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QUANTUM REACTIVITY PARAMETERS COMPUTATIONS FOR ELECTROCHEMICAL BEHAVIOR ASSESEMENT

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Introduction

Structure of 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(5-isopropyl-3,8-dimethylazulen-1-yl)pyridine (**LV**) was investigated by DFT method using computational tools, aiming to assess their molecular key parameters for reactivity and electrochemical behaviour. Energetical levels of frontier molecular orbitals, the Highest Occupied Molecular Orbital (HOMO) and of the Lowest Unoccupied Molecular Orbital (LUMO) were calculated and used to obtain global reactivity descriptors and an assessment of oxidation and reduction potentials for electrochemical applications. Some studies report correlations between the molecular orbital energies and their reduction and oxidation potentials obtained from cyclic voltammetry. Consequently, we tried to verify this assumption using Density Functional Theory (DFT) *in silico* computations on the lowest energy conformer of the above-mentioned structure.

Materials and methods

Computations were carried out with Spartan'18 Wavefunction, Inc. Irvine, CA, U.S.A using B3LYP algorithm with 6-31+G (d, p), basis set, for equilibrium geometry, at ground state. Neutral molecule presenting the energy minima is considered for quantum parameters calculations.

Results and conclusions

In Figure 1 is illustrated the structure of **LV** in 2D and 3D view obtained with molecular mechanics force fields (developed by Merck Pharmaceuticals), along with the electrostatic potential map representation supperposed with the dipole moment vector orientation. From the charge distribution calculations, the resulted minimum value of electrostatic potential map at the electron density surface (MinElPot) is -162.13 kJ/mol. Red area is illustrated on the nitrogen atom, indicating the most susceptible region where the complexation with positive metal ions can occur. This assumption is consistent with the value of the dipole moment and the orientation of its vector. The maximum value of electronic potential map at the electron density surface (MaxElPot) is 102.56 kJ/mol.

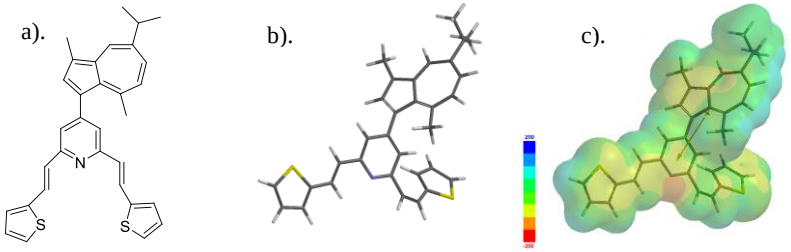
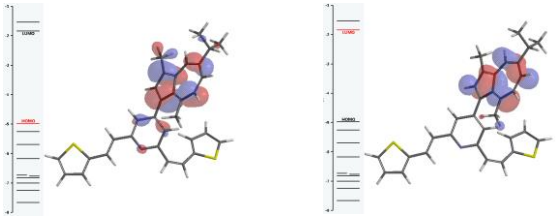


Figure 1. a) 2D Structure of **LV**; **b)** 3D optimized structure by energy minimization (having the energy of - 2089.93628 a.u.); **c)** Electrostatic potential map along with dipole moment vector



E_{HOMO} = -4.98 eV
E_{LUMO} = -1.84 eV

Figure 2. Frontier molecular orbitals energy levels for **LV**

Figure 2 represents the distribution of the frontier molecular orbitals, HOMO and LUMO and their energetical levels. Kinetic stability and reactivity of molecules can be easily predicted using relationships stated in the Koopmans' theorem, starting from calculated values of frontier molecular orbitals. Quantum reactivity parameters are depicted in Table 1.

Table 1. Calculated quantum global reactivity parameters

Parameter	Formula	Calculated value
ΔE gap	$E_{HOMO} - E_{LUMO}$	3.14
Ionization potential (*IP*)	$IP = -E_{HOMO}$	4.98
Electron affinity (*EA*)	$EA = -E_{LUMO}$	1.84
Electronegativity (χ)	$\chi = (I + A)/2$	3.41
Chemical potential (μ)	$\mu = (E_{HOMO} + E_{LUMO})/2$	-3.41
Electrophilicity index (ω)	$\omega = \mu^2 /2\eta$	9.13

Forward electrochemical measurements will be considered in order to verify our predictions regarding oxidation and reduction potentials, which are useful in complexation processes.

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