QUANTUM CHEMICAL INVESTIGATIONS ON MOLECULAR COMPLEXES OF P-CHLORANIL WITH PIPERIDINE, ANILINE, AND THEIR DERIVATIVES

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КВАНТО – МЕХАНИЧЕСКИЕ ИССЛЕДОВАНИЯ МОЛЕКУЛЯРНЫХ КОМПЛЕКСОВ П-ХЛОРАНИЛА С ПИПЕРИДИНОМ, АНИЛИНОМ И ИХ ПРОИЗВОДНЫМИ

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Аннотация. *В настоящей работе мы провели сравнение экспериментальных данных адиабатических и вертикальных потенциалов ионизации молекулярных комплексов п-хлоранила с пиперидином, анилином и их производными с результатами кванто – механических расчётов в программе Gaussian 09.*

Introduction. Classification of molecular complexes, which has been introduced and described by Mulliken [1], is based on types of molecular orbitals of the components. In the report [2], disadvantages of such classification are shown, which motivate us to return to the re-examination properties of molecular complexes. For this reason, there is a need to research the molecular complexes of one electron acceptor with a wide range of electron donor molecules. The present work aimed at analyzing linear relation the energies of charge-transfer bands of molecular complexes are related to ionization potentials of the donor components. All complexes conform to linear relations like involving both adiabatic and vertical ionization potentials of donor components. The development of photoelectron spectroscopy has led to the measurement of adiabatic and vertical ionization energies for thousands of molecules, which allow theirs to the present analysis of spectral properties molecular complexes.

Materials and research methods. We collected the information about a maximum of the charge-transfer bands of molecular complexes of p-chloranil with various donor substances and adiabatic and vertical ionization potentials from science publications [1-3]. These results were compared with calculation results. Different quantum molecular properties may be described better by different computational methods, depending on the sophistication of the computational approaches. We decided to use Density Functional Theory (DFT), because DFT takes into account a part of correlation and it has been reported to provide fairly good results for the description of various molecular properties such as the energy of the Highest Occupied Molecular Orbital, the energy of the Lowest Unoccupied Molecular orbital, electronegativity, ionization potential, etc. [4]. Calculations were done at DFT/B3LYP using the 6-31++G (d, p) basis set because of using this method in most of research works in our area [4, 5].

Results. There is π-π-interaction between donor and acceptor only for the complexes of p-chloranil with the aniline, piperidine and their derivatives. The aromatic donor and quinone rings in these complexes are almost

parallel but are displaced with respect to each other [3]. We did not find a systematic distinction between a single methyl substituent at carbons orto, meta, para – isomers of piperidine. Each type of methyl decreases the amine ionization potential by 0-0,03 eV. These C-methyl substituents occupy equatorial positions in the chair conformation of piperidine. Gas-phase and nonpolar solvent studies [2] indicate a 60-70% preference for an axial lone pair in piperidine. The results of experimental and calculated ionization potentials with charge – transfer bands maximum are presented in the Table 1.

Table 1

Maxima of charge-transfer bands in the electronic absorption spectra of molecular complexes of p-chloranil and ionization potentials of N-donors

Donors	*Charge-transfer bands maximum, λmax, [nm]*	*Experimental*		*Calculated*	
		IPa	IPv	*IPa*	IPv
Piperidine	589	8,20	8,70	7,69	8,31
o-methylpiperidine	592	8,04	8,63	7,62	8,24
m- methylpiperidine	589	8,03	8,63	7,63	8,24
p- methylpiperidine	589	8,06	8,61	7,65	8,24
N- methylpiperidine	602	7,80	8,37	7,25	7,90
Aniline	530	7,74	8,05	7,47	7,78
o-Toluidine	562	7,52	7,84	7,52	7,62
m-Toluidine	550	7,55	7,66	7,55	7,62
p-Toluidine	575	7,37	7,81	7,37	7,50
N-methyl-Aniline	590	7,34	7,65	7,34	7,41

Conclusions. The spectra of molecular complexes of chloranil with anilines and piperidines have been obtained in the present work and taken from available literature. These data have been examined. The obtained calculations have some difference from the experimental ones. Despite the lower values compared with the experimental data, the calculated values have a predictable difference, which can be used as a forecasting of the properties and values of certain quantum mechanical characteristics of more complex derivatives. In the future, a more detailed quantum-mechanical study of molecular complexes is planned to calculate charge-transfer bands maximum, the distance and the mutual arrangement between molecules in the molecular complexes, which will help us better understand their properties, reactivity, etc. Also within the framework of this thesis, the need for using quantum mechanical calculations to predict the change in the properties of complexes has been confirmed, but it is necessary to study the results in other basic sets.

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