The effect of the valent state of the heteroatom on the spectrochemical evidence of conjugation in allyl compounds of sulfur and phosphorus

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The effect of valency of the heteroatom on the spectrochemical evidence of the conjugation in allyl derivatives of $S^{II,VI}$ and $P^{III,V}$ was studied by quantum chemical methods. The geometric and electronic structures of the *trans*- and *gauche*-conformers, including those for allyl compounds of P^V with equatorial or axial P—C bonds, were calculated. According to the calculations, inversion of the higher occupied molecular orbitals (MO) and the convergence of their energies resulting from the replacement of weak n,π-conjugation by strong π,σ-conjugation should occur on going from S^{II} and P^{III} to S^{VI} and P^V. Increasing the interaction between the higher occupied MO of the fragments in the non-planar conformation of the molecule causes strengthening of the spectral evidence of conjugation: a decrease in the first ionization potential and a bathochromic shift of the long-wavelength absorption band in the electronic spectrum. The increased relative stability of the *gauche*-conformers of allyl compounds of hypervalent elements was explained by the through-space interaction between the vacant d-orbitals of the S^{VI} and P^V atoms and the π-orbital of the C=C bond. Charge transfer between the molecular fragments makes the major contribution to the energy of conjugation.

Key words: MNDO and AM1 semiempirical methods, 3-21G* *ab initio* method; conjugation in allyl compounds; interaction between MO.

The conjugation between a double (or a triple) bond and a group containing a heteroatom (π,σ-conjugation) is one of the most interesting aspects of the theory of the electron structure of molecules. In those cases when the double bond and the heteroatom are separated by a methylene bridge, the interaction between the fragments of the molecule has a substantial effect on the parameters not only of the ground state, but also of the electron-excited state. The presence of conjugation is indicated by the high intensity of the C=C band in the Raman spectra and by variations in the electronic absorption spectra and in the vibrational frequencies of the double bonds.

The non-additivity in conjugated systems is in some cases much more pronounced than that in butadiene. For example, the rate of solvolysis of pentacyclononylnitrobenzoate increases by a factor of 10^{12}—10^{14} under the action of some hydrocarbon-type substituents separated by two or three C—C σ-bonds.[1] The energy of conjugation in ions and electron-excited molecules may be an order of magnitude higher than that in dienes.[2] The conjugation of an unshared electron pair of a heteroatom with the π-orbital of a double bond (n,π-conjugation) is, as a rule, less pronounced.

Allyl compounds (AC) are of great interest. The change in the spectrochemical properties of AC resulting from a conformational transition can be described in terms of the concept of conjugation of the fragments of a molecule through chemical bonds and through space.[3] Quantum chemical investigations of the effect of the nature of the heteroatom on the properties of frontier MO in divinyl and allyl compounds points to a relationship between the dominating type of interorbital interactions and the structure of the electron shell of the heteroatom (the presence of unshared electron pairs, diffuseness, and electron populations and energies of AO).[3,4] When this structure varies, the conditions of interorbital interactions and conjugation in AC also vary. Therefore, spectrochemical evidence of the conjugation must also depend on the valent state of the heteroatom.

In the present work we have studied the influence of the valent state of the heteroatom on electronic structures and relative stabilities of the planar (*trans*) and non-planar (*gauche*) sulfur- and phosphorus-containing AC (in the *trans*-conformer, the C atoms and the heteroatom lie in the same plane) by quantum chemical methods.

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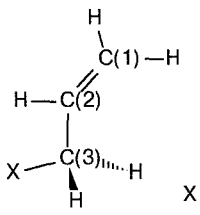
Table 1. The geometric and electronic structures of the conformers of CH_2CHCH_2SH (**1**) and $CH_2CHCH_2SO_3H$ (**2**), according to the data of semiempirical and *ab initio* calculations

