AM1 study of photoelectron spectra

7.* Allyl alcohol, allylamine, and allylmercaptane

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The correlation between the group dipole moments of substituents and the experimental values of ionization potentials has demonstarted that the position of the lower ionic π state of allylamine, allylmercaptane, allyl alcohol, and other organic allyl derivatives (except allyl bromide) was determined by the field effect. The empirically obtained conclusions were confirmed by semiempirical AM1 studies. The mechanism of destabilization of energetically unfavorable rotational isomers in the above series of compounds was considered, and it was found that this destabilization is caused mainly by electrostatic interaction.

Key words: allylamine, allylmercaptane, allyl alcohol; photoelectron spectra; semiempirical quantum chemical calculations.

To explain the changes in the ionization potentials of the π-MO of organic and organometallic β,γ-unsaturated compounds the concept of π,σ-interaction and the induction effect are widely used.[2,3] The resonance (π,σ) and field (inductive) effects are also very important for allenes.[1,4] Previously,[5] the photoelectron (PE) spectra of the allyl derivatives under our consideration have been interpreted in the framework of qualitatively analogous concepts. The authors of Ref. 5 concluded that in alcohol the inductive effect mainly occurs, while in nitrogen- and sulfur-containing molecules, n(X),π-interaction also takes place. This conclusion provokes serious objections because: (a) the shifts of the levels in allylmercaptane and allylamine are relatively small with respect to the corresponding model compounds; (b) the studied[5] allyl derivatives are conformationally nonuniform.

According to the experimental data summarized in a known monograph,[6] 57 % of the allyl alcohol present in the gas phase is the *sin*-planar (*sp*) conformer, while only 30 % of allylamine is in this form, and allylmercaptane is perhaps present almost completely in the anticlinal (*ac*) form. There are some doubts in the literature[6] concerning the conformation of the latter compound. However, the results presented below do not confirm these. Reflecting the essence of 1,3-interaction, the maximum mixing of the n(X)-AO and the π-MO should occur in the *sp* form of a molecule. In the *ac* conformers, it can change to σ(CX),π-mixing (1,2-interaction).

Evidently, the analysis of the conformational structure and the interpretation of the PE spectra have been carried out at different levels of reliability. Therefore, it is necessary to discuss again the PE spectra interpreted within the framework of the model concepts. For this purpose, two approaches were used in the present paper. The first one consists of the empirical development of the consequences of the field effect of the substituents according to the method described earlier.[4] The second one is the exact calculation of the ionization potentials by the semiempirical AM1 method taking into account the configurational interaction (CI) (see Ref. 1).

Methods of Calculation

The AM1 quantum chemical studies were carried out using the AMPAC program package (version 1.00). The nonempirical calculations were carried out using the 6-31G basis set (HONDO program). All of calculations were performed with the full optimization of the molecular geometry. It was assumed that the geometry of the radical cations (CI calculations) is identical to that of the corresponding neutral forms. The group dipole moments of the substituents R are assumed to be equal to those of RMe derivatives in the gas phase.[7,8] The sign of the group moment was specified by or determined according to the literature data.[7]

Results and Discussion

Since the AM1 semiempirical method has not been used before for the study of conformations of allyl derivatives, we compared its results with the experimental and *ab initio* calculations data (Table 1 and 2, see also Ref. 6 and references therein). This comparison is necessary due to the fact that the efficiency of 1,2- or 1,3-orbital interaction depends on the molecular conformation. This is why it must be assured that there are no calculation artifacts.

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* For Part 6, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 55—61, January, 1995.

