Physical Chemistry

A quantum-chemical approach to the analysis of intramolecular interactions using the fragment orbitals and MNDO method. Calculations for vinyl fluoride and vinyl iodide

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A new quantum-chemical method for demarcation between the basic mechanisms of mutual influence of structural fragments in complex organic molecules (inductive effect, conjugation, *etc.*) and for assessment of their significance for particular physicochemical properties is proposed. The effects of different channels of intramolecular interaction on the molecular geometry and energy, charge distribution, and the molecular orbital structures and energies were considered taking vinyl halides as examples. In systems with an interfragment bond of high polarity, separation of the contribution of the inductive effect is to a great extent meaningless, while π-conjugation can be considered independently. The method allows a more valid interpretation of the results of quantum-chemical calculations in terms of theoretical organic chemistry.

Key words: semiempirical quantum-chemical calculations; AM1, MNDO, and PM3 methods; fragment orbitals, conjugation, inductive effect, vinyl halides.

Modern quantum-chemical methods have considerable computational opportunities and are widely used for calculations of the properties of particular molecules. At the same time, much less attention is paid to the interpretation of the results of quantum-chemical calculations in terms of such basic concepts used in chemistry as the chemical bonding, molecular structure, and mutual influence of structural fragments of a molecule. This is likely due to the fact that, physically, the quantum-mechanical description of a molecule regarded as a system of interacting electrons and nuclei requires no further interpretation and, hence, the above-mentioned chemical concepts seem to be unnecessary or even meaningless. However, these concepts are widely and successfully used in chemistry. Therefore, considering quantum chemistry as a division of chemical science rather than quantum mechanics, interpretation of the results of quantum-chemical calculations in terms of the above-mentioned basic chemical concepts is reasonable and even desirable. It would provide the possibility of using quantum chemistry not only for simply obtaining numerical data, thus considering it in essence as a

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particular form of computer experiment, but also for interpretation of the results of calculations in terms of theoretical chemistry.

In this work, we propose an approach which makes it possible to analyze the electronic structure and physicochemical properties of complex molecules in terms of the interaction between the orbitals of their radical fragments (FO). The use of the fragment orbitals in quantum-chemical calculations presents of course no innovation (see, *e.g.*, Refs. 1—10); on the other hand, it seems likely that such an approach has not been applied systematically to the analysis of intramolecular interactions in terms of chemical bonding, molecular structure, and mutual influence of structural fragments. A method, which is formally very similar to the approach proposed in this work, has been applied[6] to the analysis of the indications of the inductive and mesomeric effects in molecules (in particular, acrolein). Unfortunately, the method uses some approximations, which impose essential restrictions on the area of its application. For instance, no variational calculations for the molecular fragments are carried out; rather, preliminarily constructed hybrid orbitals are used, which to a great extent reduces the potentialities of the method in studying, *e.g.*, the influence of the effects under consideration on the molecular geometry. As far as we know, no studies on the development of this method have been reported.

Since in organic chemistry the mutual influence of structural fragments is usually considered qualitatively or, at best, semiquantitatively, it seems appropriate to use modern semiempirical quantum-chemical methods (e.g., the MNDO,[11] AM1,[12] and PM3[13] methods) as basic tools for our studies. For any one of them, it is an easy matter to write the expressions for the matrix elements of the Hartree—Fock operator in the FO basis for a molecule represented as comprising two radical fragments (I and II):

$$F_{ij}^{\mathrm{I,I}} = \varepsilon_i^0(\mathrm{I})\delta_{ij} + \sum_{\mathrm{B}\in\mathrm{II}} V_{ij,\mathrm{B}} + \sum_{k',l'\in\mathrm{II}} n_{k'l'}(ij|k'l') + \sum_{k,l\in\mathrm{I}} (n_{kl} - n_{kk}^0\delta_{kl})[(ij|kl) - 0.5(ik|jl)] = \varepsilon_i^0(\mathrm{I})\delta_{ij} + F_{ij}^{\mathrm{PolI}} + F_{ij}^{\mathrm{Pol2}},$$

