the prevailing interactions of the active centers, the XH_n group, and the double bond, through intermediate bonds in the AC of S^{II} and P^{III}, and through space in the AC of S^{VI} and P^{V}. The relative stability of nonplanar and planar conformers is determined by the possibility of overlapping of the fragment orbitals (C=C and heteroatom group) in the AC molecule and the steric repulsion of bulky terminal groups. The increase in relative stability of *gauche*-conformers of the AC with the hypervalent heteroatom compared to the P^{III} AC has been explained[5] by the interaction through space of the C=C bond π-orbital with the vacant d-AO of S^{VI} and P^{V} atoms. The mixing of the π-MO of the C=C bond with vacant d-orbitals of the heteroatom results in transfer of ~0.1 of the electron charge to the heteroatom with the increase of conjugation energy (estimated as the difference between total energies of *trans*- and *gauche*-conformers).

A comparison[5] of the AC of S^{II} and S^{VI}, P^{III} and P^{V} with different ligands (H, F, O, OH) at the heteroatom (S or P) is not worthwhile, because the question of the role of ligands is left open. To what extent do conclusions based on the role of the heteroatom vacant d-AO in conjugation effects depend on the surroundings of S or P atoms? To clarify this problem it is desirable to carry out calculations of the AC with the heteroatom in various valence states, but with the same ligands. We performed such calculations for a model molecule $AllPH_4$ (**1**) and compared the data obtained with those found earlier for the $AllPH_2$ analogue (**2**).



n = 2 (**2**), 4 (**1**)

The results of *ab initio* calculations using the GAUSSIAN-80 program with the 3-21G* basis on the geometry and electronic structure of *trans*- and *gauche*-conformers are presented in Table. 1. As expected, the P atom in molecule **1** has a positive effective charge (as in hydrides PH_5 and AsH_5). The electronic density is transferred from the P atom to adjacent H and C(3) atoms; the negative charge on atom C(3) is 0.2 au higher than that in structure **2**. Unlike the PF_4 substituent in the compound $AllPF_4$ (**3**), which can be considered as a π-acceptor, the PH_4 group in the *gauche*-conformer of **1** behaves as a σ-acceptor. The positive charges on the P atom and on all PH_4 groups decrease at the conformational *trans* → *gauche* transition at the expense of electron density from the allyl fragment, but in this case the effect is weaker than in the $AllPF_4$ molecule. It is noteworthy that the *ab initio* calculations apparently strongly overestimate the polarity of the P—C(3) bond. More realistic effective charges on C(3) atom in molecules **1** and **2**, equal to −0.3 and −0.2, are given by the semiempirical AM1 method.

Let us compare the frontier MO of molecules **1**—**3**. The MO analysis in terms of basis AO allows one to point out the MO localized mainly on the fragment bonds of CH_2=CH— and CH_2—Y (where Y is the group with the heteroatom). The assignment of fragment orbitals (FMO) based on their localization is shown in Fig. 1. The orbital of the P atom lone pair n(P) in structure **2** is higher in energy than the C=C bond π-orbital (see Fig. 1). The orbitals of the P^{III} atom lone pair are modified in P^{V} compounds and participate in the formation of valence bonds. However, the σ-MO localized on the P—F bonds in the compound $AllPF_4$ (**3**) is lower on the energy scale than the π-MO and σ-MO of the P—C bond. Thus the energies of the frontier MO can be described by the series σ(P—F) < σ(P—C) < π(C=C) < σ^*(P—C) < π^*(C=C). In molecule **1** the σ-MO localizes on P—H bonds; on the contrary, its energy is substantially higher than the π-MO and σ-MO of P—C: σ(P—C) < π(C=C) < σ(P—H) < σ^*(P—H) < π^*(C=C); the electron affinity of the PH_4 group is significantly less than that of the PF_4 substituent. As a result, violation of the skeleton planarity and mixing of σ- and π-MO leads to less transfer of the electron density to vacant d-AO of P atom of the PH_4 group.

The relative stability of *trans*- and *gauche*-conformers correlates with the amount of charge transferred at the conformational transition between fragments in structures **1** and **3**. At the *trans* → *gauche* transition in **3** and **1** the portion of electron transferred is 0.11 and 0.07 respectively; thus the total energy of molecule **3** de-

Table 1. Geometry and electronic structure of $AllPH_4$ (**1**) and $AllPH_2$ (**2**) molecule conformers according to the *ab initio* SCF MO LCAO calculations with the 3-21G* basis

Conformer	Bond lengths/Å			Valence angle/deg		Effective charge (au)				
	C(1)—C(2)	C(2)—C(3)	P—C(3)	C—C—C	P—C—C	C(1)	C(2)	C(3)	P	$PH_4(PH_2)$
trans-**1**, $(P—C)_{ax}$	1.32	1.51	1.99	125	115	−0.49	−0.13	−0.87	0.65	0.43
gauche-**1**, $(P—C)_{ax}$	1.32	1.49	2.01	126	110	−0.47	−0.18	−0.86	0.61	0.36
trans-**1**, $(P—C)_{eq}$	1.32	1.51	1.91	124	115	−0.48	−0.14	−0.82	0.66	0.23
gauche-**1**, $(P—C)_{eq}$	1.32	1.51	1.91	125	109	−0.45	−0.19	−0.80	0.63	0.17
trans-**2**	1.33	1.50	1.92	123	118	−0.35	−0.19	−0.64	−0.11	0.05
gauche-**2**	1.33	1.50	1.93	124	116	−0.33	−0.19	−0.64	−0.12	0.03