Table 1. Relative energies (ΔE/kcal mol^{-1}) and dihedral angles (θ/deg) of the conformers of allyl derivatives with two axes of internal rotation

Method	Parameter	Conformer				
		ac,−sc	*sp,sc*	*sp,ap*	*ac,ap*	*ac,sc*
		$CH_2=CH-CH_2-OH$				
Experiment[6]	Composition	43 % (*ac*)	57 % (*sp*)			
4-21G[9]	ΔE	0.54	0.0	1.34	2.25	2.39
	θ	128, −60	12, 65	0, 180	137, 176	124, 61
4-31G[10]	ΔE	0.0	0.18	0.99	1.37	1.81
	θ	127, −60	11, 65	180, 180	132, 176	121, 65
6-31G**//4-31G[10]	ΔE	0.0	0.14	1.07	1.35	1.64
AM1	ΔE	0.0	0.30	2.60	Unstable	Unstable
	θ	159, −58	8, 56	0, 180		
		$CH_2=CH-CH_2-OMe$				
AM1	ΔE	0.0	0.90	1.66		
	θ	158, −58	15, 75	0, 180		
		$CH_2=CH-CH_2-NH_2$				
Experiment[6]	Composition	70 % (*ac*)	30 % (*sp*)			
4-31G[11]	ΔE	0.05	0.91	0.0	0.22	2.11
AM1	ΔE	2.58	2.32	0.0	0.24	2.22
	θ	136, −75	14, −74	0, 179	135, 177	139, 68
		$CH_2=CH-CH_2-SH$				
Experiment[6]	Composition	~100 % (*ac*)				
6-31G	ΔE	0.0	1.99	2.86	1.17	1.49
	θ	121, −55	18, 57	2, 180	117, 172	111, 50
AM1	ΔE	0.0	Unstable	Unstable	1.13	0.38
	θ	120, −56			120, 175	111, 50
		$CH_2=CH-CH_2-SMe$				
AM1	ΔE	0.0	Unstable	Unstable	0.48	0.25
	θ	123, −72			119, 175	116, 73
		$CH_2=CH-CH_2-CH=CH_2$				
Experiment[6]	Composition	*ac,−ac*			*ac,sp*	*ac,ac*
	ΔE	0.0			0.36	0.0
	θ	129, −129			117, 4	122, 122
AM1	ΔE	0.0			0.71	0.11
	θ	134, −134			130, −11	131, 133

The characteristics of the rotational isomers presented in Tables 1 and 2 indicate that the method used qualitatively describes the structure and the relative stability of the most stable rotamers in a wide series of β,γ-unsaturated compounds. The rotational isomerism of allylamine and allyl alcohol is the most varied. In the analysis of the PE spectra of these allyl derivatives it is necessary to take into account the possibility of their existence as an ensemble of two (R = OH) or three (R = NH_2) rotational isomers with similar energies, but with different statistical factors. For allylmercaptane, according to the *ab initio* (6-31G basis set) calculation (see Table 1), a quite large (>1 kcal mol^{-1}) energy gap separates the most stable rotamer (*ac,−sc*; the second index corresponds to rotation around the H_2C-R bond) from the others. The AM1(CI) calculated ionization potentials of the *ac,−sc* conformer reproduce with high accuracy (r = 0.989) (Table 3) the values obtained from the PE spectrum of this compound. In addition, the calculations show that two low ionic states of allylmercaptane of π and σ symmetry are practically unperturbed by configurational interactions.

Table 2. Relative energies (ΔE/kcal mol^{-1}) and dihedral angles (θ/deg) of conformers of allyl derivatives ($CH_2=CH-CH_2-X$) with a single axis of internal rotation

X	Parameter	Experiment[6]		AM1 calculation	
		sp	*ac*	*sp*	*ac*
F	ΔE	0.0	0.83	0.0	0.71
	θ	0	127	180	121
Cl	ΔE	0.62	0.0	0.81	0.0
	θ	0	121	0	120
Br	ΔE	0.79	0.0	1.41	0.0
	θ	0	—	0	111
CN	ΔE	0.0	1.31	0.0	0.86
	θ	0	120	0	126
Me	ΔE	0.52	0.0	0.67	0.0
	θ	0	120	0	133

Table 3. Calculated and experimental ionization potentials (IP_i/eV) of the most stable conformers of allylmercaptane, allylamine, and allyl alcohol