$$F_{i'j'}^{\mathrm{II,II}} = \varepsilon_{i'}^0(\mathrm{II})\delta_{i'j'} + \sum_{\mathrm{B}\in\mathrm{I}} V_{i'j',\mathrm{B}} + \sum_{k,l\in\mathrm{I}} n_{kl}(i'j'|kl) + \sum_{k',l'\in\mathrm{II}} (n_{k'l'} - n_{k'k'}^0\delta_{k'l'})[(i'j'|k'l') - 0.5(i'k'|j'l')] = \varepsilon_{i'}^0(\mathrm{II})\delta_{i'j'} + F_{i'j'}^{\mathrm{PolI}} + F_{i'j'}^{\mathrm{Pol2}},$$

$$F_{ij'}^{\mathrm{I,II}} = \beta_{ij'} - 0.5\sum_{k\in\mathrm{I},l'\in\mathrm{II}} n_{kl'}(ik|jl') \qquad (1)$$

where the primed and unprimed indices refer to different fragments; $\varepsilon_i^0(\mathrm{I})$ and $\varepsilon_{i'}^0(\mathrm{II})$ are the energies of the ith and i'th FOs of isolated fragments I and II, respectively; n_{kk}^0 and $n_{k'k'}^0$ are the populations of the kth and k'th FOs in the isolated fragments, respectively; n_{kl}, $n_{k'l'}$, and $n_{kl'}$ are the elements of the density matrix of the molecule in the FO basis; $V_{ij,\mathrm{B}}$ and $V_{i'j',\mathrm{B}}$ are the matrix elements of the operator of the interfragment electron-core interaction (the indices given by capital letters refer to the nuclei and the indices given by small letters refer to the FOs); and $(ij|k'l')$, $(ij|kl)$, $(i'j'|k'l')$, and $(i'j'|kl)$ are the integrals of the inter- and intrafragment electron-electron interactions. The following notations are also used:

$$F_{ij}^{\mathrm{PolI}} = \sum_{k,l\in\mathrm{I}} (n_{kl} - n_{kk}^0\delta_{kl})[(ij|kl) - 0.5(ik|jl)],$$

$$F_{ij}^{\mathrm{Pol2}} = \sum_{\mathrm{B}\in\mathrm{II}} V_{ij,\mathrm{B}} + \sum_{k',l'\in\mathrm{II}} n_{k'l'}(ij|k'l'). \qquad (2)$$

The formulas for calculating the quantities $F_{i'j'}^{\mathrm{PolI}}$ and $F_{i'j'}^{\mathrm{Pol2}}$ are derived analogously to expressions (2).

The $\varepsilon_i^0(\mathrm{I})$, $\varepsilon_{i'}^0(\mathrm{II})$, n_{kk}^0, and $n_{k'k'}^0$ values, as well as the FO sets, are found from preliminary calculations of isolated radical fragments. The matrix elements of the operators of the electron-core and electron-electron interactions in the FO basis are calculated using the corresponding values found in the basis of atomic orbitals (AOs), which are specific to the computational scheme employed. For instance, the expression for the integrals of the electron-electron interaction has the form:

$$(ij|kl) = \sum_{p,q\in\mathrm{A},r,s\in\mathrm{B}} C_{ip}^0 C_{jq}^0 C_{kr}^0 C_{ls}^0 (pq|rs),$$

where the indices i, j, k, and l refer to the FO; the indices p, q, r, and s refer to the AOs; and C_{ip}^0, C_{jq}^0, C_{kr}^0, and C_{ls}^0 are the coefficients at the AOs in the FO. The self-consistent solution of the Hartree—Fock equation with the operator (1) gives a set of molecular orbitals (MOs) in the FO basis and the orbital energies. By setting particular terms in expression (1) equal to zero, we can try to separate the contributions, which to some extent correspond to such concepts as conjugation and the inductive effect, and to assess their significance for different properties of the molecule.

