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An ab initio Evaluation of the Role of *p*,π Interaction: II.[1] Molecules of the CH_3COX Series

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Abstract—The RHF/6-311G(d) and MP2/6-311G(d) calculations with full geometry optimization were performed for CH_3COX molecules (X = F, Cl, Br, CH_3). Variations in the populations of the p_y orbitals of their halogen and carbon atoms (orbitals whose symmetry axes are perpendicular to the molecular plane) from X = F to X = Cl, Br, and CH_3 are not associated with variations in the extent of the *p*,π conjugation between the lone electron pair of the halogen atom and the π-electron system of the carbonyl group. The bonding molecular orbitals formed by these atomic p_y orbitals are not determined by this interaction. The RHF/6-311G(d) and MP2/6-311G(d) calculations give similar results.

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The abnormally low ^{35}Cl NQR frequency in compounds RCOCl is attributed by some authors to *p*,π conjugation between the lone electron pair of the Cl atom and the π-electron system of the carbonyl group [2–5]. This concept is consistent with large asymmetry parameters of the electric field gradient on the ^{35}Cl nuclei in these compounds [2, 5]. However, these parameters do not characterize the extent to which the lone electron pair of the chlorine atom is involved in any kind of conjugation and merely characterize the asymmetry of the electron distribution in the vicinity of the atomic nucleus (see, e.g., [6, 7]). If this conjugation actually occurs, different halogen atoms should participate in it to a different extent, because of different volume of these atoms and different sizes of their valence orbitals. To follow the trends observed in the series of halogens and to elucidate whether this conjugation actually occurs, we performed ab initio calculations of $C^2H_3C^1OX$ molecules (X = F, Cl, Br, CH_3). We showed previously that the ^{35}Cl NQR frequencies [8, 9] of chlorinated organic and organoelement molecules calculated from the populations of the less diffuse constituents of the chlorine valence *p* orbitals by the RHF, B3LYP, and MP2 methods using the 6-31G(d) basis set and the ^{79}Br NQR frequencies of brominated molecules [10] calculated by the same methods using the 6-311G(d) basis set are close to the experimental values. Hence, the electron distribution in these molecules is satisfactorily described by the Mulliken populations of the atomic orbitals determined by the above calculation methods. Presumably, when studying electronic effects in molecules, it is necessary to use methods taking into account the electron correlation. At the same time, we showed in our previous paper [1] that the electron distribution data obtained for ethylene derivatives by the restricted Hartree–Fock (RHF) method and by the Hartree–Fock method with the electron correlation taken into account using the second-order Møller–Plesset perturbation theory (MP2) differ insignificantly. Therefore, when studying *p*,π conjugation, there is no need in more time-consuming MP2 calculations. Nevertheless, in this study we used both methods: RHF/6-311G(d) and MP2/6-311G(d). The calculations were done with full geometry optimization using the GAUSSIAN-94W program [11]. The halogen or methyl carbon (at X = CH_3) atom was chosen as the origin of the coordinate system; the *z*-axis was oriented along the X–C^1 bond, and the *y*-axis, perpendicular to the molecular plane.

The calculations by both methods show that all the CH_3COX molecules studied are planar. One of the C–H bonds of the methyl group lies in the molecular plane. The dihedral angle involving this bond and the C^1–X bond is 180.00°. The other two C–H bonds of this group deviate from the molecular plane by 58.89° (RHF) or 58.75° (MP2). With X = CH_3, the molecule has a twofold symmetry axis and a symmetry plane passing through the carbonyl group. The results of the geometry optimization for all the molecules are, on the whole, consistent with the experimental data [12–15] obtained by a combination of gas-phase electron

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[1] For communication I, see [1].

Table 1. Calculated [RHF/6-311G(d), MP2/6-311G(d)] and experimental [12–15] bond lengths (*d*) and bond angles (ω) in $C^2H_3C^1OX$ molecules

Xe	Method, references	*d*, Å			ω, deg		
		$X–C^1$	$C^1=O$	$C^1–C^2$	XC^1O	XC^1C^2	OC^1C^2
F	RHF	1.325	1.162	1.494	120.44	110.84	128.72
	MP2	1.363	1.188	1.496	120.58	110.02	129.40
	[12]	1.348	1.181	1.503	–	110.18	128.21
	[13]	1.362	1.185	1.505	120.7	110.5	–
Cl	RHF	1.795	1.159	1.501	119.83	112.40	127.77
	MP2	1.808	1.189	1.501	120.58	111.38	128.05
	[14]	1.797	1.186	1.506	120.19	112.10	127.27
	[15]	1.796	1.185	1.505	121.2	111.6	–
Br	RHF	1.975	1.156	1.502	119.56	112.31	128.13
	MP2	1.999	1.186	1.502	120.42	111.04	128.53
	[14]	1.974	1.183	1.516	120.48	109.29	129.40
	[15]	1.974	1.181	1.516	122.3	111.0	–
CH_3	RHF	1.514	1.187	1.514	121.76	116.48	121.76
	MP2	1.516	1.218	1.516	121.86	116.28	121.86

