Peculiarities of the effects of trifluoromethyl and alkoxycarbonyl groups on the structure and reactivity of acrylates

1. Monosubstituted acrylates

Yu. A. Borisov, A. F. Kolomiets, and A. V. Fokin*[†]

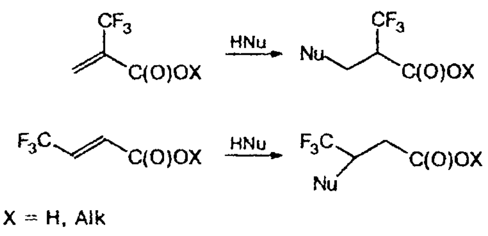
A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: yabor@ineos.ac.ru

Ab initio quantum-chemical calculations of molecules of CF_3-substituted acrylates and their non-fluorinated analogs were carried out by the restricted Hartree—Fock (RHF) method and at the second-order Møller—Plesset (MP2) level of perturbation theory using the 6-31G* basis set with full geometry optimization. Peculiarities of their molecular and electronic structure were revealed and the dipole moments, the polarizability and first molecular hyperpolarizability tensors, harmonic vibrational frequencies, electrostatic potentials, and local electron densities in the vicinity of the carbon atoms of the C=C bond were calculated. It was shown that CF_3-substituted acrylates are conjugated systems similar to their nonfluorinated analogs. Peculiarities of the structure and properties of CF_3-substituted acrylates are explained by p—π-interaction between the CF_3 group and the conjugated system.

Key words: *ab initio* calculations; methylacrylate; α- and β-methyl acrylates; α- and β-trifluoromethyl acrylates; molecular and electronic structure; polarity; polarizability; first molecular hyperpolarizability; conjugation.

Theoretically, CF_3-substituted acrylic acids and their esters were considered previously[1—8] only as convenient models for a qualitative study of the influence of two strong electron-acceptor groups (CF_3 and COOR) on the polarization of the C=C bond and the sequence of addition of various reagents to this bond. By now, it has been shown that the introduction of the CF_3 substituent in α- or β-position with respect to the carboxylic or alkoxycarbonyl group of the acrylic system does not change the β-orientation of the addition, characteristic of nonfluorinated analogs (Scheme 1).

Scheme 1



X = H, Alk

The established[4—8] regiospecificity of β-addition of hydrogen halides and ammonia[4—6] and also thiol compounds[7,8] to β-CF_3-substituted acrylic systems indicates that the trifluoromethyl substituent has a much weaker effect on the polarization of the C=C bond than the carboxylic and alkoxycarbonyl groups.

At the same time, the introduction of the CF_3 group into the acrylic system results in a substantial change in the reactivity type of the latter.[1—8] For instance, α-trifluoromethylacrylic acid and its esters are the most active acrylic compounds. Under mild conditions (at T below 20 °C) they add hydrogen halides, water, and alcohols[1] and exothermically react with thiol acids.[7,8] When moderately heated, they react with thiols,[7,8] ureas, thioureas,[2] and other weak nucleophiles. The abnormally high electrophilicity of the C=C bond in these systems manifests itself as the ability to compete with the C=O bond of the carboxylic group in reactions with lithium aluminum hydride and organometallic compounds.[3]

On the contrary, β-trifluoromethylacrylic acid and its esters are examples of the most inert compounds of the acrylic series. They do not react with hydrogen halides and nucleophilic reagents under standard conditions. In the absence of catalyst, they add ammonia[4—6] and thiol acids[7,8] only after prolonged heating to 100—120 °C. They undergo thiolation with alkanethiols and arenethiols only if the reaction is catalyzed by an acid[7] or base.[8] Addition of HBr also occurs under severe conditions[5] where homolysis of the H—Br bond is possible and the reaction can occur according to a free-radical mechanism.

[†] Deceased.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 652—657, April, 1999.