The approach outlined above was implemented using original software for the IBM PC written in the Fortran-90 programming language. The control module of the program allows calculations both including and excluding particular contributions to the Hartree—Fock operator (1) and any FO subsets. In this work, we used the MNDO semiempirical scheme[11] with the corresponding parametrization[14—16] and the "half-electron" approximation by Dewar[17] for radicals. Comparison with other semiempirical computational schemes will be given elsewhere. Calculations were carried out taking the molecules of vinyl fluoride (**1**) and vinyl iodide (**2**) as examples. Molecules **1** and **2** belong to the simplest systems with the double C=C bond and have substituents with strongly different electronegativities, for which one would expect large contributions of n,π-conjugation and the inductive effect. Hereafter, a vinyl halide molecule is represented as two radical fragments, $CH_2{=}CH^{\bullet}$ (Vin$^{\bullet}$) and Hal$^{\bullet}$, and the notation of the corresponding molecular orbital (MO) includes an indication of the FO which makes the major contribution to the MO, *e.g.*, the $\pi_{C=C}$ MO, $\pi^*_{C=C}$ MO, n^{π}_{Hal} MO (n^{π}_{Hal} is the halogen

orbital composed mainly of the contributions of the p-AOs of the same orientation as that of the π-FO of the Vin˙ radical), *etc.*

Let us consider the following channels of interfragment interaction:

1) the formation of an interfragment σ-bond by mixing a singly filled FO of a fragment with all FOs of the other fragment;

2) the inductive effect, *e.g.*, the mixing of the FOs of one fragment, accompanied by electron density redistribution caused by (i) the charge induced on the fragment at the formation of the interfragment chemical bond (this charge is first of all dependent on the energy difference between the singly filled FOs) and (ii) the charge distribution over the other fragment; these contributions are described by the F^{Pol1} and F^{Pol2} terms, respectively;

3) conjugation, *e.g.*, the mixing of doubly filled and vacant FOs of particular types (the π,π-, nπ-, nπ*-FO *etc.*) of both fragments.

The initial calculations involve merely the $F^{I,II}_{ij}$ matrix elements for the orbitals indicated in paragraph 1 and the resultant values are denoted as "Chm." Those resulting from calculations involving the F^{Pol1} and F^{Pol2} matrix elements are suitably denoted as "Ind," whereas the values calculated using the $F^{I,II}_{ij}$ matrix elements for the n- and σ-FOs are denoted as "Sgm" and those calculated using the $F^{I,II}_{ij}$ matrix elements for the π-, π- and π*-FOs are denoted as "Nπ" and "Nπ*" (nσ-, nπ-, and nπ*-conjugation, respectively). The contribution of particular channels to the value of a particular molecular parameter will be represented as a difference. For instance, the changes in the $\pi_{C=C}$-orbital energy relative to the Vin˙ radical energy due to (i) the formation of the interfragment chemical bond, (ii) the inductive effect, (iii) nσ-conjugation, (iv) nπ-conjugation, and (v) nπ*-conjugation will be respectively denoted as

$$\Delta\varepsilon_\pi(\mathrm{Chm}) = \varepsilon_\pi(\mathrm{Chm}) - \varepsilon_\pi(\mathrm{Vin}),$$

$$\Delta\varepsilon_\pi(\mathrm{Ind}) = \varepsilon_\pi(\mathrm{ChmInd}) - \varepsilon_\pi(\mathrm{Chm}),$$

$$\Delta\varepsilon_\pi(\mathrm{Sgm}) = \varepsilon_\pi(\mathrm{ChmSgm}) - \varepsilon_\pi(\mathrm{Chm}),$$

$$\Delta\varepsilon_\pi(\mathrm{N}\pi) = \varepsilon_\pi(\mathrm{ChmN}\pi) - \varepsilon_\pi(\mathrm{Chm}),$$

and

$$\Delta\varepsilon_\pi(\mathrm{N}\pi^*) = \varepsilon_\pi(\mathrm{ChmN}\pi^*) - \varepsilon_\pi(\mathrm{Chm}).$$

