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An ab initio Evaluation of the Role of *p*,π Interaction: I. Ethylene Derivatives

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Abstract—The RHF/6-311G(d) and MP2/6-311G(d) calculations with full geometry optimization were performed for $XCH=CH_2$ molecules (X = F, Cl, Br, CH_3, CH_2CH_3, CH_2F, CHO). The p_y electron density distribution in these molecules and the bonding molecular orbitals formed by the p_y orbitals of atoms of the planar fragment of these molecule (atomic orbitals whose symmetry axes are perpendicular to this plane) are not determined by the *p*,π conjugation between the lone electron pair of the heteroatom in substituent X and π electrons of the C=C bond. Changes in the population of the p_y orbitals of the halogen and carbon atoms in going from X = F to X = Cl and Br are not associated with changes in the extent of this *p*,π interaction. Taking into account the electon correlation in the MP2 method does not noticeably alter the features of the electron density distribution in these molecules estimated by restricted Hartree–Fock calculations.

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The results of the population analysis of valence *p* orbitals of Cl in the $Cl_2C=CHOMe$ molecule, according to RHF/6-31G(d) calculations, are consistent with the conclusions made from the experimental measurements of the electric field gradient on the ^{35}Cl nuclei in compounds $Cl_2C=CHOR$ that there is no *p*,π conjugation between the lone electron pairs of chlorine and π electrons of the C=C bond [1, 2]. The RHF/6-31G(d) calculations of fluoro and chloro derivatives of ethylene showed that these molecules have *p*,π-bonding molecular orbitals formed by the orbital of the lone electron pair of the halogen atom and π orbitals of the carbon atoms, in agreement with the concept of the *p*,π conjugation between these orbitals [1, 3]. According to our RHF/6-31G(d) calculations, the $Cl_2C=CHOMe$ molecule also has a bonding molecular orbital with an energy of 15.362 eV, formed by the π orbitals of the carbon atoms involved in the double bond and by the p_y orbitals of the Cl and O atoms, whose symmetry axes are perpendicular to the molecular plane. These orbitals also participate in formation of a number of other molecular orbitals. It can be assumed that, in unsaturated heteroatomic molecules, the *p*,π interaction between the lone electron pairs of heteroatoms and adjacent C=C π bond occurs along with atomic interactions of other types. This interaction makes a certain contribution to the electron distribution in the molecule and affects the related properties of the compound. According to the concept considering the chemical bonding as a result of the overlap of definite orbitals of adjacent atoms, it can be assumed that in going from X = F to X = Cl and Br the extent of the overlap between the orbital of the lone electron pair of the halogen atom and the π orbital of the adjacent carbon atom should decease, because of an increase in the volume of the valence p orbitals of the halogen atom in this series. It can also be assumed that the populations of constituents of these orbitals will vary differently in the series F–Cl–Br. To examine the capability of halogen atoms for *p*,π interaction, we performed the RHF/6-311G(d) calculations of haloethylenes $XC^1H=C^2H_2$ (X = F, Cl, Br) with full geometry optimization by the GAUSSIAN-94W program [4]. It can be expected that the calculations taking into account the electron correlation will provide a more adequate description of such interactions. Therefore, we also performed MP2/6-311G(d) calculations for these molecules. The origin of the coordinate system in all the cases coincided with the position of the nucleus of the halogen atom, the *z*-axis was oriented along the X–C^1 bond, and the *y*-axis, perpendicular to the molecular plane (in [1–3] this axis lay in the molecular plane).

The results of the optimization of the molecular geometries by both methods show that all the molecules are essentially planar (all the dihedral angles are 0° or 180°). The optimized geometric parameters of the molecules are given in Table 1. These parameters reasonably agree with the experimental data [5, 6]. For example, according to the gas-phase electron diffraction data [6], the carbon–halogen bond lengths are

Table 1. Bond lengths (*d*, Å) and bond angles (ω, deg) in $XC^1H=C^2H_2$ molecules (X = F, Cl, Br), according to RHF/6-311G(d) and MP2/6-311G(d) calculations

Bond, angle	F		Cl		Br	
	RHF	MP2	RHF	MP2	RHF	MP2
$X=C^1$	1.352	1.344	1.741	1.732	1.896	1.890
$C^1=C^2$	1.307	1.329	1.310	1.333	1.310	1.334
XC^1C^2	122.50	122.32	123.25	123.07	123.27	122.99
HC^1C^2	125.64	125.60	124.17	123.74	124.07	123.71
$C^1C^2H_{cis}$	121.48	121.12	122.46	122.01	122.75	122.37
$C^1C^2H_{trans}$	119.71	119.42	119.56	119.35	119.55	119.28