Table 1. Geometric parameters and total energies of molecules MA, **1a**,**b**, and **2a**,**b** calculated by the HF/6-31G* method (the results of MP2/6-31G* calculations are given in parentheses)

Parameter	MA	**1a**	**2a**	**1b**	**2b**
			Bond length/Å		
1—2	1.319 (1.340)	1.322 (1.343)	1.322 (1.342)	1.320 (1.339)	1.316 (1.338)
1—10	1.073 (1.084)	1.072 (1.083)	1.076 (1.088)	1.072 (1.083)	1.073 (1.085)
1—11	1.075 (1.085)	1.075 (1.086)	—	1.072 (1.083)	—
1—12	—	—	1.499 (1.495)	—	1.496 (1.490)
2—3	1.484 (1.481)	1.495 (1.489)	1.480 (1.476)	1.494 (1.491)	1.489 (1.482)
2—11	—	—	1.075 (1.087)	—	1.073 (1.085)
2—12	1.074 (1.086)	1.506 (1.501)	—	1.507 (1.503)	—
3—4	1.190 (1.223)	1.191 (1.224)	1.191 (1.223)	1.187 (1.220)	1.188 (1.222)
3—5	1.325 (1.356)	1.325 (1.356)	1.327 (1.359)	1.321 (1.352)	1.321 (1.353)
12—13	—	1.083 (1.092)	1.083 (1.093)	1.326 (1.355)	1.319 (1.350)
12—14	—	1.084 (1.093)	1.087 (1.095)	1.319 (1.348)	1.323 (1.354)
12—15	—	1.084 (1.093)	1.087 (1.095)	1.319 (1.348)	1.323 (1.354)
			Bond angle/deg		
1—2—3	124.3 (124.1)	121.0 (121.2)	124.4 (124.4)	122.8 (123.5)	123.6 (123.4)
10—1—11	117.2 (117.6)	117.1 (117.6)	—	117.7 (118.3)	—
10—1—12	—	—	116.5 (117.3)	—	114.7 (115.6)
3—2—12	113.7 (114.0)	114.9 (114.7)	—	115.7 (115.2)	—
3—2—11	—	—	113.7 (114.1)	—	114.2 (114.9)
2—3—4	122.9 (123.7)	122.9 (123.5)	123.1 (123.9)	123.5 (124.0)	122.4 (123.3)
			Total energy (au)		
E_{tot}	−304.6798 (−305.5340)	−343.6980 (−344.7066)	−343.7062 (−344.7065)	−640.2975 (−641.7861)	−640.3010 (−641.7886)

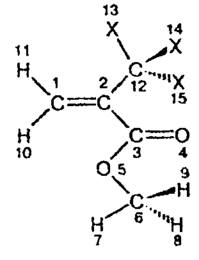
It should be noted that the ability of nonfluorinated acrylic compounds to add at the C=C bond monotonically decreases on going from acrylic acid to methacrylic acid and further to crotonic acid. In this case their reactivity is of the same type: all these compounds add hydrogen halides (HCl, HBr), thiol acids, ammonia, and primary and secondary amines under mild conditions in the absence of catalyst, and, if the reaction is catalyzed by a base, they add water, alcohols, and thiols.[9,10]

Such unusual peculiarities of the reactivity of fluorine-containing acrylic acids are undoubtedly due to specific effects of carboxylic (alkoxycarbonyl) and CF_3 groups on the state of the C=C bond in the conjugated system of these compounds.

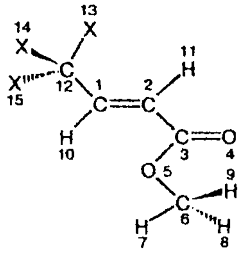
Table 2. Effective charges (q_i) on the atoms of molecules MA, **1a**,**b**, and **2a**,**b** calculated by the RHF/6-31G* method

Atom	q_i (e)				
	MA	**1a**	**2a**	**1b**	**2b**
C(1)	−0.35	−0.39	−0.11	−0.36	−0.31
C(2)	−0.25	−0.05	−0.31	−0.28	−0.27
C(3)	0.79	0.81	0.81	0.85	0.81
O(4)	−0.58	−0.58	−0.59	−0.55	−0.56
H(10)	0.22	0.22	0.22	0.24	0.27
H(11)	0.20	0.19	0.22	0.24	0.26
C(12)	0.22(H(12))	−0.49	−0.52	1.20	1.13
X(13)	—	0.17	0.18	−0.38	−0.36
X(14)	—	0.19	0.18	−0.36	−0.36
X(15)	—	0.19	0.18	−0.36	−0.36