Conformer	Calculation method	Bond length/Å			Bond angle*/deg		The effective charge (au)				
		C(1)=C(2)	C(2)—C(3)	S—C(3)	C—C—C	S—C—C	C(1)	C(2)	C(3)	S	SH(SO_3H)
trans-**1**	AM1	1.33	1.48	1.74	122.8 (126.6)	109.8 (113.5)	−0.22	−0.16	−0.23	0.03	0.05
	MNDO	1.34	1.50	1.73	125.3 (129.9)	111.6 (115.3)	−0.05	−0.12	−0.04	0.06	0.03
	3-21G*	1.32	1.50	1.89	122.5 (127.6)	111.5 (112.9)	−0.42	−0.21	−0.69	0.07	0.14
gauche-**1**	AM1	1.33	1.48	1.74	123.7	109.2	−0.21	−0.16	−0.23	0.03	0.04
	MNDO	1.34	1.50	1.74	126.7	109.7	−0.04	−0.12	−0.04	0.05	0.02
	3-21G*	1.32	1.50	1.90	124.1	109.8	−0.40	−0.21	−0.69	0.06	0.12
trans-**2**	AM1	1.34	1.48	1.81	121.8 (131.0)	113.6 (121.6)	−0.17	−0.21	−0.27	1.41	−0.10
	MNDO	1.35	1.49	1.85	123.9 (135.1)	118.0 (125.0)	0.0	−0.16	−0.08	1.51	−0.04
	3-21G*	1.33	1.50	1.97	120.6 (131.2)	118.5 (127.1)	−0.37	−0.26	−0.73	1.45	−0.15
gauche-**2**	AM1	1.34	1.47	1.80	123.2	113.3	−0.14	−0.21	−0.29	1.42	−0.09
	MNDO	1.35	1.48	1.86	126.4	115.6	0.04	−0.17	−0.08	1.50	−0.13
	3-21G*	1.34	1.48	2.00	121.2	112.3	−0.33	−0.25	−0.72	1.35	−0.30

Note. The average values for the experimental bond lengths for related compounds are: $d_{C=C}$ = 1.34 Å, d_{C-C} = 1.53 Å, $d_{S^{II}-C}$ = 1.84 Å, $d_{S^{VI}-C}$ = 1.94 Å.
* The data for *cis*-conformers are given in parentheses.



X = SH, SO_3H, PH_2, PF_4

The geometries and electronic structures of conformers of AC containing lower-valence (S^{II}, P^{III}) or higher-valence (S^{VI}, P^{V}) sulfur or phosphorus were calculated by MNDO[5] and AM1[6] semiempirical methods and also by the SCF MO LCAO *ab initio* method in the 3-21G* basis set. The results of the calculations are presented in Tables 1 and 2.

The S and P atoms in the highest valent states act as electron donors, readily forming bonds with the atoms of electronegative elements. In organic compounds, these are, as a rule, halogen and oxygen atoms. In this connection, we considered the $CH_2CHCH_2SO_3H$ and $CH_2CHCH_2PF_4$ molecules as model AC containing S^{VI} and P^{V}.

As can be seen from the data of Table 1, the introduction of the bulky SO_3H group results in C—C—C and S—C—C bond angles in the *cis*-conformer of the AC that are 7—11° greater than the corresponding values in the *trans*-conformer, due to the repulsion between the closely spaced substituent and the terminal C atom, although for CH_2CHCH_2SH, the analogous difference between the angles is noticeably lower. The smaller S—C—C bond angle in the *gauche*-conformation is an indication of the through-space interaction between the orbitals of the molecular fragments. According to the data of semiempirical methods, this interaction is not great: the *gauche*-conformer of the CH_2CHCH_2SH molecule is more stable than its *trans*-conformer by less than 1 kcal mol^{-1}. In the case of $CH_2CHCH_2SO_3H$, the relative stability of the *gauche*-conformer, according to MNDO calculations, increases to 3 kcal mol^{-1}.

However, the calculation scheme of the semiempirical methods used does not take into account the d-AO, which are known[7] to be extremely significant in coordination compounds of S^{VI}. When the d-orbitals of the S atom are included in the consideration, the results of the calculation of the S^{VI} AC conformers fundamentally change, whereas the calculated geometric and electronic characteristics of S^{II} AC remain virtually unaffected. The S—C (or P—C, see below) bond lengths calculated by semiempirical and *ab initio* methods are dissimilar, since the corresponding calculation schemes are different. The addition of d-orbitals to the basis set results in an improvement in the agreement between the calculated and experimental bond lengths.[8] The *ab initio* calculation in the 3-21G* basis set, which involves the diffuse d-orbitals, predicts a 6° decrease in the S—C—C bond angle in the *gauche*-conformer of the $CH_2CHCH_2SO_3H$ molecule compared with that in its *trans*-conformer (see Table 1). The diffuse d-AO of the S atom in $CH_2CHCH_2SO_3H$ may substantially overlap

Table 2. The geometric and electronic structures of the conformers of the $CH_2CHCH_2PH_2$ (**3**) and $CH_2CHCH_2PF_4$ (**4**), according to the data of semiempirical and *ab initio* calculations