Such an approach (Scheme 1) should be considered to be preferable, since in this case the terms of "mixed nature" (hereafter, mixed terms) will of course make the smallest contributions to the calculated values. On the other hand, we will also use other computational schemes and, in particular, Scheme 2, which does not separate the contributions of the formation of the interfragment chemical bond and that of the inductive effect:

$$\Delta\varepsilon_\pi(\mathrm{ChmInd}) = \varepsilon_\pi(\mathrm{ChmInd}) - \varepsilon_\pi(\mathrm{Vin}),$$

$$\Delta\varepsilon_\pi(\mathrm{Sgm}) = \varepsilon_\pi(\mathrm{ChmIndSgm}) - \varepsilon_\pi(\mathrm{ChmInd}),$$

$$\Delta\varepsilon_\pi(\mathrm{N}\pi) = \varepsilon_\pi(\mathrm{ChmIndN}\pi) - \varepsilon_\pi(\mathrm{ChmInd}),$$

$$\Delta\varepsilon_\pi(\mathrm{N}\pi^*) = \varepsilon_\pi(\mathrm{ChmIndN}\pi^*) - \varepsilon_\pi(\mathrm{ChmInd}).$$

It is possible to assess the extent to which the channels can be considered independent by comparing the sum of the contributions, Add (*e.g.*,

$$\mathrm{Add} = \Delta\varepsilon_\pi(\mathrm{ChmInd}) + \Delta\varepsilon_\pi(\mathrm{Sgm}) + \Delta\varepsilon_\pi(\mathrm{N}\pi) + \Delta\varepsilon_\pi(\mathrm{N}\pi^*))$$

with the Δ(Scf) value obtained using the results of the MNDO calculations for the entire molecule and for a particular fragment (*e.g.*, $\Delta(\mathrm{Scf}) = \varepsilon_\pi(\mathrm{MNDO}) - \varepsilon_\pi(\mathrm{Vin}^\cdot)$). It should be noted that the first equalities in Schemes 1 and 2 characterize the choice of the reference, which is dictated by chemical considerations and by salient features of the property in question. Further, we will use both the radical fragments and the "molecules-fragments," namely, the ethylene and methyl halide molecules.

Let us analyze how different channels of intramolecular interaction affect the molecular geometry. To this end, we will optimize the geometry of the fragment under study or the length of the interfragment chemical bond only at the desired level of approximation using the molecular geometry obtained from calculations with full optimization as initial approximation. Here, the ethylene and methyl halide molecules calculated with full geometry optimization will serve as references.

Calculations performed for molecule **2** according to Scheme 1 showed that the above-mentioned channels of intramolecular interaction are not independent since their contributions to the changes in the C=C and C—I bond lengths are less than the sum of the mixed terms. For molecule **1**, this nonadditivity is more pronounced: optimization of the C—F bond length (the Chm version) leads in fact to the bond cleavage, whereas simultaneous consideration of the inductive effect (the ChmInd version) leads to an R_{C-F} value which is only ~0.1 Å longer than that obtained from complete MNDO calculations. The situation for the C=C bond in molecule **1** is much the same as for molecule **2**.

Table 1. Changes in the C=C and C—Hal bond lengths (ΔR) in the vinyl fluoride (**1**) and vinyl iodide (**2**) molecules caused by different channels of intramolecular interaction (calculated according to Scheme 2)

Interaction channel	ΔR/Å			
	Molecule **1**		Molecule **2**	
	C=C	C—F	C=C	C—I
ChmInd(mol)*	0.023	0.079	0.002	0.005
Sgm	−0.012	−0.081	−0.001	−0.041
Nπ*	0.006	−0.032	0.002	−0.016
Add	0.017	−0.034	0.003	−0.052
ΔScf(mol)*	0.016	−0.023	0.002	−0.048
ΔScf − Add	−0.001	0.011	−0.001	0.004

* All values are given relative to the corresponding bond lengths in the ethylene and MeHal molecules.