This work is dedicated to the analysis of these peculiarities using a comparative study of the molecular and electronic structure, the dipole moments, and polarizability of methylacrylate (MA), methylmethacrylate (**1a**), methylcrotonate (**2a**), methyl-α-trifluoromethylacrylate (**1b**), and methyl-γ,γ,γ-trifluorocrotonate (**2b**) molecules, as well as the electronic state of their reaction centers. The structures of compounds **1a**,**b** and **2a**,**b** and the numbering of atoms are shown below.



1a,b



2a,b

X = H (**a**), F (**b**)

Calculation procedure

Ab initio calculations were performed by the restricted Hartree—Fock (RHF) method[11] and at the second-order Møller—Plesset (MP2) level of perturbation theory[12] in the 6-31G* basis set with full geometry optimization using the GAMESS [13] and GAUSSIAN-94 [14] programs on a CRAY J-90 supercomputer (Berkeley, California, USA). Selected param-

Table 3. Dipole moments (μ/D) and their components (μ_X/D, μ_Y/D, μ_Z/D) and the elements of polarizability (α, au) and first molecular hyperpolarizability (β, au) tensors of molecules MA, **1a,b**, and **2a,b** calculated by the RHF/6-31G* method

Molecule	μ	μ_X	μ_Y	μ_Z	α_{XX}	α_{YX}	α_{ZX}	α_{YY}	α_{YZ}	α_{ZZ}
MA	2.46	−0.65	2.38	0.00	54.28	−7.57	0.00	51.66	0.00	24.62
1a	2.05	−2.00	0.46	0.01	68.52	1.96	0.00	58.64	0.05	33.85
2a	2.89	−2.86	0.39	0.00	73.00	9.29	−0.01	58.44	0.01	34.50
1b	4.51	−3.58	2.74	0.00	66.28	2.22	0.00	57.37	0.00	34.07
2b	2.71	−0.54	2.66	0.00	69.89	7.56	0.00	56.89	−0.01	34.56
	β_{XXX}	β_{YXX}	β_{ZXX}	β_{XYY}	β_{YYY}	β_{ZYY}	β_{XZZ}	β_{YZZ}	β_{ZZZ}	
MA	−36.44	7.19	0.00	21.71	−58.98	0.03	−21.88	11.20	−0.03	
1a	56.27	−33.37	−0.33	2.74	−15.76	0.00	−43.55	−8.00	0.10	
2a	44.68	−53.03	−0.07	−57.51	−33.03	0.02	10.72	−7.25	0.01	
1b	96.31	−32.94	0.00	−3.46	−43.81	−0.01	−14.50	−14.83	0.05	
2b	6.19	−44.91	0.07	−27.81	−40.58	0.02	−24.78	−14.90	−0.03	

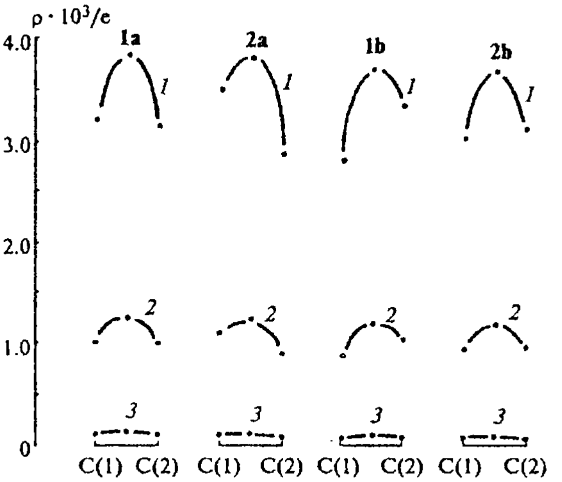


Fig. 1. Change in the electron density ρ in molecules **1a,b** and **2a,b** along the lines connecting the projections of the nuclei of the C(1) and C(2) atoms on the planes parallel to the molecular plane. The separations between the planes are 1.7 (*1*), 2.0 (*2*), and 2.5 Å (*3*).

