AM1 study of photoelectron spectra

6.* Alkoxyallenes. Interaction of distant fragments

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A correlation was found between the group dipole moments of substituents determined from the dipole moments of ethylene derivatives and the second ionization potentials of allene derivatives corresponding to the π'-MO of the C(β)—C(γ) bond. It was shown that the concept of the effect of the substituent field cannot completely explain the observed phenomena, and the energies of the second ionic states of bromoallene and alkoxyallenes are lowered because of the interaction between nonbonded fragments through the σ systems of the compounds. It has been found that, in terms of orbital approximation, this interaction causes electronic destabilization of the *anti*-planar (*trans*) conformers of methoxyallene and methyl vinyl ether compared to their *sin*-planar (*cis*) forms.

Key words: allene derivatives; photoelectron spectra; semiempirical quantum chemical calculations.

The photoelectron spectra of allene derivatives including alkyl allenyl ethers have been widely studied[2—8] (see also the references therein). The effect of the substituent on the highest occupied π-MO of allene can be readily interpreted in terms of resonance and short-range inductive effects. Perturbation of the π-MO of the C(β)—C(γ) bond distant from the substituent (π'-MO) in conformationally rigid allenes (R = Et, Me, H, Cl, Br, and CN) is due to the field (strong inductive) effect.[4] This fact is confirmed by the linear correlation between the ionization potentials of the allene π'-MOs and the group dipole moments of substituents determined from the dipole moments of benzene derivatives.

This correlation is also valid for methoxyallene, a conformationally labile allene.[4] However, this approach is inadequate for analyzing the mechanism of the interaction between nonbonded fragments in alkoxyallenes as a whole, because the corresponding benzene derivatives simulate only one possible stable molecular conformation. From this standpoint, monosubstituted ethylenes would be better models of allenes.

Another reason why benzene derivatives are poor models of allenes is that the π'-MO of allene in a planar (with respect to heavy atoms) conformation can mix with a substituent σ-MO of suitable symmetry[4,6] (see also references in the well-known monograph, Ref. 7). This mixing is absent in the corresponding benzene derivatives,** and, in monosubstituted ethylenes, the σ-MO of the terminal CH_2 group, $\sigma(CH_2)$, can act as a π'-MO.

Because of the different orientations of the σ-bond orbitals of the substituent and the π'-MO or $\sigma(CH_2)$-MO of allenyl and vinyl ethers in the *sin*-planar (*sp*) and *anti*-planar (*ap*) conformations, the extent of this mixing is different for different rotational isomers. This can result in the model effect when using the dipole moments of monosubstituted benzene derivatives as an empirical measure of electrostatic interactions. Hence, earlier conclusions[4] require independent confirmation by results based on another approach.

It is known that the four-electron interactions that occur in occupied MOs destabilize a molecular system. Hence, the search for experimental manifestations of the mixing of fragment orbitals in the alkoxyallene σ system may be closely related to the explanation for the preferability of their rotational *sin* (*anti*) isomers. The role of the σ system of unsaturated ethers has never been studied before. According to present theoretical data,[9] the reason one of the rotational isomers of methyl vinyl ether, which is the simplest unsaturated ether, is energetically preferred is due to the compromise between the electronic destabilizing and stabilizing (charge transfer) interactions in its π system.

It should be taken into account that the mixing of fragment orbitals in the ground state and the electronic configurations in the ionic state may be different. Hence, the fact that photoelectron spectroscopy (PES) shows mixing does not prove unambiguously that mixing occurs in the neutral molecule. In this connection, we analyzed published photoelectron spectra of alkyl allenyl

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* For Part 5, see Ref. 1.

** In this case, it is the a_2-MO that can participate in mixing.

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Table 1. Ionization potentials (*IP*/eV) of allenes $RCH{=}C{=}CH_2$