Table 2. Changes in the formation energies (ΔE) of the vinyl fluoride (**1**) and vinyl iodide (**2**) molecules caused by different channels of intramolecular interaction (calculated according to Scheme 2)

Interaction channel	ΔE/kcal mol^{-1}	
	Molecule **1**	Molecule **2**
ChmInd(rad)*	−83.7	−66.8
Sgm	−34.2	−9.7
Nπ^*	−14.7	−3.6
Add	−132.6	−80.1
ΔScf(rad)*	−130.6	−79.4
ΔScf − Add	2.0	0.7

* All values are given relative to the corresponding energies of the Vin$^\cdot$, F$^\cdot$, and I$^\cdot$ radicals.

The changes in the optimized C=C and C—Hal bond lengths in molecules **1** and **2**, which are due to different channels of intramolecular interaction (calculations according to Scheme 2) are listed in Table 1. As should be expected, n,π-conjugation makes no contribution; hence the corresponding row was not included in Table 1. As can be seen, n,π^*-conjugation causes a lengthening of the C=C double bond and an appreciable shortening of the C—Hal ordinary bond, the effect for molecule **1** being more pronounced than for molecule **2**. It should be noted that the contributions of n,π^*-conjugation calculated according to Scheme 1 are close to those listed in Table 1, whereas the contributions of n,σ-conjugation (Sgm) differ appreciably.

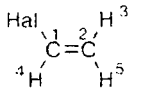
This suggests that the mixed terms are mainly due to the changes in the character of the interfragment chemical bond (Chm), the inductive effect (Ind), and n,σ-conjugation (Sgm), whereas the contribution of n,π^*-conjugation can be considered to some extent independent (especially for molecule **2**). For the C—Hal interfragment chemical bond, this appears to be pronounced to an extent that separation of independent interaction channels except for, probably, different types of π^*-conjugation seems to be meaningless. This is consistent with the interpretation of the inductive effect as a result of the electric field effect of one molecular fragment on the other fragment, but not on the interfragment chemical bond (see, *e.g.*, Refs. 18, 19).

The results discussed below refer to the molecular structures of vinyl halides, which were obtained after full geometry optimization in complete MNDO calculations. Unlike the calculations carried out above, hereafter the radical fragments (Vin$^\cdot$, F$^\cdot$, and I$^\cdot$) are used as references instead of the ethylene and methyl halide molecules, because in this case the interpretation of results is apparently much easier.

As for the bond lengths, calculations of the contributions of different channels of intermolecular interaction to the formation energies of the vinyl halide molecules, carried out according to Scheme 1, also revealed an important role of the mixed terms. Therefore, in Table 2 we present the results obtained using Scheme 2, which is more appropriate in this case. It should be noted that for both compounds the contributions of n,π^*-conjugation calculated using the two schemes differ appreciably. This is due to the fact that the nonadditivity of the interaction channels under study affects the energy parameters of the molecules more pronouncedly than their geometries. On the other hand, the energy effect of n,π^*-conjugation for molecule **1** is much stronger than for molecule **2** (see Table 2). As should be expected, the contributions of n,π-conjugation are very small; because of this, they are not listed in Table 2.

Table 3 lists the atomic charges of molecules **1** and **2** found 1) assuming the noninteracting radical fragments, 2) taking into account the formation of the interfragment chemical bond, 3) as in the preceding case with inclu-

Table 3. Calculated total, σ-, and π-charges (q) on the atoms of vinyl fluoride (**1**) and vinyl iodide (**2**) molecules



Atom	Charge type	q/au							
		Isolated fragment		Chm		ChmInd		Scf	
		1	**2**	**1**	**2**	**1**	**2**	**1**	**2**
C(1)	σ	−0.152	−0.143	0.129	0.042	0.080	−0.188	0.139	−0.183
	π	0.070	0.070	0.070	0.070	−0.039	−0.103	−0.029	−0.107
	Total	−0.082	−0.073	0.199	0.113	0.041	−0.291	0.110	−0.290
C(2)	σ	−0.061	−0.066	−0.077	−0.089	−0.095	−0.081	−0.084	−0.080
	π	−0.070	−0.070	−0.070	−0.070	0.039	0.103	−0.030	0.088
	Total	−0.131	−0.136	−0.147	−0.160	−0.056	0.022	−0.113	0.008
Hal	σ	0	0	−0.247	−0.093	−0.248	0.084	−0.250	0.090
	π	0	0	0	0	0	0	0.059	0.019
	Total	0	0	−0.247	−0.093	−0.248	0.084	−0.191	0.110
H(3)	Total	0.061	0.058	0.061	0.053	0.074	0.054	0.063	0.051
H(4)	Total	0.092	0.088	0.071	0.036	0.108	0.076	0.074	0.073
H(5)	Total	0.059	0.063	0.063	0.051	0.082	0.055	0.057	0.049