1.348 (X = F), 1.728 (X = Cl), and 1.904 Å (X = Br). The lengths of the double bonds in these molecules optimized by the RHF/6-311G(d) method are somewhat smaller than the experimental values; the MP2/6-311G(d) optimization provides better agreement. For example, the C=C bond length in chloroethylene is 1.332 Å according to microwave spectroscopy [5] and 1.355 Å according to gas-phase electron diffraction [7]. The results of RHF/6-311G(d) optimization of the molecular geometry of chloroethylene are close to those obtained previously by the RHF/6-31G(d) method [3].

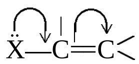
To examine the *p*,π interaction in ethylene derivatives, we used the Mulliken population analysis of atomic orbitals; this method described the electron distribution in molecules most adequately. This is confirmed, e.g., by the agreement between the experimental NQR parameters of a large number of halogen-containing and organoelement compounds and the parameters calculated from the populations of the less diffuse constituents of the valence *p* orbitals of the halogen atoms, determined by ab initio calculations (see our previous papers [1]).

The populations of the valence *p* orbitals of the halogen and carbon atoms in substituted ethylenes and of the constituents of these orbitals, according to the RHF/6-311G(d) and MP2/6-311G(d) calculations, are listed in Table 2. In the 6-311G(d) basis set, each valence *p* orbital of an atom is represented as a combination of three orbitals of different sizes (see, e.g., [8]). Therefore, its population is the sum of the populations of three constituents (denoted as 2*p*, 3*p*, and 4*p*, according to an increase in their diffuse character). The populations and their constituents calculated by both methods are essentially the same. For example, for the p_y orbitals of the carbon atoms in unsubstituted ethylene, the RHF/6-311G(d) calculation gives the populations of 0.148, 0.402, and 0.439 e, and the MP2/6-311G(d) calculation, the populations of 0.147, 0.398, and 0.445 e. The populations of these p_y orbitals forming the π-electron system of the C=C bond vary in going to halo derivatives $XC^1H=C^2H_2$ differently: with X = F, the total population of the p_y orbital of the C^1 atom decreases and that of C^2 increases; with X = Cl and Br, the trends are opposite. With X = F, the populations of the two least diffuse constituents of the valence p_y orbitals of the C^1 and C^2 atoms are virtually the same, and that of the most diffuse constituent for C^1 is somewhat lower compared to C^2. With X = Cl and Br, the populations of all the constituents for C^1 are somewhat higher compared to C^2. All these facts indicate that the halogen atoms exert different effects on the π-electron density distribution in these molecules. In going from unsubstituted ethylene to any of the haloethylenes under consideration, the populations of the two least diffuse constituents of the valence p_y orbitals of the C^1 and C^2 atoms increase, and those of the third, most diffuse constituent decrease (except for C^2 with X = F). This trend is inconsistent with the concept that the extent of *p*,π conjugation decreases in going from X = F to X = Cl and Br. The total populations of the p_y orbitals of the halogen atoms, capable of *p*,π conjugation, are somewhat lower than those of the p_x orbitals lying in the molecular plane and incapable of such conjugation. This difference in the populations might be, in principle, attributed to the *p*,π conjugation. In going from X = F to X = Cl and Br, the total populations of the p_z orbitals of the halogen atoms decrease, in agreement with a decrease in the halogen electronegativity. At the same time, the populations of the p_y orbitals of the halogen atoms increase, which is consistent with a decrease in the extent of their participation in the *p*,π conjugation with the π-electron system of the C=C bond. However, the populations of the halogen p_x orbitals incapable of the *p*,π conjugation also increase in the series F–Cl–Br. The populations of the p_x and p_y orbitals increase to approximately the same extent. Therefore, the observed increase in the population in going from

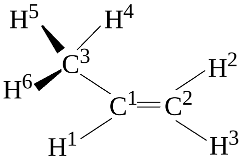
Table 2. Populations of the valence *p* orbitals (ΣNp) of the halogen and methyl carbon atoms, of the p_y orbitals of the vinyl carbon atoms, and of constituents of these orbitals in molecules of the series $XC^1H{=}C^2H_2$, according to RHF/6-311G(d) and MP2/6-311G(d) calculations