R	MO[a]	Ionic state	Predominant configuration	*IP*(CI)	*IP*(PES)[b]	Δ*IP*
$CH{=}CH_2$[c]	π_4	$^2A''$	$0.98\pi_4$	8.32	8.88	0.56
	$\pi_3'(CH_2{=}C{=})$	$^2A'$	$0.95\pi_3$	9.56	10.04	0.48
	π_2	$^2A''$	$0.82\pi_2{}^d$	10.67	11.37	0.70
	$\sigma_1(CH{=}CH_2)$	$^2A'$	$0.94\sigma_1$	11.62	12.55	0.93
	$\sigma_2(CH_2{=}C{=}CHCH{=}CH_2)$	$^2A'$	$0.87\sigma_2{}^d$	13.22	13.90	0.68
	$\pi_1(CH_2)$	$^2A''$	$0.73\pi_1(CH_2)^d$	13.53	13.90	0.37
C≡N	π_5	$^2A''$	$0.98\pi_5$	9.74	10.35	0.61
	$\pi_4'(CH_2{=}C{=})$	$^2A'$	$0.96\pi_4'$	10.32	11.16	0.84
	$\pi_3'(C{\equiv}N)$	$^2A'$	$0.94\pi_3'$	12.32	12.21	
	$\pi_2(C{\equiv}N)$	$^2A''$	$0.86\pi_2{}^d$	13.11	12.95	
	$\sigma_1(N{-}C)$	$^2A'$	$0.73\sigma_1{}^d$	13.45	13.16	
	$\pi_1(CH_2)$	$^2A''$	$0.82\pi_1(CH_2)^d$	14.30	~15.30	1.00
$CH_2{-}CH_3$[c]	π_4	$^2A''$	$0.99\pi_4$	9.09	9.22	0.13
	$\pi_3'(CH_2{=}C{=})$	$^2A'$	$0.94\pi_3'$	9.52	9.96	0.46
	$\sigma_1(CH_2)$	$^2A'$	$0.92\sigma_1$	11.48	12.10	0.62
	$\sigma_2(CH_3)$	$^2A'$	$0.86\sigma_2{-}0.32\pi_2$	12.33	12.70	0.37
	$\pi_2(CH_3)$	$^2A''$	$0.82\pi_2{+}0.33\sigma_2$	12.92	~13.20	0.30
	$\pi_1(CH_2)$	$^2A''$	$0.86\pi_1(CH_2)^d$	14.14	14.20	0.00
Cl	π_4	$^2A''$	$0.98\pi_4$	9.35	9.57	0.22
	$\pi_3'(CH_2{=}C{=})$	$^2A'$	$0.97\pi_3$	10.09	10.55	0.46
	n(Cl)	$^2A'$	0.95n	11.02	11.54	0.52
	π_2	$^2A''$	$0.88\pi_2$	12.51	12.87	0.36
	$\pi_1(CH_2)$	$^2A''$	$0.75\pi_1{}^d$	14.20	15.10	0.90
	$\sigma_1(CCCCl)$	$^2A'$	$0.65\sigma^d$	15.53	16.10	0.47
Br	π_4	$^2A''$	$0.98\pi_4$	9.44	9.46	0.02
	$\pi_3'(CH_2{=}C{=})$	$^2A'$	$0.95\pi_3'$	9.97	10.38	0.41
	n(Br)	$^2A'$	0.93n	10.29	10.87	0.58
	π_2	$^2A''$	$0.89\pi_2$	11.54	12.08	0.54
	$\sigma_1(CCCBr)$	$^2A'$	$0.88\sigma_1{}^d$	13.59	14.35	0.76
	$\pi_1(CH_2)$	$^2A''$	$0.68\pi_1{}^d$	14.29	~15.00	0.70

[a] Sequence of occupied MOs of the ground state; assumed numbering of the σ-MOs is the reverse of the numbering of the π-MOs. [b] Data from Refs. 4 and 7. [c] Anticlinal (*ac*) conformation. [d] Mixing with non-Koopmans configurations.

ethers. Their orbital structures and ionic states were interpreted using calculations by the conventional semiempirical AM1 method and the configuration interaction method AM1(CI).

Experimental

Photoelectron spectra were recorded on an ES-3201 electron spectrometer. The spectrum was excited using the helium(I) resonance band (21.21 eV). The energy scale was calibrated with respect to the first ionization potential of argon (15.76 eV). For the allowed bands, the error of the determination of ionization potentials was 0.05 eV.

Quantum chemical calculations were performed using the AMPAC program package (version 1.00). Unless otherwise specified, full geometry optimization of molecules was performed. In calculations, the geometries of radical-cations and their corresponding molecules were assumed to be identical. Since the AM1(CI) method has never been applied to allenes, we calculated the ionization potentials of some compounds with known or obvious conformations (the results are given in Table 1). The average deviation between the calculated and experimental ionization potentials was −0.5 eV (except for the nitrile group).