Substituent	Conformer	MO	AM1 calculation			Experiment:
			IP_i(KT)*	IP_i(CI)	Predominant configuration (CI)	$IP_i(\mathrm{PES})^{3,5}$
SH	*ac,−sc*	n(S)	8.98	8.50	0.92n(S)	9.25
		π	10.36	9.98	0.90π	10.05
		σ_1(CS)	11.57	11.25	0.77σ_1(CS); 0.54σ(CC)	11.90
		σ(CC)	12.37	12.01	0.56σ(CC); 0.42σ_1(CS)	12.70
		σ_2(CS)	13.85	13.37	0.74σ_2(CS); 0.45π(CH_2S)	13.60
		π(CH_2S)	14.61	13.80	0.66π(CH_2S); 0.33σ_2(CS)	14.60
NH_2	*ac,−sc*	n(N)	9.55	8.97	0.93n(N)	9.44
		π	10.56	10.17	0.92π	10.04
		σ_1(CC)	11.82	11.43	0.97σ_1(CC)	12.50
		σ_2(CC)	13.20	12.77	0.95σ_2(CC)	13.40
		σ(CN)	13.73	13.42	0.94σ(CN)	14.60
		π(CH_2)	15.64	14.85	0.59π(CH_2)	14.90
NH_2	*ac,ap*	n(N)	9.92	9.35	0.84n(N); 0.52π	9.44
		π	10.33	10.01	0.84π; 0.51n(N)	10.04
		σ_1(CC)	12.18	11.81	0.96σ_1(CC)	12.5
		σ_2(CC)	12.70	12.30	0.78σ_2(CC)**	13.4
		π(CH_2N)	14.41	13.82	0.77σ(CH_2N)	14.6
		σ(CN)	14.76	14.51	0.81π(CN)	14.9
NH_2	*sp,ap*	n(N)	9.99	9.73	0.97n(N)	9.44
		π	10.20	9.81	0.99π	10.04
		σ_1(CC)	12.74	12.02	0.97σ_1(CC)	12.50
		π(CH_2N)	13.04	12.64	0.96π(CH_2N)	13.40
		σ_2(CC)	13.30	13.02	0.96σ_2(CC)	14.60
		σ(CN)	15.69	15.42	0.93σ(CN)	14.90
OH	*ac,−sc*	π	10.28	9.89	0.99π	10.16
		n(O)	11.26	10.66	0.95n(O)	10.93
		σ(CC)	12.40	11.87	0.90σ(CC)	12.20
		σ_1(CO)	12.97	12.43	0.92σ_1(CO)	13.30
		π(CH_2O)	14.77	14.34	0.80π(CH_2O); 0.23σ_2(CO)	14.20
		σ_2(CO)	15.54	14.96	0.82σ_2(CO); 0.32π(CH_2O)	15.20
OH	*sp,sc*	π	10.23	9.84	0.99π	10.16
		n(O)	11.32	10.78	0.96n(O)	10.93
		σ(CC)	12.24	11.76	0.95σ(CC)	12.20
		σ_1(CO)	13.36	12.99	0.95σ_1(CO)	13.30
		σ_2(CO)	14.00	13.69	0.98σ_2(CO)	14.20
		π(CH_2)	15.62	15.17	0.82π(CH_2)**	15.20

* According to the Koopmans theorem. ** Mixing with non-Koopmans configurations.

Statistical processing of the correlation between the calculated and experimental ionization potentials of allylamine (see Table 3) showed that the best agreement is achieved for the *ac* forms of this compound (below the second index corresponds to the orientation of the bonding electron pair):

ac,−sc: $IP_i(\mathrm{CI}) = 0.920 IP_i(\mathrm{PES}) + 0.45$, $r = 0.974$;

ac,ap: $IP_i(\mathrm{CI}) = 0.876 IP_i(\mathrm{PES}) + 1.04$, $r = 0.989$;

ac,ap: $IP_i(\mathrm{CI}) = 0.881 IP_i(\mathrm{PES}) + 1.11$, $r = 0.945$.