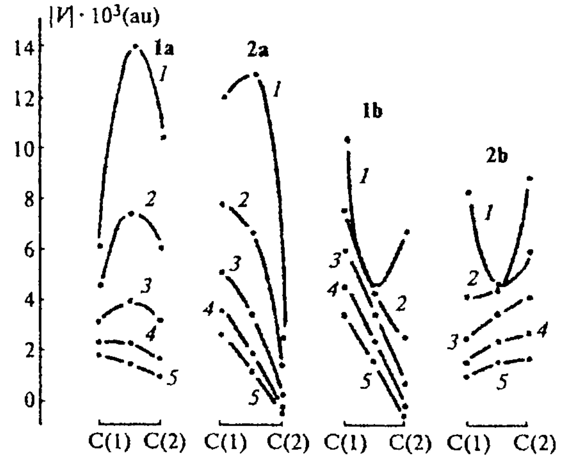


Fig. 2. Change in the electrostatic potentials *V* along the lines connecting the projections of the nuclei of the C(1) and C(2) atoms on the planes parallel to the molecular plane. The separations between the planes are 2.0 (*1*), 2.5 (*2*), 3.0 (*3*), 3.5 (*4*), and 4.0 Å (*5*) (the *V* values for **1a** and **2a** are negative, and those for **1b** and **2b** are positive).

eters characterizing the structure of the molecules under study are listed in Table 1. The effective charges on the atoms, dipole moments of the molecules, and the components of the corresponding polarizability and the first molecular hyperpolarizability tensors are listed in Tables 2 and 3. Characteristics of the electronic state of the C=C bond are given in Table 4 and in Figs. 1 and 2.

Results and Discussion

The structures of acrylates **1a,b** and **2a,b** shown above correspond to global energy minima and all molecular skeletons are planar. The CF_3 group in compounds **1b** and **2b** is oriented in such a way that one of the fluorine atoms (F(13)) lies in the molecular plane, while the other two fluorine atoms (F(14) and F(15)) lie in a plane orthogonal to the former, symmetrically with respect to the C(1)=C(2) bond. Such an arrangement of CF_3 substituents is rigidly fixed: the energy barrier to rotation about the C—C(12) bond exceeds 2 kcal mol^{-1}. In calculations of polarizability and hyperpolarizability of the molecules it was assumed that the nucleus of the C(1) atom is at the origin of the Cartesian system, the *X* axis of which coincided with the axis of the C(1)—C(2) bond, the *Y* axis lay in the molecular plane, and the *Z* axis lay in the orthogonal plane.

From Table 1 it follows that only in CF_3-substituted acrylates is the C=C bond length close to that of ethylene.*

The lengths of the C—H bonds at the C(1) and C(2)

The lengths of the C=C and C—H bonds in the ethylene molecule calculated by the HF/6-31G and MP2/6-31G* methods are equal to 1.317, 1.076 and 1.336, 1.085 Å, respectively. The values obtained by the MP2/6-31G* method are very close to experimental ones.

atoms correspond to their s-type (as in ethylene). In structures **1a**, **2a**, and even in MA the s-type of the C=C bond is somewhat lower than in ethylene.

In the molecules of all compounds under study the bond angles at the C=C bond are appreciably smaller than in the ethylene molecule (by 1.7—5.1° at the C(1) atom and by 4.4—6.0° at the C(2) atom). This indicates that the C=C bond participates in the conjugation with the substituents; an appreciably shorter distance between the substituents at the C(2) atom compared to that for the substituents at the C(1) atom suggests that conjugation is maximum between the C=C bond and the COOMe group and that all compounds under study have a conjugated system of C=C—C=O atoms. At the same time it is reasonable to assume the existence of direct polar conjugation between the vicinal CF_3 and COOMe groups at the C=C bond in molecule **2b** with a highly symmetric arrangement of substituents (see Table 1). This is somewhat less pronounced for the derivative **2a**, containing vicinal Me and COOMe groups at the C=C bond.

