CALCULATION OF SOME CHARACTERISTICS OF SUBSTITUTED BENZENES

II. A Study of Nitrobenzene-Type Molecules by the MO LCAO Method

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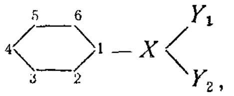
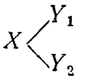
Investiya Vuz. Fizika, No. 5, pp. 5–8, 1965

Compounds of the $C_6H_5XY_1Y_2$ type have been examined, and the dependence of energy and wave functions on α_Y, β_{XY}, and β_{CX} has been studied. Numerical calculations have been carried out and tables compiled.

We shall examine compounds of the type



where the  $X\langle^{Y_1}_{Y_2}$ group has an even number of π-electrons distributed among three atoms. NO_2, COOH, etc., are included here.

The object of this paper is to clarify the behavior of the energy spectrum and the wave functions in relation to the types of atoms S, Y_1, and Y_2, which we characterize by Coulomb and exchange integrals.

CALCULATION OF SUBSTITUTED BENZENES OF THE $C_6H_5XY_1Y_2$ TYPE

As indicated in [1], the MO LCAO parametric method can be used for calculating many effects which play an important part in quantum chemistry, including the nonorthogonality of the atomic functions, exchange integrals with nonadjacent atoms, etc. The calculations given here therefore are of considerable importance for speeding up and simplifying the use of quantum-chemical methods. In our case the equation which describes the behavior of the system assumes the form

$$\sum_{q'=1}^{9} H_{qq'} c_{q'} = \varepsilon c_q. \qquad (1)$$

The energy is determined by solving the equations

$$|H_{qq'} - \varepsilon\delta_{qq'}| = 0, \qquad (2)$$

where

$$H_{11} = H_{22} = H_{33} = H_{44} = H_{55} = H_{66} = \alpha,$$

$$H_{12} = H_{23} = H_{34} = H_{45} = H_{56} = H_{61} = \beta,$$

$$H_{XX} = \alpha_X,\ H_{Y_1Y_1} = H_{Y_2Y_2} = \alpha_Y,$$

$$H_{CX} = \beta_{CX},\ H_{XY_1} = H_{XY_2} = \beta_{XY}.$$

Introducing the values $x = \alpha - \varepsilon$, $\delta_X = \alpha_X - \alpha$ and $\delta_Y = \alpha_Y - \alpha$ and expanding determinant (2), we get

$$\{x^6 + (\delta_X + \delta_Y) x^5 + (\delta_X \delta_Y - 2\beta^2_{XY} - \beta^2_{CX} - 5\beta^2) x^4 -$$
$$- [\delta_Y \beta^2_{CX} + 5(\delta_X + \delta_Y)\beta^2] x^3 + [10\beta^2 \beta^2_{XY} - 5\delta_X \delta_Y \beta^2 +$$
$$+ 3\beta^2 \beta^2_{CX} + 4\beta^4] x^2 + [3\beta^2 \beta^2_{CX} \delta_Y + 4\beta^2(\delta_X + \delta_Y)] x +$$
$$+ 4\delta_X \delta_Y \beta^4 - 8\beta^4 \beta^2_{XY}\} (x^2 - \beta^2)(x - \delta_Y) = 0. \qquad (3)$$

The following parameters were used for calculating (3): $\delta_X = 1.4\beta$, while β_{CX}, β_{XY} and δ_Y were varied respectively within the limits 0.4β to 1.5β, 0.7β to 2β, and -1β to 1β. After solving the equation we obtained the parametric family of energies ε_i $(\beta_{CX}, \delta_Y, \beta_{XY})$ and the wave functions C_{qi} $(\beta_{CX}, \delta_Y, \beta_{XY})$. Values of ε_i and $\sum_i^{\text{occ.}} |c_{qi}|^2$ are given in Tables 1 and 2.

DISCUSSION OF RESULTS AND THEIR UTILIZATION

The behavior of the levels for this class of molecules is more complicated than that for the molecules considered in [1]; nevertheless since the general regularities noted there are also observed here, we shall not give a more detailed description here. As an example of the use of the tables for calculating the molecular characteristics, we give the relevant calculations for nitrobenzene.

According to Peacock [2], the values for δ_N, δ_O, β_{CN} and β_{NO} are respectively 1.4β, 0.8β, 0.5β, 0.54β. Interpolating the values from the tables we get, disregarding self-consistency, the following energy values:

$$\alpha + 2.65\beta,\ \alpha + 1.96\beta,\ \alpha + 1.00\beta,\ \alpha + 0.99\beta,\ \alpha + 0.80\beta;$$

$$\alpha - 0.49\beta,\ \alpha - 1.00\beta,\ \alpha - 1.10\beta,\ \alpha - 2.02\beta.$$

The energy values obtained by Peacock, after carrying out the self-consistency procedure, are respectively: $\alpha + 2.6\beta$, $\alpha + 1.91\beta$, $\alpha + 1.34\beta$, $\alpha + 1.27\beta$, $\alpha + 0.83\beta$, $\alpha - 0.73\beta$, $\alpha - 1.02\beta$, $\alpha - 1.20\beta$, $\alpha - 1.72\beta$.