This fact is in agreement with the experimental data concerning the predominance of *ac* conformers in allylamine. However, based on the calculations using the CI formalism and the analysis of the whole PE spectrum we

Table 4. Energies of two-center electrostatic interactions (ΣE_{AB}) of unbonded valence atoms of the C(1)=C(2)—C(3)H_2—XY fragment in the most stable conformers of organic allyl derivatives and their π-MO orbital energies (ε_π)

Compound	Substituent	X	Y	Conformer	$\Sigma E_{AB}{}^{el}$/eV	ε_π/eV	p_π-AO coefficients C(1)	C(2)	−C(3)	C(X)
1a	CH_2=CH	C	C	*ac,−ac*	0.720	$9.94^{a,b}$ $10.22^{a,b}$	0.47 0.49	0.42 0.47	0.24 0.05	0.35 0.24
1b	CH_2=CH	C	C	*ac,ac*	0.785	$9.91^{a,b}$ $10.31^{a,b}$	0.48 0.48	0.42 0.46	0.18 0.12	0.18 0.00
2a	CH_2Cl	C	Cl	*ac,ap*	0.559	10.31	0.66	0.62	0.22	0.15
2b	CH_2Cl	C	Cl	*ac,sc*	0.616	10.23	0.67	0.62	0.21	0.13
3	CN	C	N	*sp*	0.363	10.47	0.67	0.63	0.23	0.05
4	OMe	O	C	*ac,−sc*	0.618	10.24	0.67	0.61	0.22	0.07
5a	SMe	S	C	*ac,−sc*	0.585	10.18	0.64	0.58	0.23	0.16
5b	SMe	S	C	*ac,sc*	0.539	10.04^{a}	0.61	0.55	0.26	0.34
6a	OH	O	—	*ac,−sc*	0.572	10.28	0.65	0.59	0.23	0.12
6b	OH	O	—	*sp,sc*	0.613	10.23	0.65	0.59	0.25	0.13
7a	NH_2	N	—	*sp,ap*	0.605	10.20	0.67	0.60	0.26	0.05
7b	NH_2	N	—	*ac,−sc*	0.907	10.56^{a}	0.59	0.60	0.02	0.39
7c	NH_2	N	—	*ac,ap*	0.592	10.33	0.63	0.59	0.19	0.13
8	Me	C	—	*ac,ap* (H)	0.642	10.01	0.68	0.62	0.22	0.13
9a	F	F	—	*ap*	0.348	10.35	0.65	0.60	0.24	0.18
9b	F	F	—	*sp*	0.394	10.28	0.65	0.61	0.24	0.17
10	Cl	Cl	—	*ac*	0.291	10.48	0.66	0.63	0.16	0.20
11	Br	Br	—	*ac*	0.219	10.35^{a}	0.64	0.59	0.18	0.29

[a] π-MO perturbed by the interfragment orbital interactions ($C(X)^2$ or $C(Y)^2 > 0.1$). [b] An average value was used in comparison with $\Sigma E_{AB}{}^{el}$.

were unable to find out exactly what type of *ac* conformer dominates. One can only give some preference to the *ac,ap* form of allylamine characterized by mixing of the two lowest single ionized configurations.

In contrast to allylamine, for allyl alcohol a comparison of only the theoretical and observed ionization potentials does not allow one to reliably differentiate even the *sp* and *ac* forms:

$$ac,-sc\colon\ IP_i(\mathrm{CI}) = 1.02IP_i(\mathrm{PES}) + 0.54,\ r = 0.987;$$

$$sp,sc\colon\ IP_i(\mathrm{CI}) = 1.01IP_i(\mathrm{PES}) + 0.44,\ r = 0.996.$$

Thus, the orbital ionization potentials of allyl alcohol are not very sensitive to the details of the structure of its most stable rotational isomers. They are not sensitive to the configurational interactions either (see Table 3), *i.e.*, their correlation corrections are insignificant.