The conjugated system of C=C—C=O atoms in the compounds studied is also characterized (see Table 1) by C(2)—C(3) bond lengths (1.476—1.491 Å) approaching the C_{sp2}—C_{sp2} bond length (1.47 Å), shortened C=O bond (1.222—1.224 Å), and the C(2)—C(12) bonds of length 1.501 to 1.503 Å in **1a** and **1b** (*cf.* the C_{sp3}—C_{sp2} bond length, 1.51 Å), as well as by close values of the C(1)—C(2)—C(3) and C(2)—C(3)—O(4) angles, which provide almost parallel arrangement of the C=C and C=O bonds in the molecules (the deviation for **1b** and **2a,b** lies in the range 0.1 to 0.5° and is 1.9° for **1a**). The C(1)—C(12) bonds in derivatives **2a** and **2b** are appreciably shorter (1.490—1.495 Å) than the C_{sp3}—C_{sp2} bond, which confirms the assumption of a direct polar conjugation between the vicinal CF_3, Me, and COOMe groups at the C=C bond. The degree of conjugation in the C=C—C=O system decreases in the order **2b** > **2a** > **1b** > **1a**. The presence of the CF_3 group in the molecule causes a shortening, whereas the presence of the Me group causes a lengthening of the C=O, C(3)—O(5), C(1)—H, and C(2)—H bonds, which is in agreement with the electron-acceptor and electron-donor nature of these substituents, respectively.

The distribution of the effective atomic charges (see Table 2) is consistent with the presence of the conjugated system characteristic of MA in molecules **1b** and **2b** and confirms the electron-acceptor effect of the CF_3 group on the characteristics of the C=O, C(3)—O(5), C(1)—H, and C(2)—H bonds. However, the values of the charges on the carbon atoms of the C=C bond in derivatives **1b** and **2b** do not reflect the electron-acceptor properties of the substituent, since no considerable shift of the negative charge toward the C(2) (or C(1)) atom due to the CF_3 group is observed; in fact, the CF_3 substituent stabilizes charges characteristic of MA on the atoms of the C=C bond irrespective of its position in the molecule. At the same time, the electron-donor properties of the Me group in compounds **1a** and **2a** affect first of all the values of the charges of the C(1) and C(2) atoms; in turn, this affects the charges on the atoms at the C=C bond. By inducing an increased charge on the distant C atom of the multiple bond the Me group either decreases the conjugation in the C=C—C=O system (in molecule **1a**) or substantially increases it (in molecule **2a**).

Table 4. π-Electron populations of the C=C bond (*n*, e), one-electron energies (*E*), and ionization potentials (*IP*) of molecules MA, **1a,b**, and **2a,b**

Molecule	*n*(C(1))	*n*(C(2))	*E*/eV			*IP*
			σ-MO	π-MO	π*-MO	/eV
MA	1.024	0.879	−12.12	−10.70	3.15	10.70
1a	0.988	0.917	−12.03	−10.20	3.34	10.20
2a	1.070	0.836	−11.95	−10.21	3.38	10.21
1b	1.075	0.838	−12.59	−11.57	2.52	11.57
2b	0.962	0.942	−12.67	−11.54	2.37	11.54

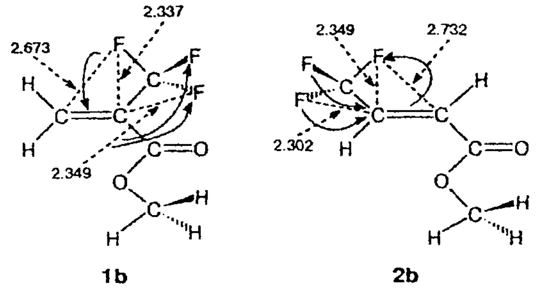
Peculiarities of the distribution of effective charges between the C(1) and C(2) atoms in molecules **1b** and **2b** are rationalized by the p—π-interaction of the CF_3 group with the conjugated system, which was postulated to explain the conjugation in CF_3-substituted aromatic compounds.[15] According to these concepts, the excess electron density induced by the CF_3 group on the adjacent C atom is accepted by F atoms and then partly returned to the π-system. Thus, the p—π-interactions between the CF_3 substituent and the conjugated system produce a compensating flow of electron density, thus partly decreasing the −I-effect of the former.