The energy differences, although they are not too large, are a result of changes in δ_N, δ_O, β_{CN} and β_{NO} on carrying out a self-consistent solution, which we did not do, and of the effect of distant neighbors. Agreement with Peacock's results will be complete if these effects are taken into account. We shall devote a special paper to this problem, and hence will not deal with it in more detail here. The coefficients of the atomic functions obtained by both methods of calculation are also close to each other. We think that this approach is a promising one, since it allows accurate calculation of the spectra and wave functions of various

Table 1

Energy Levels of Nitrobenzene-Type Substituted Benzenes (in β)

δ_Y	β_{CX}	β_{XY}	$\varepsilon_1 - \alpha$	$\varepsilon_2 - \alpha$	$\varepsilon_3 - \alpha$	$\varepsilon_4 - \alpha$	$\varepsilon_5 - \alpha$	$\varepsilon_6 - \alpha$	$\varepsilon_7 - \alpha$	$\varepsilon_8 - \alpha$	$\varepsilon_9 - \alpha$
—1.0	0.4	0.7	2.08	1.76	1,00	0.94	—1.00	—1.00	—1.00	—1.37	—2,01
—1.0	1.5	0,7	2.81	1.74	1.00	0.58	—1.00	—1,00	—1.00	—1.52	—2.20
—1,0	0.4	2.0	3.32	1.99	1.00	0.99	—1.00	—1.00	—1.00	—2.00	—2,89
—1.0	1.5	2.0	3.77	1.89	1.00	0.85	—1.00	—1,00	—1.00	—1.94	—3.18
0	0.4	0.7									
0	1.5	0.7	2.86	1.76	1.00	0.69	0.00	—0.39	—1.00	—1.35	—2.17
0	0.4	2.0	3.61	2.02	1.00	0.99	0.00	—0.99	—1.00	—2.12	—2.12
0	1.5	2.0	4.03	1.92	1.00	0.92	0.00	—0.89	—1.00	—1.84	—2.74
0.8	0.7	1.2	2.85	1.93	1.00	0.99	0,80	—0.49	—1.00	—1.10	—2.02
1.0	0.4	0.7	2.30	1.96	1.00	1.00	1.00	0.18	—1.00	—1.02	—2.01
1.0	1.5	0,7	2.95	1.82	1.00	1.00	1.00	0.11	—1.00	—1.32	—2.16
1.0	0.4	2.0	4.06	2.00	1.00	1.00	1.00	—0.97	—1.00	—1.67	—2.01
1.0	1.5	2.0	4.36	1.96	1.00	1.00	1.00	—0.73	—1,00	—1.71	—2.48

Table 2
Electron-Density Distribution of Nitrobenzene-Type Substituted Benzenes

δ_Y	β_{CX}	β_{XY}	No. of atom								
			1	2	3	4	5	6	7	8	9
−1	0.4	0.7	1.00	0.99	0,97	0.96	0,97	0.99	1.82	1.12	1,12
−1	1,5	0.7	0.90	0.79	0,99	1.08	0,99	0.79	1.60	1,43	1,43
−1	0.4	2,0	0.82	0,98	1.02	1.08	1,02	0,98	1,37	1.30	1.30
−1	1.5	2,0	0.92	1.02	1.00	1.02	1,00	1,02	1.37	1.29	1.29
0	1.5	0.7	0.93	1.03	1.00	1.01	1.00	1,03	1.43	1.28	1.28
0	0.4	2.0	0.99	0.99	1.02	1.02	1,02	0.99	1.21	1.37	1.37
0	1.5	2.0	0.97	1.00	1.00	1.01	1.00	1.00	1.19	1.43	1.43
1	0,4	0.7	0.96	0.92	1.00	0.98	1.00	0.92	1.24	1.45	1.45
1	1.5	0.7	0.91	0.87	0.99	0.85	0.99	0.87	1.17	1.67	1.67
1	0.4	2.0	0.99	0.99	1.00	1.00	1.00	0.99	1.07	1.46	1.46
1	1.5	2.0	1.01	0.97	1.00	0.97	1.00	0.97	1.06	1.50	1.50

molecules with a certain structure: the only time taken up in calculation is that spent on choosing the parameters, whereas several days were previously required for manual calculation. We consider it essential to compile similar tables for all classes of molecules.

In conclusion the authors would like to thank N. A. Prilezhaev and V. I. Danilov, who helped us daily in carrying out this work.

REFERENCES

1. V. A. Mikhailova and O. A. Ponomarev. Izv. vuzov SSSR, Fizika no. 4, 1965.
2. T. E. Peacock. Proc. Phys. Soc., 78, 460, 1961.

2 January 1964

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