diffraction and microwave spectroscopy (Table 1). The C=O bonds in all the molecules, according to the RHF/6-311G(d) calculation, are noticeably shorter compared to the experimental data. The calculated C–F bond length in the CH_3COF molecule is also somewhat underestimated. The MP2/6-311G(d) calculations provide better agreement of the bond lengths with the experimental data. The CH_3COCl molecule was calculated previously [16] by the MNDO, RHF/3-21G, and RHF/6-31G(d) methods. The geometry optimized by the latter method was the closest to that obtained in this study on the higher levels of theory (Table 1).

The populations of the valence *p* orbitals of the halogen and carbon atoms in the substituent X = CH_3 and of the p_y orbitals of the O, C^1, and C^2 atoms are listed in Table 2. In the 6-311G(d) basis set, each valence *p* orbital is represented as a combination of three orbitals of different sizes (see, e.g., [17]). Therefore, its population is a sum of three constituents (denoted as 2*p*, 2*p*, and 4*p*, in the order of increasing diffuse character). As expected, the results of calculation by both methods differ insignificantly. The trends in variation of these populations and their constituents in going from X = F to X = Cl, Br, and CH_3, and also the ratio of these populations in CH_3COX molecules are similar to those observed in the series of ethylene halo derivatives [1]. In going from X = F to X = Cl, Br, and CH_3, the populations of the p_z orbitals of atoms of substituent X decrease, which is consistent with a decrease in the electronegativity of these atoms. The populations of the p_y orbitals of the halogen atoms, capable of the *p*,π conjugation, are lower than those of the p_x orbitals located in the molecular plane and incapable of such conjugation. Therefore, this difference in the populations might be attributed to the *p*,π conjugation. However, the same ratio of the populations of the p_x and p_y orbitals is also observed for the C atom of the substituent X = CH_3. In CH_3COX (Table 2) and CH_2=CHX [1] molecules, the populations of the p_x orbitals of the halogen atoms are virtually the same for given X, whereas the populations of their p_y orbitals in acetyl halides are appreciably lower. In acetyl halides, the oxygen atom is an acceptor of the electron density not only from the halogen atom, but also from the C^1 atom for which the population of the p_y orbital is appreciably lower (Table 2) compared to the carbon atom bonded with the halogen in haloethylenes [1]. However, there is no correlation between the populations of the p_y orbitals of these atoms in acetyl halides. In both series of molecules, the populations of the halogen p_y orbitals increase in going from X = F to X = Cl and Br, suggesting a decrease in the extent of participation of halogen atoms in the *p*,π conjugation. However, the populations of the p_x orbitals incapable of such conjugation increase to approximately the same extent. Furthermore, the population of the oxygen p_y orbital decreases only in going from X = F to X = Cl, and then, in going to X = Br and CH_3, it remains constant. Therefore, apparently, the observed increase in the populations of the p_y orbitals of the halogen atoms in going from X = F to X = Cl and Br should not be attributed to a decrease in the

Table 2. Populations of valence p orbitals (Np) of halogen atoms or carbon atom of substituent X, their constituents, and p_y orbitals of the C^1, C^2, and O atoms in $C^3H_3C^1OX$ molecules, according to RHF/6-311G(d) and MP2/6-311G(d) calculations

X	Np	X			C^1,	C^2,	O,	X			C^1,	C^2,	O
		Np_x, e	Np_y, e	Np_z, e	Np_y, e	Np_y, e	Np_y, e	Np_x, e	Np_y, e	Np_z, e	Np_y, e	Np_y, e	Np_y, e
		RHF						MP2					
F	2p	0.422	0.401	0.320	0.124	0.202	0.256	0.422	0.402	0.315	0.120	0.201	0.256
	3p	0.874	0.838	0.708	0.352	0.587	0.595	0.871	0.838	0.700	0.341	0.586	0.593
	4p	0.646	0.659	0.456	0.195	0.373	0.524	0.653	0.667	0.476	0.203	0.376	0.532
	ΣNp	1.942	1.898	1.484	0.671	1.162	1.375	1.946	1.907	1.491	0.664	1.163	1.381
Cl	2p	0.366	0.352	0.281	0.125	0.204	0.250	0.367	0.353	0.278	0.120	0.202	0.250
	3p	1.145	1.117	0.834	0.350	0.590	0.584	1.146	1.117	0.829	0.340	0.587	0.583
	4p	0.477	0.487	0.184	0.227	0.367	0.499	0.476	0.487	0.183	0.234	0.369	0.511
	ΣNp	1.988	1.956	1.299	0.702	1.161	1.333	1.989	1.957	1.290	0.694	1.158	1.344
Br	2p	0.308	0.297	0.220	0.124	0.204	0.250	0.307	0.298	0.216	0.119	0.202	0.251
	3p	1.094	1.067	0.810	0.344	0.592	0.586	1.093	1.067	0.806	0.334	0.589	0.585
	4p	0.608	0.613	0.235	0.223	0.368	0.498	0.604	0.614	0.240	0.230	0.370	0.511
	ΣNp	2.010	1.977	1.265	0.691	1.164	1.334	2.004	1.979	1.262	0.683	1.161	1.347
CH_3	2p	0.204	0.197	0.193	0.113	0.196	0.243	0.203	0.195	0.191	0.109	0.195	0.243
	3p	0.583	0.570	0.549	0.319	0.570	0.569	0.581	0.568	0.545	0.310	0.568	0.567
	4p	0.387	0.359	0.215	0.221	0.359	0.523	0.389	0.361	0.213	0.229	0.361	0.535
	ΣNp	1.174	1.126	0.957	0.653	1.126	1.335	1.173	1.124	0.949	0.648	1.124	1.345

