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SELF CONSISTENT FIELD MOLECULAR ORBITAL CALCULATION FOR ANILINE

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THIS note is a preliminary report on SCF calculation[1,2] for aniline. The semiempirical LCAO MO method[2] has been applied for the calculation of the ground state orbitals. In dealing with the excited states the configuration interaction has been admitted and all singly excited configurations have been included.

The main problem in the semiempirical method, always open for discussion, is the evaluation of the basic parameters of the theory. Especially, the influence of the presence of amino group on the value of core Coulomb integral for adjacent carbon atom (the inductive effect in Hückel parlance) seems to be not unambigously established. Therefore it seems us desirable to make a comparative study of different approximations on the results of semiempirical calculations.

The expression for the core Coulomb integral is[2]

$$\alpha_p = - I_p + \sum_{q \neq p} \left(p \left| V_q \right| p \right)$$

where the summation is over all atoms which participate in the conjugation. The approximations in method A and B are concerned with the evaluation of the core-attraction terms $(p|V_q|p)$. In method A we put simply[3]

$$(p|V_q|p) = -Z_q \gamma_{pq} ,$$

where Z_q is the core charge of q-th atom with respect to π-electrons. In method B we include neutral penetration integrals, i.e. we put

$$(p|V_q|p) = (p|V_q^*|p) - Z_q \gamma_{pq} ,$$

where V_q^* is the field of uncharged atom q obtained by putting Z_q electrons in the $2p\pi$-orbital χ_q. The terms $(p|V_q^*|p)$ have been evaluated theoretically[4]. One-center Coulomb repulsion integrals and atomic valence state ionization potentials for nitrogen atom have been taken from McEwen[5] ($\gamma_{NN} = 12.74$ eV, $I_N = 24.83$ eV). Two-center integrals γ_{pq} have been calculated from the formula proposed by Mataga and Nishimoto[6].

In method C the inductive effect for carbon atom C^* adjacent to $-NH_2$ group has been introduced in a straightforward manner. We have started from the method A, but we have added corrections δ_{C^*} and δ_N to the values of α_{C^*} and α_N respectively. We have found a choice: $\delta_{C^*} = -1.0$ eV, $\delta_N = +1.6$ eV as a reasonable one.

In all methods the core resonance integrals have been taken into account only for nearest neighbours: $\beta_{CC} = -2.39$ eV, $\beta_{CN} = -2.74$ eV.

The results for transition energies E_i (in eV), oscillator strenghts f_i, ionization potential $\mathcal{J}$ (in eV) and π-electronic contribution to dipole moment (in D) of the ground state, together with the experimental data are collected in Table.

TABLE

	Method A	Method B	Method C	Experiment
E_1	4.64	4.55	4.46	4.34^{a}
f_1	0.042	0.005	-	0.026^{a}
E_2	5.68	5.32	5.28	5.29^{a}
f_2	0.23	0.39	-	0.17^{a}
E_3	6.70	6.38	6.38	6.30^{a}
f_3	1.05	0.81	-	-
E_4	6.70	6.60	6.60	
f_4	0.90	0.84	-	
μ^{π}	1.62	0.93	1.826	0.7^{b}; 0.94^{c} 1.02^{d}; $\sim 1.67^{e}$
$\mathcal{J}$	8.18	8.28	7.84	7.70^{f}

[a] from H. Baba, Bull.Chem.Soc.Japan, 34, 76 (1961).

[b] I. Fischer, Acta Chem.Scand., 4, 1197 (1950).

[c] estimated in the manner suggested by H. Hamano, H.F. Hameka, Tetrahedron, 18, 985 (1962).

[d] K.B. Everard, L.E. Sutton, J.Chem.Soc., 2818 (1951)

[e] mesomeric moment of aniline; see J.W. Smith, J.Chem.Soc., 81 (1961).

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It is evident that by inclusion of the penetration integrals (method 1) one can get a satisfactory overall agreement with the experiment. Method 2, in turn, gives the best interpretation of spectra, but fails in prediction of the dipole moment of the molecule.

More detailed discussion of the subject and other results, not mentioned here, will be reported in Acta Physica Polonica.

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