The group dipole moments of substituents of allene derivatives were assumed to be equal to the dipole moments of monosubstituted ethylenes in the gas phase.[10] The group dipole moments of the OMe, OPr^n, OBu^n, OPr^i, and OBu^t fragments (Table 2) were derived from the correlation between the dipole moments of monosubstituted derivatives of ethylene and benzene in the gas phase and in benzene solutions.[10–12] The signs of the group dipole moments were obtained on the basis of the bond moments and (or) dipole moments of *cis* (*trans*) isomers of disubstituted ethylenes.[10,11]

Results and Discussion

The correlation between the group moments of the substituents and the second ionization potentials (IP_2) corresponding to the π′-MOs of allene derivatives are given in Fig. 1 (see also the data in Table 2). This dependence has some specific pecularities when compared with a similar correlation determined in Ref. 4 using dipole moments of benzene derivatives. First, the

Table 2. Group dipole moments of substituents and second ionization potentials of allenes ($RCH=CH_2$ and $RCH=C=CH_2$)

Compound	R	R—CH=CH$_2$[a]		R—CH=C=CH$_2$:
		μ_{gas}/D	μ_{benz}/D	$IP_2(\pi')$/eV[b]
1	Et	0.44		9.96
2	Me	0.36		10.06
3	CH=CH$_2$	0.00		10.04
4	H	0.00		10.07
5	OMe	−1.2[c]	−1.11	10.30
6	OEt	−1.27	−1.19	10.17
7	OPr^n	−1.3[c]	−1.19	10.15
8	OBu^n	−1.3[c]	−1.25	10.18
9	Br	−1.41	−1.36	10.38
10	Cl	−1.44		10.55
11	OPr^i	−1.6[c]	−1.48	10.09
12	OBu^i	−1.9[c]	−1.79	9.90
13	CN	−3.89		11.16

[a] Data from Refs. 10 and 12. [b] Photoelectron spectra from Refs. 4 and 8. [c] Estimated value (see Experimental).

partial correlation (Eq. (1); R = Et, Me, C_2H_3, H, Cl, and CN) and the total correlation (Eq. (2); R = Et, Me, C_2H_3, H, OMe, Br, Cl, and CN) differ significantly in their regression coefficients (*r*):

$$IP_2 = 10.10 - 0.277\mu_R,\ r = 0.995,\ n = 6; \quad (1)$$

$$IP_2 = 10.07 - 0.271\mu_R,\ r = 0.985,\ n = 8. \quad (2)$$

Deviations of points corresponding to allenes with R = OMe and Br from the regression line (1) exceed 2Δ in the energy scale (where Δ is the error of photoelectron spectroscopy). Second, the characteristics of the other alkoxyallenes (see Table 2) fit neither one, nor another correlation at all (see Fig. 1). Hence, the field effect alone provides the explanation for the variation of IP_2 in the series of compounds that fit partial correlation (1).

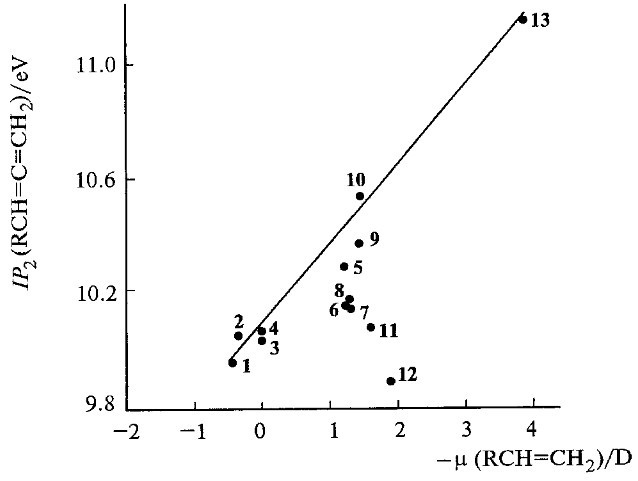


Fig. 1. Correlation between the group dipole moments of the substituents and the second ionization potentials of allene derivatives (for the numbering of the compounds see Table 2).

Scheme 1

π′-MO
$CH_2=C=CHCl$

π′-MO
$CH_2=C=CHBr$

As can be seen from the data in Table 1, the first excited state of the monobromoallene radical-cation is adequately described by an electronic configuration with the unoccupied π′-MO. Consequently, in its ground state there must be mixing of fragment orbitals. A comparison of the π′-MOs of haloallenes (Scheme 1) shows that when R = Br this mixing is enhanced.