The short distance between the F atoms and the conjugated system (2.3—2.7 Å), which is much less than the sum of the effective van der Waals radii (3.05 Å), favors the p—π-interactions in molecules **1b** and **2b**. Taking into account this characteristic of their geometry as well as the specificity of the C—F bonds and the charge distribution between the F atoms, the following scheme of p—π-interactions in compounds **1b** and **2b** seems to be logical (Fig. 3). In the first compound, the excess electron density on the C(2) atom (from the C(2)—C(3) bond) is accepted by the F(14) and F(15) atoms lying in a plane perpendicular to the molecular plane and transferred to the π-orbital of the C=C bond through the F(13) atom lying in the molecular plane. In this case, the directions of the effects of the COOMe group and the compensation flow of the electron density coincide; this causes a particularly strong effect of the CF_3 substituent on the effective charges on the C(3) and O(4) atoms and on the parameters of the C=O and C(3)—O(5) bonds in derivative **1b**. In compound **2b** the excess π-electron density from the C=C bond is accepted by the F(13) atom lying in the molecular plane and is returned to the conjugated system through the F(14) and F(15) atoms lying in a plane perpendicular to the molecular plane. In this case the direction of the compensating flow is opposite to that of the effects of the COOMe group, which leads to a direct polar conjugation between the CF_3 and COOMe substituents. A lower deficiency of the electron density on the C(12) atom in molecule **2b** compared to that in **1b** is consistent with this mechanism of p—π-interactions.

Hence it follows that the CF_3 substituent in derivatives **1b** and **2b** is included in the conjugated atomic system irrespective of its position at the C=C bond. This determines the electron-acceptor properties of this system, which are common to these compounds. Distinctions between **1b** and **2b** are due to the opposite directions of the effects of p—π-interactions (depending on the position of the CF_3 group at the C=C bond), which should primarily affect the state of this bond, which is the reaction center of the molecules under consideration. The results of calculations given below are in complete agreement with these concepts.

According to HF/6-31G* calculations of the frequencies of normal vibrations of compounds under study, the frequency of the stretching vibration of the C=O bond increases in the series **1a** < **2a** < **1b** < **2b** (ν(C=O) is 1996, 2002, 2018, and 2024 cm^{-1}, respectively) and the electron-acceptor derivatives **1b** and **2b** are characterized by appreciably higher vibrational frequencies. On the contrary, changes in the frequency of the stretching vibration of the C=C bond in the same series (ν(C=C) is 1871, 1878, 1873, and 1913 cm^{-1}, respectively) reflect radical distinctions in the state of this bond in the molecules under study.

In this regard, data on the polarity (dipole moments) and polarizability of the molecules of compounds considered (see Table 3) are illustrative. The dipole moments of nonfluorinated acrylates increase in the order **1a** < MA < **2a**. They respectively increase or decrease as the Me group strengthens or weakens the effect of the COOMe substituent on the distribution of effective charges between the C(1) and C(2) atoms. For derivatives **1b** and **2b** the change in polarity compared to MA correlates with the direction of the compensating flow of the electron density through the CF_3 group. The extremely high dipole moment of molecule **1b** (4.51 D) due to large contributions of its *X* and *Y* components is determined by adding the effects of CF_3 and COOMe substituents in geminal positions with respect to the C=C bond. The opposite directions of the effects of these substituents in vicinal positions at the C=C bond cause a drastic decrease in the polarity of derivative **2b** (compared to that of **1b**), primarily due to the decrease of the contribution of the *X* component of the dipole moment.



