Extended Hückel Calculations Including the Outer Orbitals: Ethylene, Methyl Chloride and Related Compounds

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LCAO calculations including the outer atomic orbitals (AO) have been carried out for small molecules by several authors.[1,2] In this note, the extended Hückel method proposed by Hoffmann[3] is modified so that the molecular orbitals (MO) are constructed not only by the valence AO's but also by the outer AO's. The calculations are made for planar ethylene, twisted ethylene, methyl chloride, and the transient species, $(Cl\cdots CH_3\cdots Cl)^-$, appearing in S_N2-type reactions. The calculations are carried out by several methods. The following AO's are included in each method:

A: valence AO's

B: valence AO's + $3s_C$, $3p_C$ AO's,

C: valence AO's + $3s_C$, $3p_C$ AO's + $2s_H$, $2p_H$ AO's,

D: valence AO's + $3s_C$, $3p_C$ AO's + $3d_C$, $3d_{Cl}$ AO's,

where $3s_C$ and $3p_C$ refer to the 3s and 3p AO's of the carbon atom and so on.

The adopted values of the Coulomb integrals of the outer AO's are as follows: −3.75 eV. for the carbon 3s AO; −2.35 eV. for the carbon 3p AO's;[4] −3.40 eV. for the hydrogen 2s, 2p AO's, and −1.47 eV. and −1.60 eV. for the carbon and chlorine 3d AO's respectively.[5] The orbital exponents of these AO's, derived from the rule in Ref. 2, which are necessary in calculating the overlap integrals, are 0.500 for the hydrogen AO's, 0.483 for the carbon AO's, and 2.0333 for the chlorine AO's. The geometries of the treated compounds have already been given in our previous paper,[6,7] where the adopted configurations for the transient species, $(Cl\cdots CH_3\cdots Cl)^-$, were denoted by the notations b-IV and b-VI.[7]*

The calculated values of the total electronic energy, the highest occupied (HO), the lowest vacant (LV), and the next LV orbital energies of the normal and twisted ethylene molecules are listed in Table I (a), along with the methods adopted. The same quantities calculated for the methyl chloride and the transient species are given in Table I (b). Remarkable effects of the inclusions of the outer AO's are seen on the lowerings of the vacant MO energies. For normal ethylene, the first π-σ^* transition energies are

TABLE I. THE CALCULATED TOTAL ENERGIES, E, THE HO, LV AND THE NEXT LV ORBITAL ENERGIES (in eV.)

(a)	C_2H_4	E	HO	LV	Next LV
Normal	A	−210.83	−13.24	−8.25	+8.14
	B	−212.47	−13.24	−8.46	−5.17
	C	−215.75	−13.24	−8.80	−5.87
Twisted	A	−207.33	−10.39	+11.02	+12.94
	B	−208.99	−10.41	−5.17	−3.61
	C	−214.19	−10.75	−5.71	−5.04

(b) CH_3Cl and the species b-IV, b-VI

	Method	E	HO	LV
CH_3Cl	A	−249.79	−13.80	+1.09
	B	−250.20	−13.80	−4.43
	D	−250.47	−13.81	−4.96
b-IV	A	−388.77	−13.76	−3.77
	B	−389.43	−13.79	−5.51
	D	−389.82	−13.82	−6.05
b-VI	A	−386.01	−12.61	−3.52
	B	−386.83	−12.68	−5.45
	D	−387.43	−12.78	−5.89

TABLE II. THE ATOMIC ORBITAL BOND POPULATIONS, $N(r-s)$, OF THE C–Cl BONDS IN THE b-VI COMPOUNDS

Method	s/r	$N(r-s)$			
		$2s_C$*	$2p\sigma_C$	$3s_C$	$3p\sigma_C$
B	$3s_{Cl}$*	−0.042	0.053	0.035	−0.022
	$3p\sigma_{Cl}$	−0.043	0.189	0.0	0.003
D	$3s_{Cl}$	−0.031	0.056	0.028	−0.022
	$3p\sigma_{Cl}$	−0.040	0.191	0.0	0.002

* The notation $2s_C$ denotes the carbon 2s AO, and $3s_{Cl}$ is the chlorine 3s AO and so on.

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* The configurations of these compounds are as follows: for the b-IV compounds, the C–Cl$^-$ distance is 2.4 Å; for the C–Cl, 1.95 Å and the Cl–C–H angle is 100°, and for the b-VI symmetrical configuration, the C⋯Cl is 2.05 Å, and the Cl–C–H angle, 90°.

21.4 eV. by Method A, and 7.4 eV. by Method C. As to the total energies, the lowerings in the twisted ethylene are larger than those in normal ethylene.

The same tendencies are found in the methyl chloride and its anions. Namely, the differences between the HO and LV orbital energies of methyl chloride are 15 eV. by Method A and 9 eV. Method D, whereas the corresponding observed value is about 8 eV.(7) The largest lowering of the total energy of the compounds in Table I (b) is found in the species with a symmetrical configuration, b-VI. Further, by population analysis of the above compounds it is shown that the carbon 3s AO participates in the C—Cl bondings while the 3pσ AO does not, as Table II shows. In other words, it may be suggested that the hybrids formed by the carbon 2pσ and 3s AO's take part mainly in the C—Cl bonding at the transition state of S_N2-type reactions. The contributions of the 3d AO's to the ground state of chlorinated compounds are found to be negligibly small.

Accordingly, it may be concluded that the inclusion of the outer AO's improves especially the excited states of the normal molecules and the ground states of the unstable compounds or of those containing atoms with unusual valencies. Hence, the improvement made in Methods B, C and D may be useful in discussing the σ-σ^* transition and the ^{13}C–H coupling constants in NMR of various compounds. Full details of these results will be published in the near furture.

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