Orbital interactions cause the lowest $^2A'$ state of the bromoallene ion to be stabilized by 0.12±0.05 eV.

According to theoretical data, the orbital structure and photoelectron spectra of OAlk-substituted allenes is much more complicated than those for R = Me, Hal, or CN. On the one hand, the σ-orbital, which is mixed with the π′-MO in these compounds, is more strongly localized on the substituent and has higher orbital energy than the σ-MO of the C—Br bond. On the other hand, the efficiency of this mixing depends on the conformation of the alkoxyallene and the length (branching) of the hydrocarbon chain of the radical, and increases upon ionization (Tables 3 and 4). As a result of the set of factors mentioned, the field effect slowly varying in the series of alkoxyallenes is masked by the resonance stabilization of their ionic states with the unoccupied π′-MO (see Fig. 1).

The amount of stabilization of the ionic state is larger for *ap* conformers. However, it is impossible to relate this directly to the problem of the electronic destabilization (stabilization) of one of the alkoxyallene rotational isomers, because the Koopmans theorem fails for these molecules (see Table 3). Thus, at the level of only ionization energies, photoelectron spectroscopy and AM1(CI) calculations are incapable of providing even qualitative information on the preferability of *sp* or *ap* forms of alkoxyallenes or its causes (*cf.* Eqs. (3)—(5)):

sp (Me, Et, Pr^i, Bu^t): $IP(\text{PES}) = 0.32 + 0.973IP(\text{CI})$, $r = 0.981,\ n = 24$; (3)

ap (Me, Et, Pr^i, Bu^t): $IP(\text{PES}) = 0.82 + 0.932IP(\text{CI})$, $r = 0.980,\ n = 24$; (4)

sp (Me, Et), *ap* (Pr^i, Bu^t): $IP(\text{PES}) = 0.56 + 0.954IP(\text{CI})$, $r = 0.983,\ n = 24$. (5)

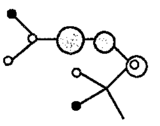
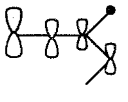
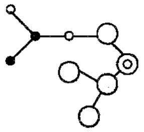
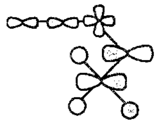
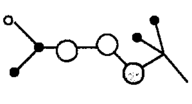
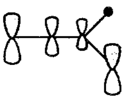
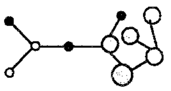
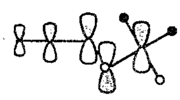
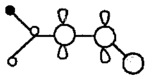
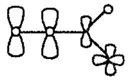
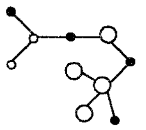
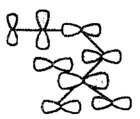
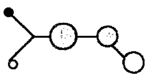
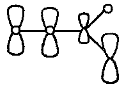
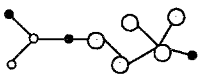
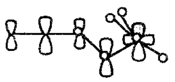
The role of nonbonded fragments in the electronic stabilization of one of the rotational isomers of the considered compounds can be analyzed most completely for methyl vinyl ether and allenyl methyl ether. Other