X	*Np*	X			C^1, Np_y, e	C^2, Np_y, e	X			C^1, Np_y, e	C^2, Np_y, e
		Np_x, e	Np_y, e	Np_z, e			Np_x, e	Np_y, e	Np_z, e		
		RHF					MP2				
F	2*p*	0.421	0.412	0.311	0.160	0.163	0.421	0.413	0.308	0.160	0.160
	3*p*	0.871	0.853	0.694	0.439	0.439	0.870	0.853	0.689	0.436	0.433
	4*p*	0.650	0.654	0.466	0.361	0.468	0.653	0.659	0.476	0.370	0.471
	ΣNp	1.942	1.919	1.471	0.960	1.070	1.944	1.924	1.473	0.966	1.064
Cl	2*p*	0.369	0.361	0.276	0.165	0.152	0.369	0.361	0.277	0.163	0.150
	3*p*	1.136	1.131	0.789	0.450	0.413	1.137	0.131	0.787	0.446	0.409
	4*p*	0.478	0.476	0.159	0.420	0.416	0.476	0.474	0.156	0.427	0.424
	ΣNp	1.983	1.968	1.224	1.035	0.981	1.982	1.966	1.220	1.036	0.983
Br	2*p*	0.312	0.306	0.219	0.165	0.150	0.312	0.306	0.219	0.163	0.148
	3*p*	1.088	1.083	0.749	0.447	1.408	1.089	1.083	0.747	0.442	0.404
	4*p*	0.609	0.603	0.183	0.424	0.411	0.607	0.601	0.179	0.431	0.419
	ΣNp	2.009	1.992	1.151	1.036	0.969	2.008	1.990	1.145	1.036	0.971
CH_3	2*p*	0.200	0.198	0.191	0.146	0.155	0.198	0.196	0.191	0.145	0.154
	3*p*	0.571	0.568	0.546	0.400	0.417	0.568	0.565	0.544	0.396	0.413
	4*p*	0.372	0.347	0.207	0.400	0.462	0.373	0.349	0.206	0.405	0.469
	ΣNp	1.143	1.113	0.944	0.946	1.034	1.139	1.110	0.941	0.946	1.036

X = F to X = Cl and Br cannot be attributed to a decrease in the capability of the lone electron pairs of the halogen atoms for the p,π conjugation with the π orbitals of the C=C carbon atoms. In parallel with an increase in the populations of the halogen p_x and p_y orbitals, the populations of the p_y orbitals of the C^1 atoms (bonded with halogen) increase also, whereas the populations of the C^2 orbitals decrease. The total excess of the electron density on the carbon p_y orbitals is substantially smaller than the electron density deficiency on the halogen p_y orbital (Table 2). Therefore, the changes in these populations cannot be attributed to the p,π conjugation. Apparently, the populations of these orbitals and their constituents do not characterize the extent of their participation in the p,π conjugation. Additional information on this matter can be derived from analysis of the coefficients at the atomic orbitals forming the π-bonding molecular orbital (Table 3). These coefficients are sums of coefficients at all the three constituents of the valence p_y orbitals of the corresponding atoms. The energies of these molecular orbitals, their shapes, and the coefficients at the atomic orbitals forming these molecular orbitals, calculated by the RHF/6-311G(d) and MP2/6-311G(d) methods, differ insignificantly. Each of the molecules $XC^1H{=}C^2H_2$ (X = F, Cl, Br) has two molecular orbitals formed by the p_y orbitals of the halogen and carbon atoms. One of them, with a lower energy, is the π-bonding orbital. Certain contribution to it is also made by the vacant d orbitals of the halogen and carbon atoms. In going from X = F to X = Cl and Br, the coefficient at the atomic orbitals of halogen in this molecular orbital decreases, that at the C^1 orbitals, on the contrary, increases, and that at the C^2 orbitals passes through a maximum at X = Cl. A decrease in the coefficient at the p_y orbital of the halogen atom in the π-bonding molecular orbital is consistent with a decrease in the extent of the participation of the X atom in the p,π conjugation in going from X = F to X = Cl and Br. However, trends in variation of the coefficients at the carbon p_y orbitals are inconsistent with this assumption. The variations in the populations of the carbon p_y orbitals in going from ethylene to its halo derivatives, in the populations of the halogen and carbon p_y orbitals, and in the coefficients at these orbitals in the π-bonding molecular orbitals of halo-substituted ethylenes do not fit in the scheme commonly accepted for the p,π conjugation (see, e.g., [9]):