The question of what kind of interactions perturb the π system of allyl derivatives with varying substituents requires two levels of consideration: one at the orbital level and one within the framework of the concept of the state. In the first case, it is assumed that the orbital energies of the π-MO (ε_π) of organic allyl derivatives will be used (Table 4), and the energy of the electrostatic interactions ($\Sigma E_{AB}{}^{el}$) of pairs of unbonded valence atoms on the C=C—CH_2XY (X and Y are heavy atoms) fragment calculated according to the technique of the partitioning of the total energy of a molecular system (see Ref. 1 and references therein) will be used as the measure of the field effect. In the second case, the ionization

Table 5. Ionization potentials (IP_π) of allyl derivatives and group dipole moments (μ) of the substituents

Compound	Substituent	$\mu_R/D^{7,8}$	IP_π(PES)/$eV^{3,5}$
1	CH_2=CH	−0.36	9.55^{a} 9.95^{a}
3	CN	−3.97	10.55
6	OH	−1.70	10.16
7	NH_2	−1.28	10.04
8	Me	0.00	9.77
9	F	−1.85	10.38
10	Cl	−1.86	10.30
11	Br	−1.82	10.00
12	SH	−1.26	10.05
13	Pr^i	0.13	9.63
14	H	-0.40^{b}	9.88

[a] An average value was used in comparison with μ_R. [b] Moment of C—H bond (*cf.* Ref. 1).

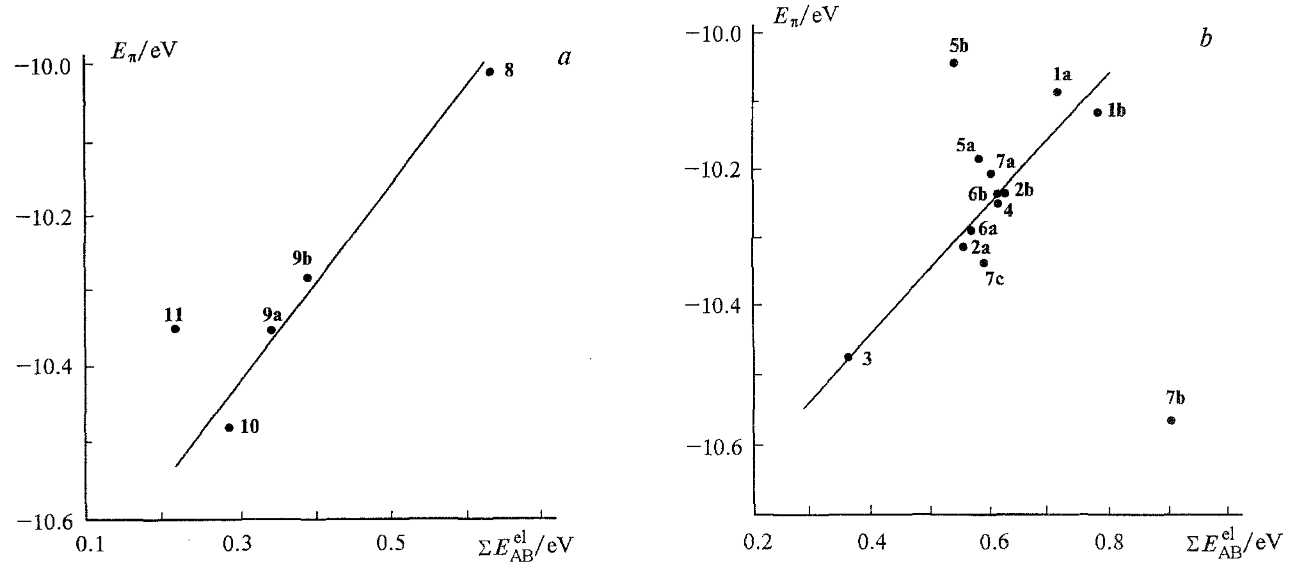

Fig. 1. Correlation of the orbital energies and the energies of electrostatic interactions of unbonded valence atoms of the $C=C-CH_2XY$ fragment of allyl derivatives (for the numbering of the compounds see Table 4).