Table 3. Energhies (–E, eV) of particular molecular orbitals formed by the atomic p_y orbitals and coefficients k at these atomic orbitals in $C^3H_3C^1OX$ molecules (X = F, Cl, Br, CH_3), according to RHF/6-311G(d) and MP2/6-311G(d) calculations

X	–E, eV	k				–E, eV	k			
		X	C^1	C^2	O		X	C^1	C^2	O
		RHF					MP2			
F	19.894	0.973	0.361	0.162	0.260	19.540	0.976	0.353	0.180	0.254
	16.914	–0.531	0.132	0.672	0.231	16.584	–0.544	0.125	0.674	0.213
	14.514	–0.410	0.412	–0.302	0.860	14.405	–0.394	0.421	–0.292	0.871
Cl	17.762	0.202	0.427	0.526	0.485	17.592	0.204	0.402	0.557	0.440
	15.321	0.233	0.389	–0.542	0.650	15.099	0.279	0.410	–0.509	0.673
	12.706	1.114	–0.085	–0.047	–0.412	12.724	1.103	–0.104	–0.040	–0.439
Br	17.720	0.127	0.416	0.544	0.497	17.551	0.124	0.391	0.577	0.450
	15.330	0.118	0.398	–0.524	0.704	15.089	0.134	0.423	–0.486	0.743
	11.508	1.177	–0.014	–0.072	–0.287	11.534	1.176	–0.019	–0.072	–0.291
CH_3	17.050	0.429	0.333	0.429	0.352	16.954	0.440	0.314	0.440	0.318
	15.303	–0.532	0.000	0.532	0.000	15.288	–0.532	0.000	0.532	0.000
	13.466	–0.271	0.466	–0.271	0.836	13.195	–0.252	0.479	–0.252	0.857

capability of their lone electron pairs for the p,π conjugation with the π-electron system of the carbonyl group.

Each acetyl halide molecule has three molecular orbitals formed by the p_y orbitals of the halogen, carbon, and oxygen atoms. The energies of these molecular orbitals and the coefficients at their constituent atomic p_y orbitals are given in Table 3. These coefficients are sums of the coefficients at the three constituents of the valence p_y orbitals of the corresponding atoms. The results obtained by the two calculation methods differ insignificantly. The molecular orbital of the lowest energy is bonding. The contribution of the halogen p_y orbital to this molecular orbital decreases, and that of the oxygen p_y orbital, increases in going from X = F to X = Cl and Br. With X = F, the contribution of the p_y orbital of the methyl carbon atom is insignificant, but with X = Cl and Br it becomes prevalent. With X = CH_3, the contribution of the p_y orbitals of the methyl carbon atoms to the bonding molecular orbital is also prevalent. The above data show that these molecular orbitals are not determined by the p,π conjugation between the lone electron pair of substituent X and the π-electron system of the carbonyl group. The results obtained by the RHF/6-311G(d) and MP2/6-311G(d) methods differ insignificantly.

Thus, the variations in the populations of the p_y orbitals of the halogen and carbon atoms in CH_3COX molecules (X = F, Cl, Br, CH_3), i.e., of the orbitals whose symmetry axes are perpendicular to the molecular plane, observed in going from X = F to X = Cl, Br, and CH_3, are not associated with variations in the extent of the p,π interaction between the lone electron pair of the halogen atom and π-electron system of the carbonyl group. The ratio between the populations of the p_x and p_y orbitals of the halogen atoms and the bonding molecular orbitals formed by the p_y orbitals of atoms of the planar molecular fragment are not determined by such interaction. The results obtained by the RHF/6-311G(d) and MP2/6-311G(d) methods differ insignificantly.

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