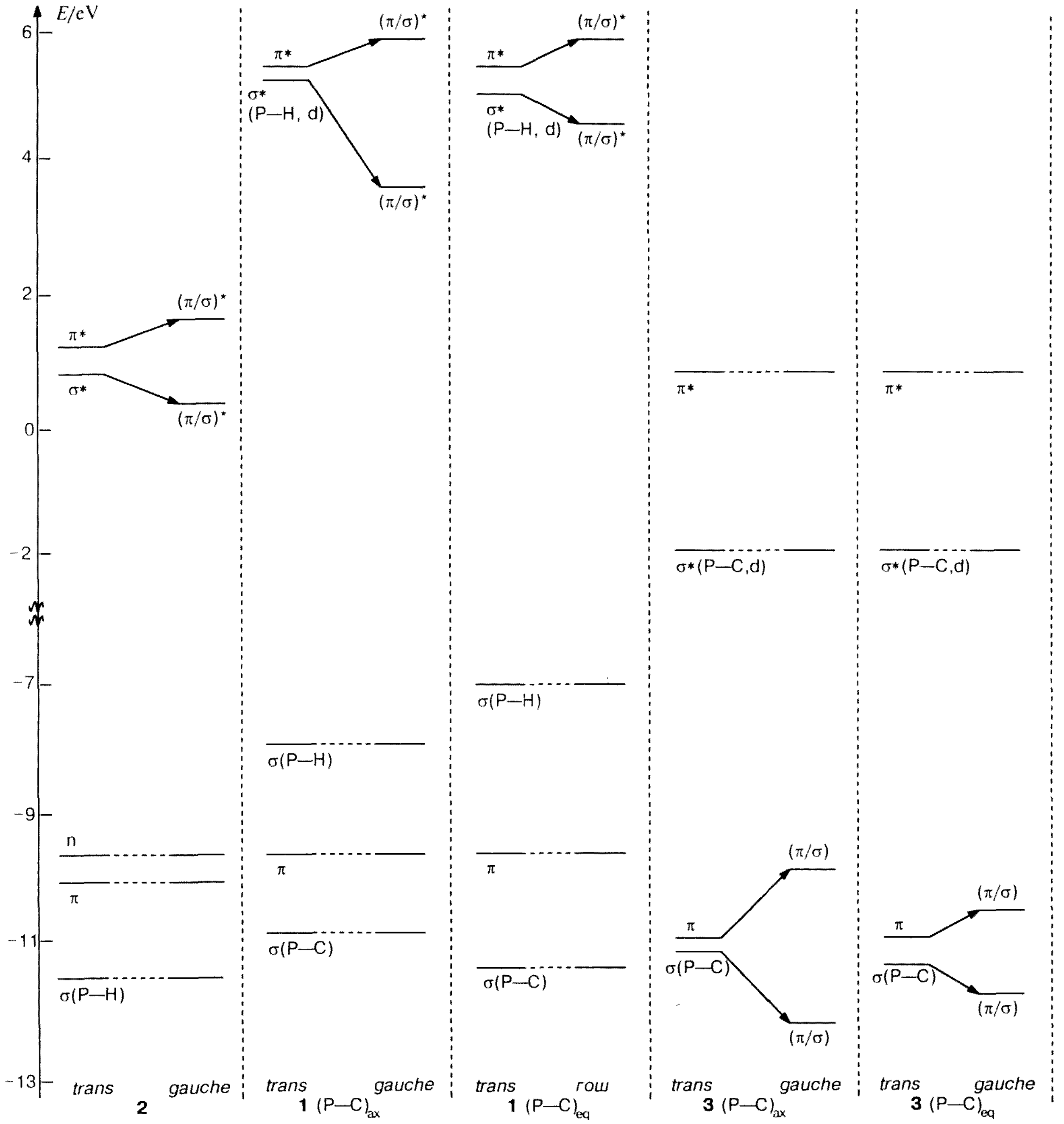


Fig. 1. Influence of the valence state of the P atom and the nature of the ligands on the FMO system in allylphosphines. The MO are assigned according to the contributions from basis AO.

creases by 7.5 kcal mol^{-1}, whereas in analog **1** it decreases by 4.5 kcal mol^{-1}.

Thus, ligands at the P atom can appreciably affect the energy of σ,π-conjugation; their influence on spectra is even more pronounced. However, the transition from flat to nonplanar structure of the C=C—C—P chain in compounds **1** and **2** does not change noticeable the HOMO energies. In molecule **2** the lone pair at the HOMO does not interact significantly with the π-orbital of the C=C bond; in molecule **1** mixing of the highest occupied σ(P—H) and π(C=C) MO is also very weak, because the MO have very different energies. Nevertheless, the bathochromic shift of the long-wave absorption band at the conformational transition in both cases should be rather significant due to a decrease in the LUMO energy as the result of mixing the π*- and σ*-orbitals.