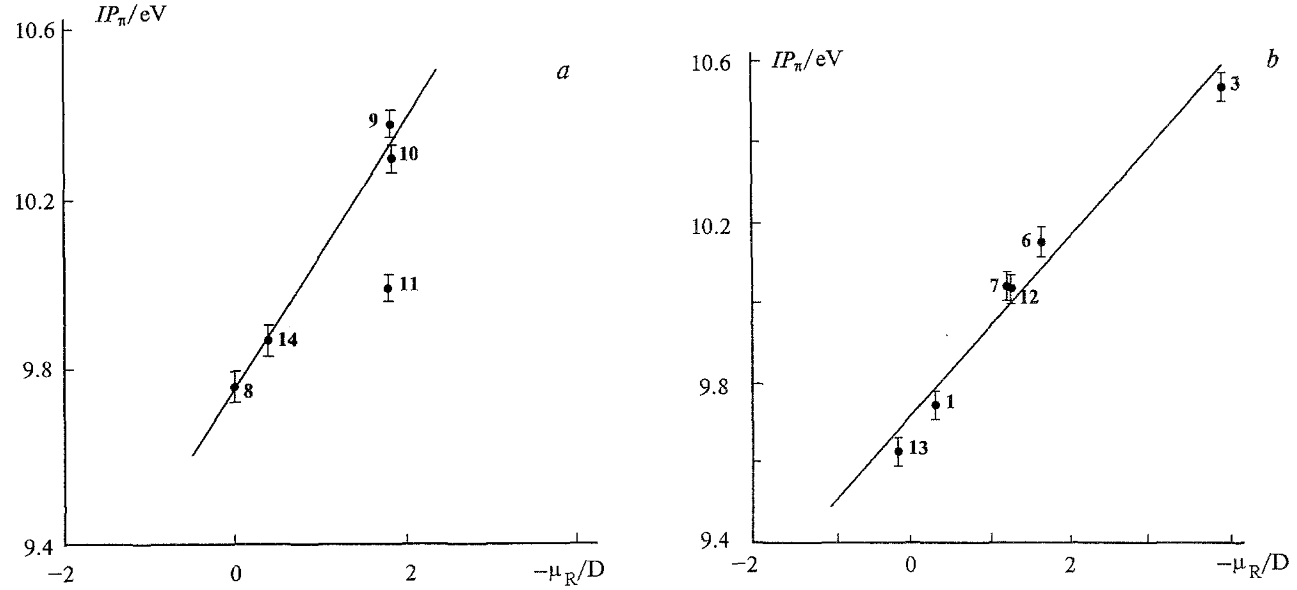

Fig. 2. Correlation of the experimental ionization potentials of π-MO of allyl derivatives and the group dipole moments of substituents (for the numbering of the compounds see Table 5).

potentials corresponding to π-MO vacancies will be used and (as the measure of the field effect) the group dipole moments of the substituents (μ_R) determined from the experimental values of μ_{RMe} (Table 5).

An analysis of the relationships between the theoretically estimated parameters of the most stable conformers made it possible to establish that there are two linear correlations between ε_π and $\Sigma E_{AB}{}^{el}$, one of which connects 1-butene, allyl fluoride, and allyl chloride (see Fig. 1, *a*). In this case, the point related to allyl bromide deviates considerably from the regression line. This is due to additional resonance interaction between the fragments (see Table 4).

Among the other investigated compounds (see Table 4), the *ac,−sp* conformer of allylamine and the *ac,sc*-conformer of allylmethyl sulfide do not obey the analogous correlation (Fig. 1, *b*). An analysis of the coefficients presented in Table 4 shows that the π-MO of the conformers mentioned above is significantly localized at the substituent. The points corresponding to these conformers deviate from the regression line shown in Fig. 1, *b*, some with higher orbital energies and some with lower. In the *ac,−sc* form of allylamine, resonance stabilization of the π-MO takes place, while in the *ac,sc* conformer of allylmethyl sulfide, in contrast, there is resonance destabilization of this orbital. Since the sign of

Table 6. Stable and energetically unfavorable rotational conformers of allyl derivatives destabilized mainly by two-center electrostatic interactions