Table 3. Ionization potentials (*IP*/eV) of alkoxyallenes $ROCH=C=CH_2$

R	*IP*(PES)	*sp,ap*(*cis*) Conformation				*ap,ap*(*trans*) Conformation			
		MO[a]	Ionic state	Predominant configuration	*IP*(CI)	MO[a]	Ionic state	Predominant configuration	*IP*(CI)
Me	8.75[b], 8.73[c], 8.77[d]	π_5	$^2A''$	$0.98\pi_5$	8.50	π_5	$^2A''$	$0.98\pi_5$	8.46
	10.33, 10.28, 10.33	π_4'	$^2A'$	$0.97\pi_4'$	9.90	π_4'	$^2A'$	$0.96\pi_4'$	9.69
	12.00, 12.02, 11.97	π_3	$^2A''$	$0.88\pi_3$[f]	11.80	π_3	$^2A''$	$0.87\pi_3$[f]	11.57
	12.20, 12.34, 12.28	$\sigma_1(OMe)$	$^2A'$	$0.85\sigma_1$[f]	12.60	$\sigma_1(OMe)$	$^2A'$	$0.58\sigma_1-0.36\sigma_2$	12.57
	13.94[e]	$\sigma_2(CCCOMe)$	$^2A'$	$0.83\sigma_2$[f]	13.40	$\sigma_2(CCCOMe)$	$^2A'$	$0.83\sigma_2$[f]	13.54
	14.06[e]	$\pi_2(CH_2)$	$^2A''$	$0.77\pi_2$[f]	13.70	$\pi_2(CH_2)$	$^2A''$	$0.77\pi_2$[f]	13.69
Et	8.47, 8.66	π_6	$^2A''$	$1.00\pi_6$	8.68	π_6	$^2A''$	$0.95\pi_6$	8.57
	10.12, 10.23	π_5'	$^2A'$	$0.74\pi_5'-0.53\sigma_1$	9.85	π_5'	$^2A'$	$0.70\pi_5'-0.63\sigma_1$	9.66
	11.41, 11.67	$\sigma_1(OEt)$	$^2A'$	$0.73\sigma_1+0.55\pi_5'$	11.64	$\sigma_1(OEt)$	$^2A'$	$0.62\sigma_1+0.58\pi_5'$	11.63
	12.08, 11.92	π_4	$^2A''$	$0.53\pi_4$[f]	11.98	π_4	$^2A''$	$0.55\pi_4-0.55\pi_3$	12.52
	12.9[e]	$\sigma_2(Me)$	$^2A'$	$0.77\sigma_2$[f]	13.07	$\pi_3(Me)$	$^2A''$	$0.65\sigma_2+0.65\pi_4$	13.28
	~13.5[e]	$\sigma_2(CCCOEt)$	$^2A'$	$0.88\sigma_3$[f]	14.10	$\sigma_2(CCCOEt)$	$^2A'$	0.80σ[f]	13.97
Pr^i	8.61	π_7	$^2A''$	$1.00\pi_7$	8.61	π_7	$^2A''$	$0.99\pi_7$	8.40
	10.09	π_6'	$^2A'$	$0.80\pi_6'-0.47\sigma_1$	10.09	π_6'	$^2A'$	$0.69\pi_6'-0.61\sigma_1$	9.65
	11.40	$\sigma_1(COPr^i)$	$^2A''$	$0.83\pi_5$[f]	11.40	$\sigma_1(COPr^i)$	$^2A''$	$0.80\pi_5$[f]	11.76
	11.58	π_5	$^2A'$	$0.79\sigma_1-0.54\pi_6'$	11.58	π_5	$^2A'$	$0.73\sigma_1+0.54\pi_6'$	11.84
	13.0[e]	$\sigma_2(CCCOPr^i)$	$^2A'$	$0.68\sigma_2$[f]$(0.6\sigma_2)$[g]	13.00[e]	$\sigma_2(CCCOPr^i)$	$^2A'$	$0.97\sigma_2$	12.96
	13.6[e]	$\pi_4(Me)$	$^2A'$	$0.96\pi_4$	13.60[e]	$\sigma_3(Me)$	$^2A'$	$0.87\sigma_3+0.39\sigma_1$	13.38
Bu^t	8.56	π_8	$^2A''$	$1.00\pi_8$	8.54	π_8	$^2A''$	$0.98\pi_8$	8.43
	9.95	π_7'	$^2A'$	$0.83\pi_7'-0.48\sigma_1$	10.00	π_7'	$^2A'$	$0.69\pi_7'-0.64\sigma_1$	9.68
	11.25	π_6	$^2A''$	$0.89\pi_6$	11.80	π_6	$^2A''$	$0.79\pi_6$[f]	11.79
	11.47	$\sigma_1(COBu^t)$	$^2A'$	$0.69\sigma_1+0.57\pi_7'-0.44\sigma_2$	11.85	$\sigma_1(COBu^t)$	$^2A'$	$0.75\sigma_1+0.50\pi_7'$	11.87
	12.7[e]	$\pi_5(Me)$	$^2A''$	$0.95\pi_5$	12.91	$\pi_5(Me)$	$^2A''$	$0.96\pi_5$	12.99
	~12.7[e]	$\sigma_2(OBu^t)$	$^2A'$	$0.85\sigma_2+0.48\sigma_1$	13.39	$\sigma_2(OBu^t)$	$^2A'$	$0.88\sigma_2$[f]	13.41

[a] See footnote[a] for Table 1. [b] Data from Ref. 5. [c] Data from Ref. 6. [d] Data from Ref. 8. [e] Results of this work. [f] Admixture of non-Koopmans configuration. [g] Non-Koopmans satellite.