sion of the inductive effect, and 4) in complete MNDO calculations. As can be seen, the formation of the C—Hal bond leads to qualitatively similar charge distribution for both molecules. Since the energy of the singly filled orbital of the Vin$^{\bullet}$ radical is higher than that of the halogen atom, a deficiency of the σ-electron density appears on the C_α atom and an excess σ-electron density appears on the halogen atom; at the same time, the π-electron distribution remains virtually unchanged. Quantitative differences can be due to the greater electronegativity of F (according to MNDO calculations, the open-shell energies of the F and I atoms and the Vin$^{\bullet}$ radical are −9.9, −6.9, and −5.1 eV, respectively).

At the same time, the inductive effect affects the charge distributions in molecules **1** and **2** in strongly different manners. In the former case, it, on the one hand, leaves the atomic charge of F virtually unchanged, and, on the other hand, favors the delocalization of the large positive charge on the C_α atom over the entire vinyl fragment (this charge appears due to the formation of the C—F chemical bond). In the latter case, this effect is responsible for the changes in the signs of the atomic charges of I and C_α and favors both the concentration of the negative charge on the C_α atom and the nearly uniform distribution of the positive charge over the other atoms of the vinyl group and the I atom. This difference between molecules **1** and **2** is most likely due to the relatively small energy difference between the singly filled FOs of the Vin$^{\bullet}$ radical and I atom (see above) and to the much wider energy gap between the singly and doubly filled FOs of the F atom compared to the I atom (~6 *vs.* ~4 eV, respectively). The inclusion of the inductive effect (the F^{Pol1} and F^{Pol2} terms) leads to the mixing of the orbitals. As a result, the energy of the singly filled FO of the I atom increases and appears to be higher than that of the singly filled FO of the Vin$^{\bullet}$ radical, which is responsible for the above-mentioned qualitative changes in the σ-electron density distribution over the I and C_α atoms.

The displacements of the σ- and π-electron densities in the vinyl halide molecules due to n,σ- and n,π-conjugation, calculated according to a modified Scheme 2, are shown in Fig. 1. The modification included simultaneous consideration of the mixing of the lone electron pair (LEP) orbital of the halogen atom with the π- and π*-orbitals of the vinyl group (separation of the contributions of n,π- and n,π*-conjugation is of no interest in discussing the charge distribution). As can be seen, the displacement patterns for molecules **1** and **2** are qualitatively similar, but quantitative changes in the former case are much more pronounced than in the latter. Comparison with the data listed in Table 3 shows