Substituent	Conformer		ΔE_t	$\Delta\Sigma E_{AB}^{el}$	$\Delta\Sigma E_{AB}^{R}$	$\Delta\Sigma E_A$
	stable	unfavorable				
$CH_2{=}CH$	*ac,−ac*	*ac,ap*	0.031	0.032	−0.024	0.023
CH_2Cl	*ac,ap*	*ac,−sc*	0.025	0.026	−0.022	0.021
	ac,ap	*sp,ap*	0.028	0.030	−0.059	0.057
	ac,ap	*sp−sc*	0.066	0.050	−0.041	0.057
Me	*ac,ap*	*sp,ap*	0.029	0.038	−0.049	0.040
CHO	*ac,−ac*	*sc,−ac*	0.034	0.026	−0.013	0.021
Cl	*ac*	*sp*	0.035	0.037	−0.065	0.063
F	*ap*	*ac*	0.031	0.022	0.057	−0.048
OH	*ac,−sc*	*sp,sc*	0.013	0.054	−0.072	0.031
	ac,−sc	*sp,ap*	0.113	0.100	0.030	−0.017
OMe	*ac,−sc*	*sp,sc*	0.039	0.045	−0.013	0.007
	ac,−sc	*sp,ap*	0.072	0.063	0.032	−0.023
SH	*ac,−sc*	*ac,sc*	0.017	0.039	−0.019	−0.003
	ac,−sc	*ac,ap*	0.049	0.100	−0.005	−0.046
SMe	*ac,−sc*	*ac,sc*	0.011	0.027	−0.043	0.027
	ac,−sc	*ac,ap*	0.021	0.066	−0.017	−0.028

Note. All energy values are in eV.

Table 7. Stable and energetically unfavorable rotational conformers of allyl derivatives destabilized mainly by two-center resonance interactions

Substituent	Conformer		ΔE_t	$\Delta\Sigma E_{AB}^{R}$	$\Delta\Sigma E_{AB}^{el}$	$\Delta\Sigma E_A$
	stable	unfavorable				
$CH_2{=}CH$	*ac,−ac*	*ac,ac*	0.005	0.025	−0.016	−0.004
CH_2Cl	*ac,ap*	*ac,sc*	0.016	0.019	−0.013	0.010
OH	*ac,−sc*	*ap,ap*	0.086	0.064	0.015	0.007
CN	*sp*	*ac*	0.037	0.093	−0.018	−0.038
NH_2	*sp,ap*	*ac,ap*	0.010	0.118	−0.033	−0.074
	sp,ap	*ac,sc*	0.096	0.116	−0.060	0.040
	sp,ap	*ac,−sc*	0.112	0.092	0.004	0.016

Note. All energy values are in eV.

the effect indicates the relative position of the perturbed level, one can suggest that 1,3-interaction is realized in the *ac,−sc* conformer of allylamine (through bond), and 1,2-interaction occurs in the *ac,sc* conformer of allylmethyl sulfide (through space).

The interrelation between the experimental values discussed above is shown in Fig. 2. Here there are also two correlations, but the only deviation is for allyl bromide. Thus, the ionization energies in the states with a vacant π-MO which were observed in the PE spectra of conformers of allyl alcohol, allylmercaptane, and allylamine are determined only by the field effect of the substituent. This makes it possible in turn to consider the *ac,ap* conformer to be more "representative" from the point of view of PE spectroscopy.

Based on the available theoretical and experimental data[6] corresponding to the rotational isomerism of $RCH_2{-}C({=}X)Y$ type molecules, it was concluded that the potential for internal rotation is not restricted to the contribution from V_3, but depends significantly on V_1 and V_2 also. The V_1 and V_2 contributions, which have some effect on the energy barrier and which to a great degree determine the position of the local minimum, are caused by electrostatic and resonance interactions respectively.

Thus, after expanding the total energy (E_t) of a molecule into its one-center (ΣE_A) and two-center (ΣE_{AB}^{el} — electrostatic and ΣE_{AB}^{R} — resonance) components, one can try to set apart those which determine the energetic unfavorability/favorability of one or another rotational isomer. The results obtained in the framework of this scheme of partitioning E_t of the conformers of the investigated compounds, including some of the most unstable ones, are collected in Tables 6 and 7. Based on these results, we can conclude that, in most cases, the conformers of organic allyl derivatives are less stable than the most stable of these because of electrostatic interactions (the changes in the other two components are either small or compensate for one another, see Table 6).

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Received June 2, 1994