To examine this effect further, we performed RHF/6-311G(d) and MP2/6-311G(d) calculations for molecules $XCH{=}CH_2$ with X = CH_3 (**I**), C_2H_5 (**II**), CH_2F (**III**), and CHO (**IV**) with the full geometry optimization. The C^1 nucleus was chosen as the origin of the coordinate system. The *z*-axis was oriented along the $C^1{=}C^2$ bond, and the *y*-axis, perpendicular to the molecular plane.



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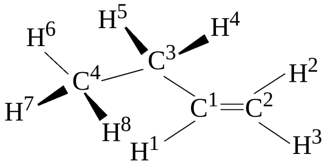

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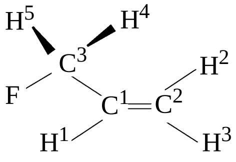

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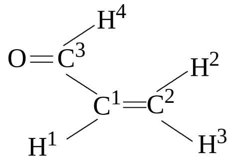

IV

Table 3. Energies (–*E*, eV) of particular molecular orbitals formed by atomic p_y orbitals and coefficients *k* at these orbitals in molecules of the series $XC^1H{=}C^2H_2$, according to RHF/6-311G(d) and MP2/6-311G(d) calculations

X	–*E*, eV	*k*		
		X	C^1	C^2
		RHF		
F	18.784	1.107	0.270	0.086
	10.447	–0.444	0.655	0.762
Cl	13.912	0.914	0.488	0.276
	10.257	0.743	–0.603	–0.671
Br	12.900	0.808	0.539	0.389
	9.963	0.900	–0.520	–0.605
		MP2		
F	18.623	1.122	0.263	0.082
	10.386	–0.433	0.662	0.761
Cl	13.920	0.928	0.437	0.261
	10.116	0.724	–0.615	–0.681
Br	12.856	0.835	0.524	0.370
	9.861	0.875	–0.538	–0.620

The optimized bond lengths and bond angles in these molecules, calculated by both methods, are given in Table 4. The core of all these molecules is essentially planar. All the dihedral angles in the vinyl group are 0° or 180°. In **I**, the $C^2C^1C^3H^4$ dihedral angle is 0.01° (RHF) or 0.00° (MP2); in **II**, the $C^1C^3C^4$ bond angle is 113.00° (RHF) or 112.7° (MP2), and the $C^2C^1C^3C^4$ and $C^1C^3C^4H^6$ dihedral angles are 180.00°; in **III**, the $FC^3C^1C^2$ dihedral angle is 179.99° (RHF) or 180.02° (MP2); in **IV**, the C^1C^3O bond angle is 124.01° (RHF) or 124.03° (MP2), the $C^1C^3H^4$ bond angle is 115.29° (RHF) or 114.99° (MP2), the $C^2C^1C^3H^4$ dihedral angle is 0.00°, and the $C^2C^1C^3O$ dihedral angle is 180.00°. The optimized geometric characteristics of **I** are mainly consistent with the experimental gas-phase electron diffraction data [10]: bond lengths C=C 1.342, C–C 1.506 Å; bond angles $C^1C^2H^3$ 121.3°, $C^3C^1C^2$ 124.3°. In this molecule, as well as in molecules **II** and **III** calculated by the RHF/6-311G(d) and MP2/6-311G(d) methods, the population ratio of the valence p_y orbitals of C^1 and C^2 is the same (Table 5) as with X = F (Table 2). With the electron-withdrawing substituent X = CHO, the populations of the p_y orbitals of these atoms are lower than 1e, and their ratio is inverse (Table 5), as in the case of X = Cl and Br (Table 2). In going from unsubstituted ethylene to its methyl, ethyl, and fluoromethyl derivatives, the populations of the p_y orbitals of the C^1 and C^2 atoms vary in the same direction as

Table 4. Bond lengths (Å) and bond angles (deg) in molecules **I**–**IV**, according to RHF/6-311G(d) and MP2/6-311G(d) calculations

