

## **Design of new organic materials based on fluorene and its heterocyclic analogues**

### Summary

The use of organic substances as optoelectronic devices is a direct consequence of their electronic structure, including the energy of HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) molecular orbitals. Among the many strategies used in the design of new optoelectronic materials based on organic systems, is the obtaining of polycyclic structures, the introduction of heteroatoms into the molecules and the substituent effect. These strategies aim to generate an intramolecular charge flow that results in changes in the electronic structure within the entire molecule. Fluorene is one of the molecular systems based on a structural skeleton, with great hopes associated with its use as optoelectronic materials. Replacing the tetrahedral carbon atom in the five-membered ring of fluorene by boron (dibenzoborol), nitrogen (carbazole), oxygen (dibenzofuran), phosphorus (dibenzophosphole) or sulfur (dibenzothiophene) leads to the formation of its heterocyclic analogues.

In this doctoral thesis, the analysis was performed on the molecular structure and intramolecular charge transfer in tetracyclic systems obtained by condensation of fluorene and five of its heterocyclic analogues (B, N, O, P, S) and successively with pentafulvene, a five-membered heterocyclic ring located in the middle of the tricyclic system and borole.

The molecular structures of the studied systems were obtained using quantum-mechanical calculations using the B3LYP density functional combined with the 6-311++(2d,2p) basis set. All the optimized geometries of the studied systems have all positive frequencies. Quantitative indexes HOMA (Harmonic Oscillator Model of Aromaticity), *p*DI (*para*-Delocalization Index) and FLU (the aromatic Fluctuation index) were calculated for the rings of the studied systems. In addition, for the amino group used as a substituent in selected systems, the cSAR (the charge of the Substituent Active Region) index was calculated.

In the four-ring systems, the individual rings were marked as A, B, C coming from the tricyclic system, while the condensed ring was marked as D. The structures of the analysed systems in most cases were planar, only in a few cases the structure of the studied systems took the shape of a bowl with the  $C_s$  point group symmetry. In each of the groups of analysed systems, a significant increase in the relative lengths of the common carbon-carbon bond formed as result of condensation, was observed. In the same systems, the smallest changes in

the relative length of carbon-carbon bonds were observed in comparison with isolated five-membered rings (before condensation). The values of the HOMA index were calculated for all four rings of the analysed systems, the *p*DI index for the A and C rings, while for the C rings in all systems, due to the large changes in  $\pi$ -electron delocalization observed in it, the FLU index values were additionally calculated. Their mutual correlation was checked on the obtained quantitative values of aromaticity indices, which showed a relative agreement of these indices in the description of changes in the level of  $\pi$ -electron delocalization in the examined rings.

The values of the aromaticity indexes showed that in all the analysed systems, in the A rings, the  $\pi$ -electron structure does not undergo major changes caused by the condensation of the fourth ring. In systems where rings B and D are the same, higher values of the HOMA index were observed for ring D. The lowest values of this index were observed for rings B and D in systems where both rings are adjacent to each other and these systems have the greatest deformation from planarity. In all analysed groups of systems condensed in such a way that a quinoid structure was formed in the C ring, the greatest changes in the  $\pi$ -electron structure of C rings were observed, leading even to the complete disappearance of their aromatic character. An attempt to rebuild their  $\pi$ -electron structure before the condensation with the fourth ring was made by applying the substituent effect with an electron-donating amino group, substituting it in two different positions of the D ring in these systems. The greatest effect of amino group substitution was observed in systems in which this group was substituted on the carbon atom in the fourth borole ring.

The calculated values of the cSAR index for the substituted amino group in systems with a condensed pentafulvene ring showed a good correlation with the HOMA index values calculated for the D ring, but much worse for the C ring. In addition, these values showed a good correlation with the length of the carbon-amine nitrogen bond and with the distance of the amino nitrogen atom from the plane defined by three atoms bound to it. In the amino-substituted systems where ring B and D were the same, the cSAR values also correlated well with the carbon-nitrogen of amino group bond lengths. However, in systems with a condensed borole ring, the calculated values of the cSAR index for the amino group also show a good correlation with the HOMA index values for the C and D rings and with the lengths of the boron- nitrogen of amino group and carbon- nitrogen of amino group bonds.

The condensation of the fourth ring results in a reduction of HOMO-LUMO energy gap ( $E_g$ ) in all cases. The biggest change was observed for the C ring - it lost its aromaticity. A

significant reduction in  $E_g$  was observed in the amino-substituted systems. From the point of view of the effectiveness of reducing the  $E_g$  gap by significantly lowering the LUMO level, the best structure was observed for borole condensed as the fourth ring.

Considering the energy aspects of the formation of tetracyclic systems, it was noticed that in the structures in which the HOMA index values for the C ring significantly decreased and the HOMO-LUMO energy gap decreased, the energy of these systems was higher by up to 35 kcal/mol.