Conformer	Calculation method	Bond length/Å			Bond angle*/deg		The 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	$PH_2(PF_4)$
trans-**3**	AM1	1.34	1.48	1.77	123.2 (129.1)	114.1 (120.5)	−0.21	−0.18	−0.20	−0.10	0.02
	MNDO	1.35	1.50	1.76	125.6 (131.4)	117.4 (122.9)	−0.04	−0.14	−0.03	0.03	0.01
	3-21G*	1.33	1.50	1.92	122.9 (130.0)	117.7 (122.2)	−0.35	−0.19	−0.64	−0.11	0.05
gauche-**3**	AM1	1.34	1.47	1.77	124.0	121.1	−0.20	−0.19	−0.20	−0.10	0.02
	MNDO	1.35	1.49	1.76	126.9	114.4	−0.03	−0.15	−0.02	0.02	0.01
	3-21G*	1.33	1.50	1.93	124.3	115.9	−0.33	−0.19	−0.64	−0.12	0.03
trans-**4** ($P—C_{ax}$)	AM1	1.34	1.46	2.03	123.4 (128.1)	111.1 (117.9)	−0.19	−0.17	−0.30	1.47	0.05
	MNDO	1.35	1.48	2.07	124.7 (133.0)	115.2 (121.2)	−0.02	−0.15	−0.05	1.59	−0.09
	3-21G*	1.34	1.50	2.13	123.1 (130.5)	115.0 (121.8)	−0.32	−0.23	−0.66	1.52	−0.21
gauche-**4** ($P—C_{ax}$)	AM1	1.34	1.45	2.02	123.9	113.8	−0.16	−0.18	−0.33	1.49	0.07
	MNDO	1.35	1.47	2.06	126.7	115.2	0.03	−0.16	−0.06	1.59	−0.09
	3-21G*	1.35	1.48	2.15	123.9	111.2	−0.30	−0.22	−0.65	1.46	−0.32
trans-**4** ($P—C_{eq}$)	AM1	1.34	1.46	1.96	123.0 (129.3)	109.1 (117.6)	−0.18	−0.19	−0.25	1.43	−0.04
	MNDO	1.35	1.49	1.97	124.6 (133.6)	113.2 (120.4)	0.0	−0.16	−0.01	1.55	−0.13
	3-21G*	1.34	1.50	2.04	123.0 (131.8)	113.5 (121.7)	−0.31	−0.24	−0.62	1.47	−0.24
gauche-**4** ($P—C_{eq}$)	AM1	1.34	1.46	1.95	123.6	111.8	−0.15	−0.20	−0.27	1.44	−0.03
	MNDO	1.35	1.48	1.97	126.6	112.0	0.04	−0.18	−0.01	1.55	−0.15
	3-21G*	1.35	1.48	2.06	123.9	109.9	−0.29	−0.23	−0.60	1.42	−0.34

Note. For related compounds, $d_{P^{III}—C}$ = 1.86 Å (2.10 Å for the axial P^V—C bond and 2.02 Å for the equatorial P^V—C bond).
* The data for *cis*-conformers are given in parentheses.

with the p-AO of the atoms of the double bond thus ensuring a weak through-space interaction of the molecular fragments. As a consequence, the transition from a planar to a non-planar conformation leads to a considerable increase in conjugation: according to calculations, the total energy of the molecule decreases by 8 kcal mol^{-1}.

A comparison of the electronic structures of conformers of CH_2CHCH_2SH and $CH_2CHCH_2SO_3H$ shows that for both compounds, the effective negative charges at the C atoms predicted by the AM1 method are greater than those determined by the MNDO method, but smaller than those found by *ab initio* calculations. However, all of these methods indicate that there is no charge transfer between the SH group and the allyl fragment in the CH_2CHCH_2SH molecule in which the distribution of the electron density practically does not depend on the conformation. A different situation is observed in the case of a conformational transition in $CH_2CHCH_2SO_3H$. The overlapping of vacant d-AO of the electron-deficient S^{VI} atom with the p-AO of the C atom of the double bond favors the transfer of electron density from the allyl fragment to the SO_3H group. According to the data of *ab initio* calculations, the *trans* → *gauche* transition is accompanied by the transfer of 0.15 au. Thus, the contribution of charge transfer to the total energy of molecule must be taken into account in evaluating the relative stabilities of the conformers.