Table 4. MOs of alkoxyallenes $ROCH=C=CH_2$

R	Conformation	$\pi(C=C)$	$\pi'(C=C)$	$\pi(COR)$	σ_1
Me	*sp,ap* (H)				
	ap (160),*ap* (H)				
CMe₃	*sp,ap* (C)				
	ap (177),*ap* (C)				

cases can be easily interpreted by successively replacing C—H bonds with C—C bonds.

As indicated by the structure of the occupied frontier MOs of methoxyallene (see Table 4), two types of or-

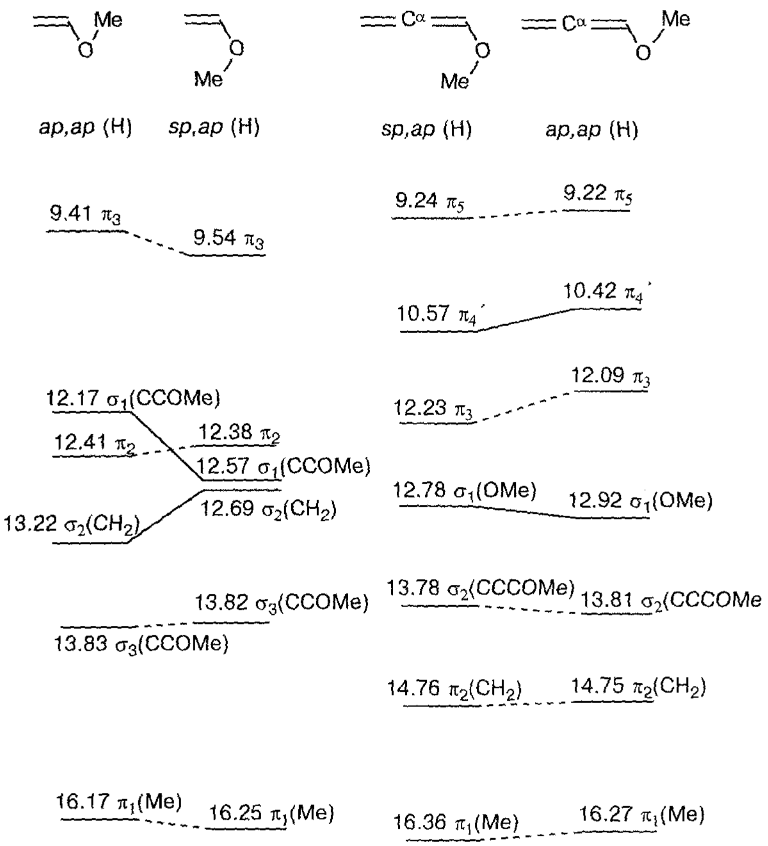


Fig. 2. Orbital energies of the occupied MOs of *ap* and *sp* conformers of methyl vinyl ether and allenyl methyl ether.

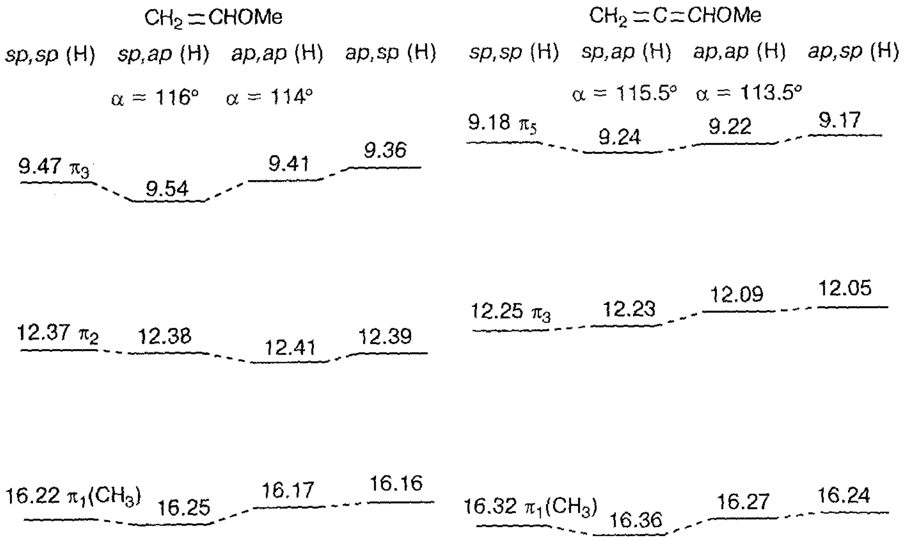


Fig. 3. Orbital energies of the occupied π-MOs of rotational isomers of allenyl methyl ether and methyl vinyl ether. Unstable *sp,sp* and *ap,ap* forms were calculated with a fixed torsion angle (θ(H) = 0°).