1b **2b**

Fig. 3. Peculiarities of the effects of p—π-interactions between the CF_3 group of acrylates **1b** and **2b** and the conjugated system.

The average values of polarizability of the molecules of the compounds under study (53.57, 55.31, 52.59, and 53.95 au for **1a**, **2a**, **1b**, and **2b**, respectively) calculated using the diagonal elements of corresponding matrices (see Table 3) indicate a lower polarizability of fluorine-containing acrylates **1b** and **2b** compared to nonfluorinated analogs. As follows from the analysis of these matrices, this is due to a lower total self-polarizability of the atoms and bonds lying in the molecular plane in the molecules of CF_3-substituted acrylates. Noteworthy is that the higher polarizability of derivative **2b** compared to that of **1b** goes together well with its larger anisotropy.

The reverse is characteristic of the first molecular hyperpolarizability (the calculation procedure was described earlier[16]). The first hyperpolarizabilities calculated for the molecules of MA and derivatives **1a**, **2a**, **1b**, and **2b** (18.40, 16.53, 31.11, 40.14, and 36.55 au, respectively) appeared to be abnormally high only for highly conjugated acrylates **2a**, **1b**, and **2b**. The maximum value was obtained for derivative **1b**, which is characterized by the minimum polarizability anisotropy and smallest differences in the absolute values of *X* and *Y* components of the first molecular hyperpolarizability (β_X and β_Y are respectively 26.11 and −30.52 for **1b** and −15.46 and −33.11 for **2b**).

Characteristics of the electronic state of the C=C bond in fluorine-containing acrylates depend strongly on the mutual arrangement of the CF_3 and COOMe groups at this bond. If these substituents occupy geminal positions (in **1b**), the total electron density above the C=C bond (at a distance from 2.5 to 1.7 Å from the molecular plane) is minimum above the C(1) atom and increases in the direction toward the C(2) atom (see Fig. 1) and the corresponding gradient substantially increases as the distance to the molecular plane decreases. The π-electron population of the C=C bond in **1b**, in which the electron density is considerably shifted from the C(1) atom toward the C(2) atom, changes analogously (see Table 4). At the same time, there is a region of positive electrostatic potentials above the C=C bond lying in the molecular plane in which the maximum potential is above the C(1) atom (see Fig. 2). The potential decreases sharply in the direction toward the C(2) atom. Such a type of the electronic state of the C=C bond must favor a nucleophilic attack on the C(1) atom and the "push—pull" mechanism of the addition of species of the Nu—H type to the C=C bond.

The type of the electronic state of the C=C bond in the case of vicinal CF_3 and COOMe groups (molecule **2b**) is quite different. The total electron density above the

C(1) and C(2) atoms is virtually equal (see Fig. 1). The tendency for the total electron density to be shifted from the C(1) atom toward the C(2) atom is observed only as the molecular plane approaches. The π-electron densities on the atoms of the C=C bond are nearly equal (see Table 4). Moreover, the region of positive electrostatic potentials near the plane of molecule **2b** is characterized by the opposite change in the potential above the C=C bond as compared to **1b**: the potentials above the C(1) atom are lower than above the C(2) atom (see Fig. 2).

Such an electronic state of the C=C bond must hinder or even prevent nucleophilic attack on the C(1) atom. The possibility of the addition of species of the Nu—H type to the C=C bond following the "push-pull" mechanism is also ruled out. This is in agreement with the extremely low activity of derivatives **2b** in reactions with nucleophiles, established experimentally; however, the reasons for entirely β-oriented addition in these processes remain unclear. It can only be assumed that an essential rearrangement of the conjugated system of molecule **2b** occurs at the formation of transition states of these reactions, which determines the order of the nucleophile addition to the C=C bond.

Distinctions in the electronic structure of the C=C bond of nonfluorinated analogs **1a** and **2a** are mainly quantitative (see Table 4, Figs. 1 and 2). For both compounds, the π-electron density distribution and the gradient of negative electrostatic potential above the C=C bond favor nucleophilic attack on the C(1) atom. Nevertheless, pronounced quantitative differences in the reactivity of these compounds can be explained only by taking into account the peculiarities of the total electron density distribution above the atoms (C(1) and C(2)) of the reaction center: in molecule **1a** the electron density above these atoms is nearly equal, whereas in molecule **2a** it is appreciably shifted toward the C(1) atom.