Changing the valent state of the S atom also has an effect on the properties of the frontier MO. In terms of their energy, the MOs in the CH_2CHCH_2SH molecule can be arranged in the following sequence: $\pi(C=C) < n(S) < \pi^*(C=C) < \sigma^*(S—C)$. The n(S) orbital of the unshared electron pair of the S atom lies at a higher energy than the π-orbital. When the planar structure changes to the non-planar σ-structure, no substantial changes in the energies of the higher occupied MO occur, which indicates the absence of n,π-conjugation. The changes in the energies of the lower unoccupied MO resulting from the *trans* → *gauche* conformational transition are typical of the case when σ*- and π*-orbitals are mixed as the planarity of an AC is disturbed. The

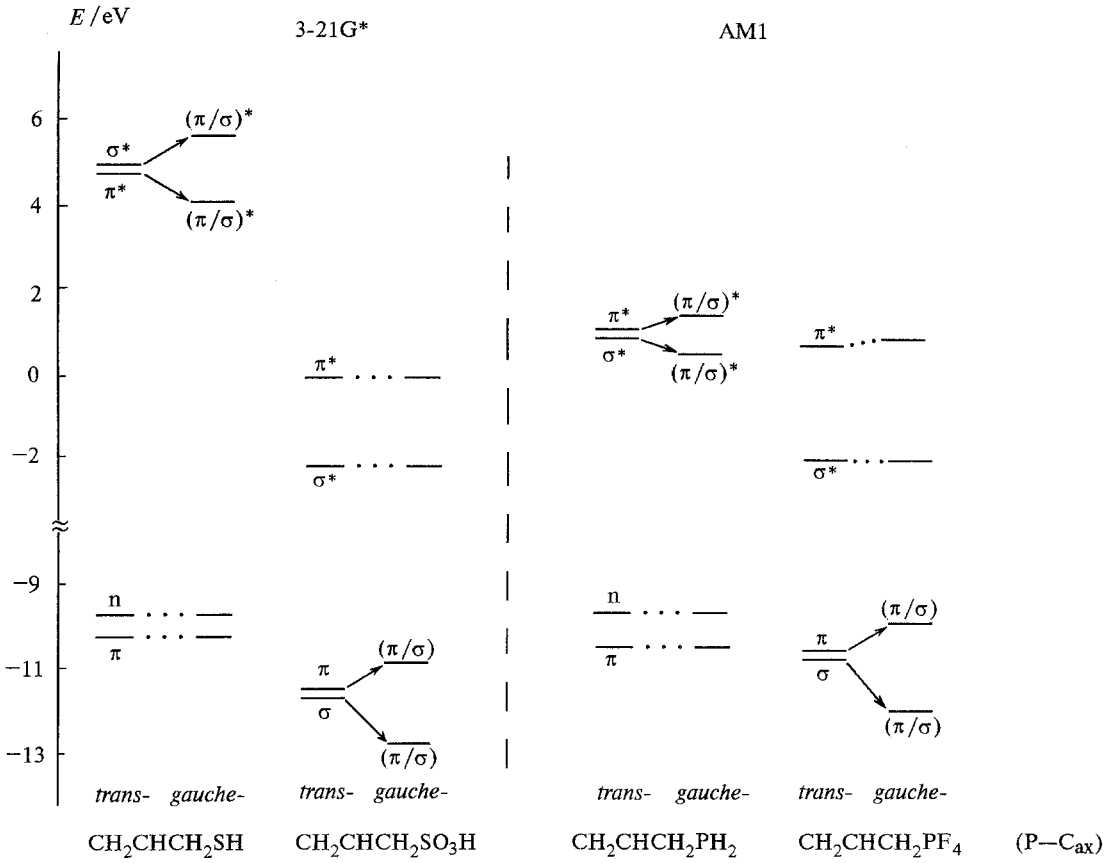


Fig. 1. The frontier MOs in molecules of allyl compounds containing S and P of various valences, according to the data of 3-21G* and AM1 calculations.

electrons of the S atom that constitute the unshared pairs in an S^{II}-containing AC are involved in the formation of the S—O bonds in the $CH_2CHCH_2SO_3H$ molecule. The σ-MO localized at the S—O bond lies lower than the π-MO and the σ-MO of the S—C bond on the energy scale; the system of frontier MOs has the following form: σ(S—C) < π(C=C) < σ*(S—C) < π*(C=C).

The inversion of MOs on the energy scale is accompanied by convergence of the higher occupied MO in the *trans*-conformation and by their mixing in the *gauche*-conformation of the molecule (Fig. 1). It can be seen from Fig. 1 that the bathochromic shifts of the long-wavelength absorption bands associated with the π → π* electronic excitation occurring during the *trans* → *gauche* transition[9] of the S^{II} and S^{VI}-AO have different causes. In the former case, it is caused by a decrease in the energy of the LUMO, while in the latter case, it is due to an increase in the energy of the HOMO.

