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QUANTUM REACTIVITY PARAMETERS COMPUTATIONS FOR ELECTROCHEMICAL BEHAVIOUR ASSESSEMENT

Alina-Alexandra Vasile[1], Amalia Stefaniu[2], Ovidiu Matica[1], Eleonora-Mihaela Ungureanu[1]*
[1]Politehnica" University of Bucharest, Gheorghe Polizu 1-7, 011061, Bucharest, Romania
[2]National Institute for Chemical - Pharmaceutical Research and Development (ICCF), 112 Vitan av., 031299 Bucharest, Romania
[*]Corresponding author: em_ungureanu2000@yahoo.com

Introduction

Structure of 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(5-isopropyl-3,8-dimethylazulen-1-yl)pyridine was investigated by DFT method using computational tools, aiming to assess their molecular key parameters for reactivity and electrochemical behaviour.

We achieved an global reactivity analysis and an assessment of oxidation and reduction potentials for electrochemical applications

Research

Computational details

- ✓ Spartan'18 Wavefunction, Inc. Irvine, U.S.A
- ✓ B3LYP algorithm with 6-31+G (d, p) basis set
- ✓ Equilibrium geometry, at ground state
- ✓ MMFF procedure for energy minimization

The results revealed that the minimum value of electrostatic potential map at the electron density surface (MinElPot) is -162.13 kJ/mol. The maximum value of electronic potential map at the electron density surface (MaxElPot) is 102.56 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.

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.

Bredas et all's empirical equations:

$$E_{HOMO} = -e\,[E_{ox}^{onset} + 4.4]$$
$$E_{LUMO} = -e\,[E_{red}^{onset} + 4.4]$$

E_{HOMO}, E_{LUMO} – energies of the Highest Occupied and Lowest Unoccupied Molecular orbital, respectively
E_{ox}, E_{red} – oxidation and reduction potential, respectively

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

Acknowledgement

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Results

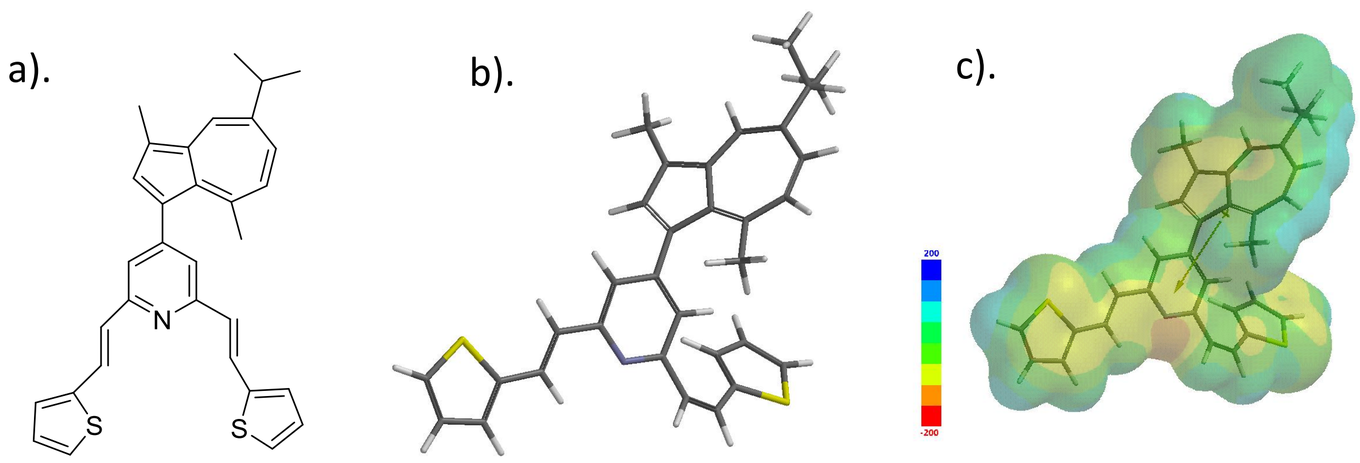
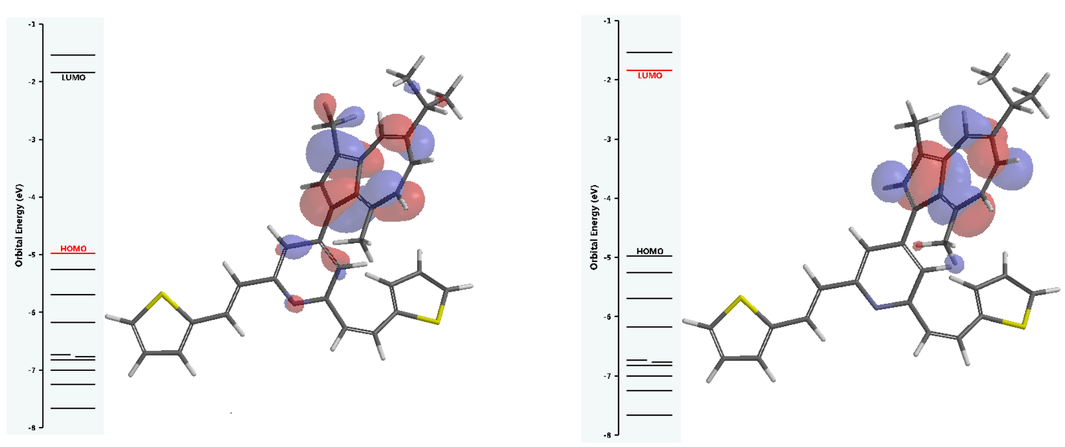