bital interactions are possible involving π and σ electron systems. The first involves the interaction between the π-MO of the allene fragment and the π-like orbitals of the methyl group,[9] and the second involves the interaction between the above-mentioned π′-MO and the σ-MO of the substituent. Interactions in the σ systems of two different methyl ethers were found to be quite similar (Fig. 2), except that, in methyl vinyl ether, the σ(CH_2)-MO of the terminal CH_2 group acts instead of the π′-MO. As can be seen from Fig. 2, the transformation of the *ap* form to the *sp* conformation is accompanied by some stabilization of the π_3 and π_1 levels and a decrease in the destabilizing four-center interactions in the σ system of the studied ethers.

A comprehensive analysis of the correlation of the π-MOs in allenyl methyl ether and methyl vinyl ether (Fig. 3) taking into account the unstable *sp,sp* and *ap,sp* conformations (the second code denotes the rotation of the methyl group), in which interactions between fragment orbitals of the methyl group and the π bond though space are impossible, indicates that a geometric factor, *viz.*, the variation in the C—O—C(α) bond angle, contributes indirectly to the π-electron stabilization of the *sp,ap* form. Hence, the second reason why the *sp,ap* conformers of allenyl methyl ether and methyl vinyl ether are more energetically stable than their *ap,ap* forms is the electronic destabilization of the σ system in the *ap,ap* forms due to the more favorable conditions for the overlap of the σ-MO of the substituent with an orbital of suitable symmetry of the terminal fragment of these ethers.

In order to see the consequences of the above-discussed interaction, we isolated the components E_A, $E_{AB}{}^{el}$, and $E_{AB}{}^R$ (one-center, two-center electrostatic, and two-center resonance components, respectively) of the total energy (E_t) of the rotational isomers of several ethers according to the procedure for partitioning the total energy from Refs. 13—15. The data in Table 5 indicate that the sign and the magnitude of the differences of the total energies of the *ap* and *sp* conformers (δ_r) are determined by the variations in their resonance components ($\delta_r\Sigma E_{AB}{}^R$). As expected, in $\Sigma E_{AB}{}^R$ the resonance energy component of the C(α)—O bond is most perturbed by rotational isomerization (Scheme 2, where (*a*) is allenyl methyl ether, (*b*) is allenyl alcohol, (*c*) is methyl vinyl ether, and (*d*) is vinyl alcohol).

Table 5. Variations of the total energy (E_t/eV) and some its components (E_A, $E_{AB}{}^{el}$, and $E_{AB}{}^R$/eV) caused by rotational isomerization

Compound	$\delta_r E_t$	$\delta_r\Sigma E_A$	$\delta_r\Sigma E_{AB}{}^{el}$	$\delta_r\Sigma E_{AB}{}^R$
CH_2=C=CHOH	0.178	−0.194	−0.166	0.206
CH_2=CHOH	0.137	−0.212	−0.091	0.259
CH_2=C=CHOMe	0.089	−0.268	0.057	0.414
CH_2=CHOMe	0.131	−0.199	−0.002	0.328