The replacement of the PH_2 group in allylphosphines by a PF_4 group exerts almost no effect on the geometry of the molecule in the planar conformation, whether the P—C bond is axial or equatorial (see Table 2). The C—C—C and P—C—C bond angles in the *cis*-conformers of $CH_2CHCH_2PH_2$ and $CH_2CHCH_2PF_4$ are similar, and the relative stabilities of the *cis*- and *trans*-conformers of both molecules are nearly identical. The semiempirical methods predict no substantial increase in the conjugation in the $CH_2CHCH_2PF_4$ molecule compared with $CH_2CHCH_2PH_2$; the P—C—C angles in the *trans*- and *gauche*-conformers as well as the heats of their formation differ only slightly.

According to the semiempirical methods, the charge distributions in $CH_2CHCH_2PH_2$ and $CH_2CHCH_2PF_4$ are also similar: the C atoms have similar effective charges, and the charges at the PH_2 and PF_4 groups are small and are approximately identical for all of the conformations of these molecules (see Table 2). The results of *ab initio* calculation indicate that in the $CH_2CHCH_2PF_4$ molecule, conjugation increases. As in the case of the S^{VI} AC, the *trans* → *gauche* conformational transition is accompanied by a transfer of electron density from the allyl fragment to the vacant d-AO of the P^V atom, which results in a 7 kcal mol^{-1} decrease in the total energy of the molecule. The changes of the frontier MO of allylphosphines during the conformational transition are the same as those found for the S-containing AC.

Figure 1 shows that for both examples considered, the transition to AC with hypervalent heteroatoms results in an inversion of the higher occupied MO on the energy scale due to the replacement of the n,π-type of

conjugation, with weak spectrochemical evidence, by strong π,σ-conjugation, which is associated with a substantial increase in the relative stability of the *gauche*-conformation of the molecule. In sulfur-containing AC, the inversion of the pair of lower unoccupied MO has also been observed.

In conformity with both semiempirical and *ab initio* calculations, no variations in the energy of the LUMO occur during conformational transitions of the sulfur- and phosphorus-containing AC.

Thus, the properties of the frontier MO and, hence, many physicochemical properties of the AC depend on the valent state of the heteroatom. The intensification of the spectrochemical evidence of conjugation that occurs with the increase in the valency of the heteroatom has several causes. The proximity of the energies of the higher occupied MO in the S^{VI} and P^{V} AC corresponds to a strong interaction of molecular fragments through chemical bonds in the *gauche*-conformation, which is exhibited as a bathochromic shift of the long-wavelength band in the electronic absorption spectra and as a decrease in the first ionization potential. A comparison of $CH_2CHCH_2PF_4$ molecules with axial and equatorial P—C bonds shows that the longer axial bond corresponds to a higher location of the σ-MO of the P—C bond on the energy scale, and, consequently, the difference between the σ- and π-MO energies is smaller than that in the case of the equatorial bond, and the spectral evidence of conjugation should be more pronounced. The HOMO in the S^{II} and P^{III} AC is occupied by an unshared electron pair, which virtually does not interact with the π-orbital of the C=C bond.

The increased relative stability of the *gauche*-conformer of AC with a hypervalent heteroatom is due to the through-space interaction between the vacant d-AO of the S^{VI} and P^{V} atoms and the π-orbital of the C=C bond. The major contribution to the conjugation energy is made by the transfer of electron density from the allyl fragment to the SO_3H and PF_4 groups.

Thus, the calculations carried out indicate that interaction through chemical bonds predominates in the S^{II} and P^{III} AC, whereas in the S^{VI} and P^{V} AC, interaction through space prevails. One may expect that in general, an increase in the valency of a hypothetical heteroatom is accompanied by intensification of its electron-donating properties and by an increase in the role of its vacant orbitals. Provided the vacant orbitals are sufficiently diffuse, through-space interaction accompanied by an increase in the spectrochemical evidence of conjugation should predominate in AC with a hypervalent heteroatom.

In conclusion it should be noted that the relative stability of the conformers is mostly determined by the through-space interaction of the orbitals of the AC fragments. Therefore, when analyzing the conjugation effects in the compounds of hypervalent elements, it is useful to take into account the d-AO, as is done for coordination compounds of transition metals. Such consideration apparently cannot be done correctly using semiempirical methods, and requires *ab initio* calculations in a basis involving polarization d-functions.

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