The CH_3 and CF_3 substituents have opposite effects on the energies of the one-electron levels of molecules **1a**, **2a** and **1b**, **2b** (see Table 4). These effects are virtually independent of the substituent position at the multiple bond. The introduction of a Me group in the α- or β-position of the MA molecule has no effect on the energy of the σ-level, whereas the energy of the filled π-level (the HOMO) increases substantially and that of the vacant π^*-level (the LUMO) increases to a somewhat lesser extent. Because of this, the energy gap for compounds **1a** and **2a** is more narrow (in absolute value) than for MA. On the contrary, the introduction of the CF_3 group in the α- or β-position of the MA molecule causes appreciable decrease in the energy of the σ-level and even more substantial change in the energy of both the HOMO and, particularly, the LUMO. As a result, the energy gap becomes much wider (in absolute value).

On the whole, consideration of the electronic states of the C=C bond makes it possible to characterize systems **1a** and **2a** as reagents of the π-donor type and derivatives **1b** and **2b** as of the π-acceptor type. This conclusion, as well as the peculiarities of the total and π-electron density distributions, and the directions and values of the gradients of electrostatic potentials provide a complete explanation for experimentally established regularities of changes in the reactivity of these compounds.

The authors express their gratitude to the Pacific Northwest National Laboratory of the U.S. Department of Energy for providing time on the CRAY J90 supercomputer (Contract No. DE-AC06-76RLO 1830).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32884).

References

1. M. W. Buxton, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 1954, 366.
2. T. Fuchikami, A. Yamanouchi, and I. Ojima, *Synthesis*, 1984, 766.
3. T. Fuchikami, Y. Shibata, and Y. Suzuki, *Tetrahedron Lett.*, 1984, **27**, 3173.
4. H. M. Walborsky and B. E. Braun, *J. Org. Chem.*, 1956, **21**, 538.
5. H. M. Walborsky and M. Schwarz, *J. Am. Chem. Soc.*, 1963, **75**, 3241.
6. P. E. Bevilacgua, D. D. Keith, and J. L. Roberts, *J. Org. Chem.*, 1984, **49**, 1430.
7. T. P. Vasil'eva, A. F. Kolomiets, E. I. Mysov, and A. V. Fokin, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1230 [*Russ. Chem. Bull.*, 1997, **46**, 1183 (Engl. Transl.)].
8. T. P. Vasil'eva, A. F. Kolomiets, and A. V. Fokin, *15th Int. Symp. on Fluor. Chem.*, Vancouver, Canada, 1997, Abstrs., F Ru C-5.
9. P. Vaculik, *Chemie Monomerü*, I, Nakladatelstvi Čescoslovenske Akademie věd, Praha, 1956.
10. S. Patai and C. Rappoport, *Nucleophilic Reactions at the Double Carbon Bond*, in *The Chemistry of Alkenes*, Ed. S. Patai, Interscience Publ., J. Wiley and Sons, London—New York—Sydney, 1964.
11. L. Salem, *Electrons in Chemical Reactions: First Principles*, J. Wiley and Sons, New York, 1982.
12. C. Møller and S. Plesset, *Phys. Rev.*, 1968, **49**, 4852.
13. M. Dupius, D. Spangler, and J. J. Wendolowski, *Nat. Resour. Comput. Chem. Software Cat. 1. Prog. QG01 (GAMESS)*, 1980.
14. M. J. Frisch, J. B. Foresman, and A. Frisch, *GAUSSIAN 94 User's Reference*, Gaussian Inc., Pittsburgh (PA), 1996.
15. A. Sheppard, *J. Am. Chem. Soc.*, 1965, **87**, 2410.
16. J. Abe and Y. Shirai, *J. Am. Chem. Soc.*, 1996, **118**, 4705.

Received May 27, 1998;
in revised form July 1, 1998