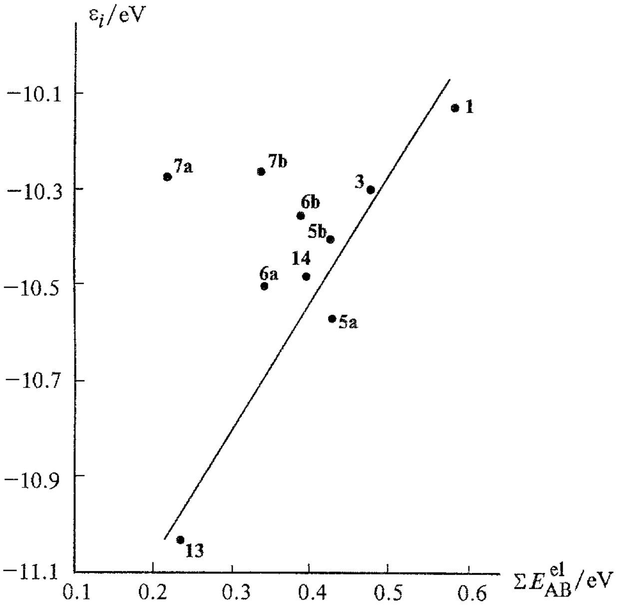


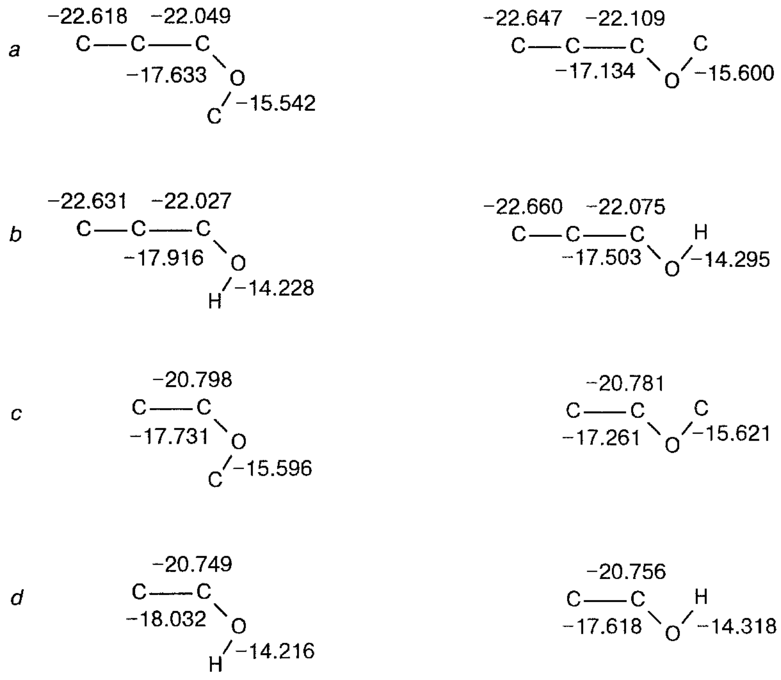
Fig. 4. Correlation between the orbital energies of allene π′-MOs and the energies of electrostatic interactions between nonbonded atoms of the fragment C(γ)—C(β)—C(α)XY (for the numbering of the compounds see Table 6).

The correlation between the orbital energies of the π′-MOs of allene derivatives and the energies of two-center electrostatic interactions of C(β, γ) atoms with

Table 6. Energies of the electrostatic interactions (E^{el}/eV) of nonbonded atoms of the CH_2=C=CH(XY) fragment in some allenes and orbital energies (ε_i/eV) of their π′-MOs

Compound	Substituent	X	Y	E^{el}/eV					$\Sigma E_{AB}{}^{el}$	ε_i
				C(γ)—C(α)	C(γ)—X	C(γ)—Y	C(β)—X	C(β)—Y		
1	CH_2Me (*ac*)	C	C	0.117	0.019	0.093	0.252	0.105	0.586	10.13
3	CH=CH_2 (*ap*)	C	C	0.098	0.030	0.091	0.281	−0.020	0.480	10.30
5a	OMe (*sp*)	O	C	0.030	0.010	0.027	0.224	0.140	0.431	10.57
5b	OMe (*ap*)	O	C	0.038	0.037	0.011	0.320	0.024	0.430	10.40
6a	OEt (*sp*)	O	C	0.030	0.013	0.010	0.227	0.065	0.345	10.50
6b	OEt (*ap*)	O	C	0.040	0.039	−0.001	0.329	−0.015	0.390	10.35
7a	OPr (*sp*)	O	C	0.027	0.021	−0.012	0.211	−0.029	0.218	10.27
7b	OPr (*ap*)	O	C	0.038	0.042	−0.016	0.333	−0.059	0.338	10.26
13	C≡N	C	N	0.070	0.010	−0.004	0.280	−0.120	0.236	11.03
14	CH_2Cl (*ac*)	C	Cl	0.126	−0.007	0.220	0.050	0.010	0.399	10.48

Scheme 2



heavy atoms of substituents is shown in Table 6 and Fig. 4. The theoretical results agree qualitatively with experimental data, thus supporting our conclusions.

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