Fig. 1 a) *2D Structure;* ***b)*** *3D optimized structure by energy minimization (having the energy of - 2089.93628 a.u.);* ***c)*** *Electrostatic potential map and dipole moment vector*



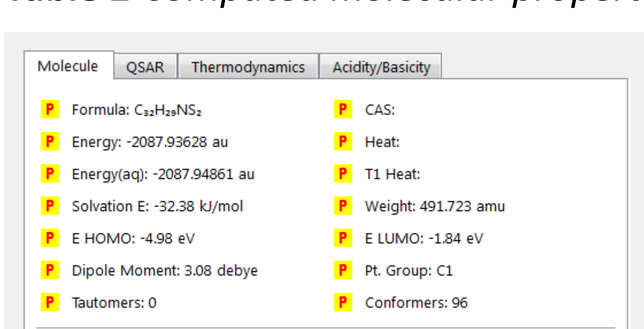
E_{HOMO} = -4.98 eV
E_{LUMO} = -1.84 eV

Fig. 2 *Frontier molecular orbitals energy levels*

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
Hardness (η)	$\eta = (I - A)/2$	1.57
Softness (σ)	$\sigma = 1/\eta$	0.64
Chemical potential (μ)	$\mu = (E_{HOMO} + E_{LUMO})/2$	-3.41
Electrophilicity index (ω)	$\omega = \mu^2 /2\eta$	9.13

Table 2 *Computed molecular properties*



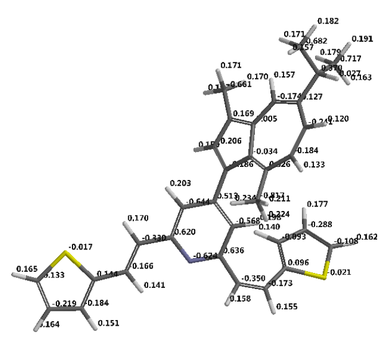


Fig. 3 *Electrostatic charges*

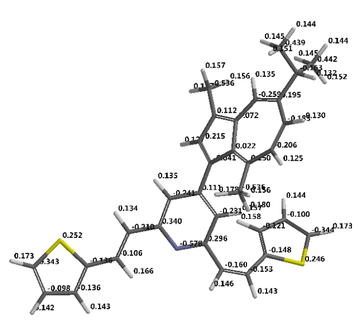


Fig. 4 *Mulliken charges*

CONCLUSION

Complexation process with heavy metals ions is expected to occur at the nitrogen atom, where the most electronegative region arises. The compound posses relatively large ΔE gap, being relatively stable. The oxidation and reduction potentials can be predicted form the calculated HOMO and LUMO energies.