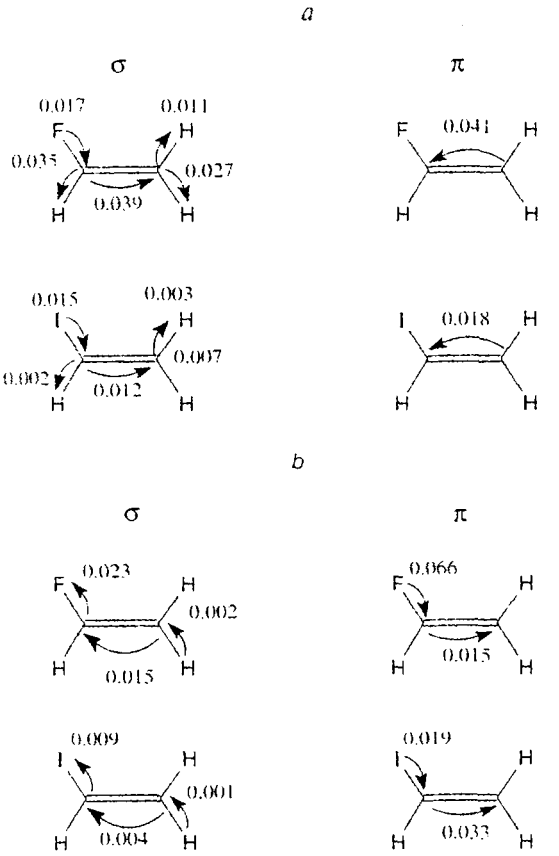


Fig. 1. Displacements of the σ- and π-electron densities in the vinyl fluoride (**1**) and vinyl iodide (**2**) molecules caused by n,σ-conjugation (*a*) and n,π-conjugation (*b*).

Table 4. Energy shifts (Δε/eV) of the orbitals of molecules **1** and **2** due to different channels of intramolecular interaction (calculated according to Scheme 2)

Interaction channel	$\Delta\varepsilon_\pi$		$\Delta\varepsilon_{\pi^*}$		$\Delta\varepsilon_{n\pi}$		$\Delta\varepsilon_n$	
	1	**2**	**1**	**2**	**1**	**2**	**1**	**2**
ChmInd(rad)*	−0.87	−0.82	−0.87	−0.81	1.35	0.01	1.30	0.09
Sgm	−0.08	−0.10	−0.08	−0.01	−0.41	−0.11	1.52	0.02
n,π	0.67	0.85	0.00	0.00	−0.67	−0.85	0.01	0.00
n,π*	0.08	0.10	0.37	0.09	−0.52	−0.17	−0.37	−0.06
Add	−0.20	0.03	−0.58	−0.81	−0.25	−1.12	2.46	0.05
ΔSCF(rad)*	−0.12	0.03	−0.62	−0.82	−0.48	−1.15	2.62	0.02
ΔSCF − Add	0.08	0.00	−0.04	−0.01	−0.23	−0.03	0.16	−0.03

* All values are given relative to the corresponding energies of the radical fragment orbitals.

that these types of conjugation act to some extent similarly to the inductive effect. For molecule **1**, they cause a substantial decrease in the negative charge on the F atom and an increase in both the positive charge on the C_α atom and the negative charge on the C_β atom. For molecule **2**, the positive atomic charge of I increases slightly, while that of C_β decreases. As can be seen in Fig. 1, n,π*-conjugation plays a key role for both molecules. It should be noted that the modified Scheme 2 (see above) used in this Section allows a satisfactory separation of the contributions of n,σ- and n,π-conjugation in the vinyl halide molecules, namely, the deviation from additivity was found to be $\sim 10^{-3}$ for vinyl fluoride and $\sim 10^{-4}$ for vinyl iodide.

Table 4 lists the energy shifts of the n- and π-orbitals of the vinyl halide molecules calculated according to Scheme 2. It should be noted that the contributions of n,π- and n,π*-conjugation calculated according to Scheme 1 are not much different from those obtained using Scheme 2, whereas the contributions of n,σ-conjugation (Sgm) calculated according to the two schemes differ appreciably. As in the case of geometry calculations, here the mixed terms are mainly due to the formation of the interfragment chemical bond (Chm), the inductive effect (Ind), and n,σ-conjugation (Sgm); at the same time, n,π- and n,π*-conjugation are to a certain extent independent (especially for molecule **2**).