Bond, angle	I		II		III		IV	
	RHF	MP2	RHF	MP2	RHF	MP2	RHF	MP2
$C^1{=}C^2$	1.318	1.339	1.318	1.340	1.316	1.338	1.320	1.343
$C^1{-}C^3$	1.502	1.501	1.515	1.513	1.504	1.504	1.480	1.478
$C^1C^2H^2$	121.91	121.44	122.02	121.58	122.25	121.97	121.56	120.93
$C^1C^2H^3$	121.59	121.48	121.55	121.45	121.39	121.17	122.03	122.10
$C^3C^1C^2$	125.33	124.60	125.22	124.71	124.55	121.99	121.35	120.73
$H^1C^1C^2$	118.73	118.79	118.39	118.57	120.63	120.75	122.29	122.43

Table 5. Populations of valence p_y orbitals (NP_y, e) in molecules **I**–**IV**, according to RHF/6-311G(d) and MP2/6-311G(d) calculations

Comp. no.	C^1	C^2	C^3	X	C^1	C^2	C^3	X
	RHF				MP2			
I	0.946	1.034	1.113	–	0.945	1.036	1.110	–
II (X = C^4)	0.954	1.028	1.118	1.114	0.953	1.030	1.115	1.111
III (X = F)	0.966	1.016	1.120	1.950	0.966	1.018	1.119	1.953
IV (X = O)	0.996	0.922	0.691	1.319	0.998	0.915	0.687	1.332

Table 6. Energies (–E, eV) of particular molecular orbitals formed by atomic p_y orbitals and coefficients k at these atomic orbitals in molecules **I**–**IV**, according to RHF/6-311G(d) and MP2/6-311G(d) calculations

Comp. no.	–E, eV	k				–E, eV	k			
		C^1	C^2	C^3	X		C^1	C^2	C^3	X
		RHF					MP2			
I	15.487	0.199	0.113	0.701	–	15.438	0.199	0.110	0.701	–
	9.821	0.682	0.736	–0.213	–	9.694	0.684	0.739	–0.209	–
II (X = C^4)	16.724	0.125	0.069	0.533	0.457	16.677	0.125	0.068	0.531	0.459
	13.689	–0.163	–0.124	–0.471	0.579	13.645	–0.162	–0.121	–0.473	0.576
	9.735	0.688	0.729	–0.260	0.034	9.602	0.691	0.732	–0.257	0.030
III (X = F)	19.226	0.077	0.038	0.494	0.868	19.033	0.078	0.038	0.495	0.869
	14.755	–0.195	–0.127	–0.497	0.842	14.783	–0.192	–0.122	–0.496	0.842
	10.254	0.691	0.725	–0.234	0.117	10.147	0.694	0.729	–0.231	0.111
IV (X = O)	15.001	0.230	0.147	0.569	0.799	14.653	0.252	0.163	0.568	0.792
	10.007	0.683	0.676	–0.062	–0.419	10.807	0.678	0.671	–0.099	–0.451

in going to the fluoro derivative. The population ratio of the p_x and p_y orbitals of the methyl carbon atom in $H_3CCH=CH_2$ is the same as in the halo derivatives (Table 2). Therefore, such a ratio in the halo derivatives cannot be attributed to the p,π conjugation. In molecules **I** and **IV**, there are two, and in **II** and **III**, three molecular orbitals formed by the p_y orbitals of all the carbon atoms and of the fluorine and oxygen atoms in **III** and **IV**, respectively (Table 6). The molecular orbitals of lower energy are bonding. The largest contribution to these bonding molecular orbitals is made by the p_y orbitals of the sp^3-hybridized carbon atoms (except **IV**) and of the fluorine and carbonyl C, O atoms in **III** and **IV**, respectively. These data show that the bonding molecular orbitals in molecules of the series $XCH=CH_2$ are not determined by the p,π conjugation between the lone electron pairs of the X atom and the C=C bond, because such orbitals are present in molecules in which the atom of substituent X bonded to the vinyl carbon atom does not necessarily have a lone electron pair (as, e.g., in **I**–**III**).

Thus, the occurrence of p,π conjugation between lone electron pairs of the X atom and the C=C bond follows neither from populations of the valence p orbitals of atoms of the planar fragment of $XCH=CH_2$ nor from the characteristics of molecular orbitals formed by the p_y orbitals of these atoms. Changes in the populations of the p_y orbitals of the halogen and carbon atoms in going from X = F to X = Cl and Br are not associated with changes in the extent of this p,π conjugation. Taking into account the electron correlation (MP2 method) does not noticeanly alter the results of RHF estimations of the electron distribution in the molecules under consideration.

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