The bathochromic shift in the electronic spectrum of the *gauche*-conformer **3** has another origin. In this case the proximity of energies of the highest occupied MO of

CH_2=CH and CH_2—PF_4 fragments favors their mixing, increases the HOMO energy, and decreases the first ionization potential; however the LUMO energy does not change at conformational transition, because the energy gap between the π*(C=C) and σ*(P—C) MOs is too large (see Fig. 1).

The conjugation energy and relative stability of the conformers are determined by the interaction through space of occupied and vacant FMO. According to the calculations, an increase in the valence of the heteroatom results in an increase in the contribution of its vacant AO in the mixing MOs, with strengthening of their interaction through space and evidence of the conjugation. However, the latter depends mainly on the energy of the frontier MO, which is determined by both the nature of the ligand and the valence of the heteroatom.

A comparison of the P^V AC with axial and equatorial P—C bonds is of special interest (see Fig. 1). According to the calculations, the longer axial bond in molecule **3** corresponds to the higher energy of the σ-MO of the P—C bond; therefore the difference in energies of the π(C=C) and σ(P—C) MO that made the main contribution to the highly occupied FMO becomes less than that in the case of the equatorial bond and their mixing in *gauche*-conformer is more pronounced, and the LUMO—HOMO gap appears to be somewhat narrower. The HOMO in **1** is the σ-MO of the P—H bonds, which are stronger in structures with the $(P—C)_{ax}$ bond. The difference in the calculated σ-MO energies of the axial and equatorial P—H bonds in molecule **1** for the $(P—C)_{eq}$ and $(P—C)_{ax}$ orientations is in qualitative agreement with the results[6] of the SCF X_α calculations of the AsH_5 molecule. In both cases the shorter equatorial X—H bond (X = As^V, P^V) should be stronger than the axial bond.

As our calculations of the PH_5 molecule shows, mixing the P d-AO with the MO localized on the axial and equatorial P—H bonds results in the MO energies moving apart. With increase in element number down the Periodic Table, the first ionization potential of the atom decreases and its electron affinity increases due to decreasing energies of the vacant AO. On going from P to As and further to Sb and Bi, the energy of the d-AO decreases, their contribution to the FMO should increase, and the difference of MO energies and lengths of axial and equatorial bonds increases in the series P < As < Sb < Bi. Thus, one can expect that the differences in the conjugation characteristics in the AC with axial and equatorial X—C bonds will increase on going to the heavier heteroatom.

As seen in Fig. 1, the HOMO of *trans*-conformer **1** with the $(P—C)_{ax}$ bond has lower energy than that of the $(P—C)_{eq}$ bond; however the energy gap of the highest occupied FMO is too large (> 2 eV) to enable them to mix appreciably at the conformational transition. At the same time, the energy lowering of the σ-MO (P—C) should result in an increase in the contribution of the P d-AO to the vacant FMO with the transfer of electron density from the allyl fragment to the PH_4 group (see Table 1). According to calculations, the *gauche*-conformer **1** with the $(P—C)_{ax}$ bond is more stable than the conformer with the $(P—C)_{eq}$ bond.

Thus, the conjugation energy in allylphosphines **1** and **3** with $(P—C)_{ax}$ bonds is higher than that in structures with $(P—C)_{eq}$; in **3** it is caused by approaching closely the frontier MO energies, and in **1** by increasing the contribution of the d-AO to the vacant FMO of the CH_2—PH_4 fragment. In the P^{III} allylphosphines the *trans* → *gauche* transition does not affect the HOMO energy, whereas in the P^V AC it does, and thus the HOMO response depends on the nature of the ligands at the heteroatom (see Fig. 1). The positive charge on the P atom in the PF_4 group is noticeably higher than that in the PH_4 substituent (1.5 and 0.6, correspondingly), and the contribution of the P d-AO to the LUMO of compound **3** is higher than that in **1** (0.15 and 0.06 %, respectively, in basis decomposition).

Mixing the diffuse P d-AO with the σ-MO of the P—C bond in **3** or the P—H bond in structure **1** results in lowering the LUMO energy while decreasing the HOMO—LUMO energy gap and in strengthening their interaction through space, which should manifest itself in an increase in the conjugation energy and bathochromic shift of the $\pi\rightarrow\pi^*$ maximum in the electronic absorption spectra.

According to the results of calculations, one can expect a substantial strengthening of the conformation effect with an increase in the valence of the heteroatom (and, certainly, on going to heavier heteroatoms) on the UV absorption spectrum of the molecule, ionization potentials, and the total energy. Deviations from additivity in the UV-spectra and in dipole moments of the P^V compounds should be more pronounced when the axial P—C bond is present. The majority of the conclusions made in this work can be applied to benzyl, indenyl, and many other compounds, in which the CH_2—XH_n group is adjacent to the π-bonds system.

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