Despite the fact that separate quantitative characterization of the influence of the formation of the interfragment chemical bond and the inductive effect for the systems under study is impossible, we believe that calculations according to Scheme 1 can allow some qualitative estimates. We found that the former factor has almost no effect on both the π-orbital energies of the vinyl fragment and the n-orbital energies of the F atom and substantially decreases the energy of the LEP orbital of the I atom, which is oriented in the plane of molecule **2**; this is accompanied by the formation of a delocalized MO with large contributions of the singly filled FOs of the Vin˙ radical and I atom. This difference between the fluoro and iodo derivatives is likely due to the fact that the n-orbital of the I atom lies on the energy scale ~5 eV closer to the singly filled FO of the Vin˙ radical than the corresponding orbital of the F atom. The inductive effect causes a substantial decrease in the $\pi_{C=C}$- and $\pi^*_{C=C}$-orbital energies in both molecules. At the same time, the n-orbital energies in the fluoro derivative increase substantially, whereas in vinyl iodide the n_π-orbital energy remains virtually unchanged, while the energy of the second LEP orbital increases appreciably. Additionally, the energy shift of the last-named orbital due to the formation of the interfragment bond (see above) is nearly compensated and the localization degree of this orbital increases from ~50% to ~90%.

Analysis of the peculiarities of the σ-electron density distribution in the vinyl halide molecules, found in calculations carried out taking into account only the formation of the C—Hal interfragment chemical bond, provides a simple and easy explanation for these manifestations of the inductive effect. As was mentioned above (see Table 3), a substantial decrease in the σ-electron density in the region of the C=C bond and its concentration on the F atom occur in molecule **1**, while only a slight excess of the σ-electron density, which has little effect on the n-orbital energies, appears on the I atom in molecule **2**. On the other hand, the σ-electron density in the region of the C=C bond decreases appreciably, though to a smaller extent than for molecule **1**. This charge redistribution apparently corresponds to the above-mentioned changes in the π- and n-orbital energies found from calculations with inclusion of the inductive effect.

As can be seen from the data listed in Table 4, n,π-conjugation affects strongly the corresponding orbital energies of both systems, the effect for molecule **2** being much stronger. Unlike this, n,π*-conjugation is pronounced for molecule **1** and insignificant for **2**. It seems likely that the closeness of the energies of the π-FO of the Vin˙ radical and the n_π-FO of the I atom is the decisive factor in the latter case, whereas for **1** the large energy difference between the $\pi_{C=C}$ and n_π^F FOs is to a great extent compensated by the appreciable displacement of the σ-electron density from the vinyl group to the F atom (see above). At the same time, n,σ-conjugation has almost no effect on the energies of these orbitals of molecule **2**, but causes a substantial decrease in the energy of the n_π-orbital and analogous increase in the energy of the other LEP orbital for **1**. Since, according to calculations, the inclusion of n,σ-interaction has virtually no effect on the structure of the n_π-orbital, changes in its energy can be explained only by a small decrease in the electron density on the F and C_α atoms (see Table 3). In contrast to this, the n-orbital, which is oriented in the plane of molecule **1**, is strongly mixed with several σ-FOs of the Vin˙ radical. The energies of these σ-FOs are fairly close to that of the n-orbital; because of this, the energy differences between the new, nearly completely delocalized MOs and the n-orbital of the F atom appear to be appreciable. Since the LEP orbital energies of the I atom are much higher, no similar effects should be observed for molecule **2** (see Table 4).

The results obtained show that the approach proposed in this work provides the possibility for detailed analysis of different mechanisms of the mutual influence of structural fragments in polyatomic molecules. Taking vinyl halides as examples, we assessed the significance of different types of conjugation and the inductive effect for the equilibrium molecular geometries, formation energies, charge distributions, and the MO structures and energies. In principle, this approach allows analysis of the dependences of any physicochemical quantities, whose values can be calculated using semiempirical quantum-chemical methods based on the Hartree—Fock approximation, on the molecular structure in terms of theoretical organic chemistry. Studies on the reactivity of molecules using this method in the framework of, *e.g.*,

the frontier orbital model also seem to be natural. In some cases (*e.g.*, in studying molecules with an interfragment bond of high polarity), the investigators can face problems; however, one should keep in mind that sometimes separation of particular contributions appears to be meaningless. We believe that the implementation of this approach in the framework of the existing *ab initio* methods, which are based on the Hartree—Fock approximation, should not present serious problems; however, the possibility and utility of combining it with the manybody approaches are still to be clarified.

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