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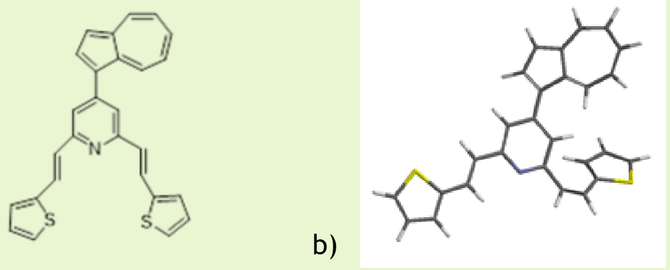
REACTIVITY ANALYSIS FOR 4-(AZULEN-1-YL)-2,6-BIS((E)-2-(THIOPHEN-2-YL)VINYL)PYRIDINE USING CALCULATED QUANTUM PARAMETERS

Ovidiu-Teodor Matica,[1*] Cristian Omocea,[1,2] Roxana Luisa Popescu,[3] Eleonora-Mihaela Ungureanu,[1] Amalia Stefaniu[4]

[1] "University Politehnica of Bucharest, Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry, Bucharest, Romania
[2] Water Basin Administration Dobrogea - Litoral, Constanta, Romania
[3] National Research and Development Institute for Industrial Ecology – Ramnicu Valcea Subsidiary
[4] National Institute of Chemical-Pharmaceutical Research and Development (ICCF), Bucharest, Romania
[*] Corresponding author: email: maticaovidiu@yahoo.co.uk



a) b)

2D (a) and 3D optimized geometry (b) structures of 4-(azulen-1-yl)-2,6-bis((e)-2-(thiophen-2-yl)vinyl)pyridine

COMPUTATIONAL PROCEDURE

- ✓ 3D stucture generation
- ✓ Geometry optimization: energy minimization, MMFF
- ✓ Density functional theory (DFT) method
- ✓ Functionals: B3LYP (a global hybrid functional) [1]
- ✓ Equilibrium geometry at ground state
- ✓ Spartan Software, Wavefunction Inc, Irvine, USA [2]

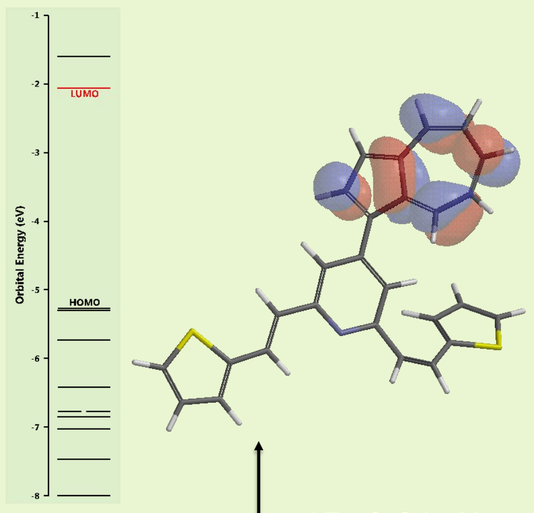
Global reactivity parameters from Koopmans' theorem [3]

FMOs energy gap, ΔE(eV)	$\lvert E_{HOMO} - E_{LUMO} \rvert$
Ionization potential, *IP* (eV)	$IP = - E_{HOMO}$
Electron affinity, *EA* (eV)	$EA = - E_{LUMO}$
Electronegativity, *x* (eV)	$x = (I + A)/2$
Global hardness, η (eV)	$\eta = (I - A)/2$
Local softness, σ (eV)	$\sigma = 1 / \eta$
Chemical potential, μ(eV)	$\mu = (E_{HOMO}+E_{LUMO})/2$
Global electrophilicity index, ω(eV)	$\omega = \mu^2 / 2\eta$

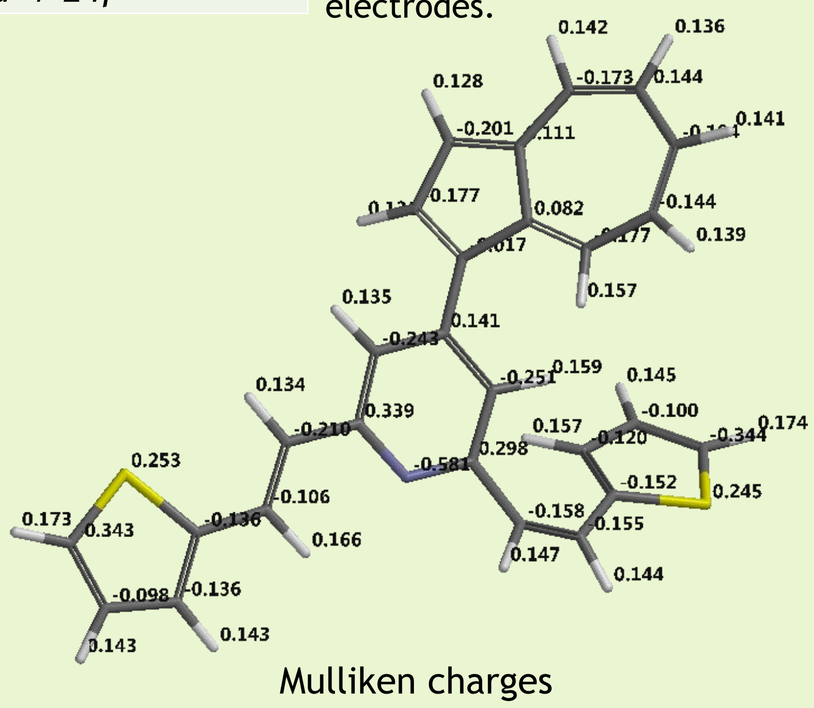
Calculated global reactivity parameters according to Koopmans' theorem

Parameter	E_{HOMO}	E_{LUMO}	ΔE	*IP*	*EA*	*x*	η	σ	μ	ω
Value (eV)	-5.27	-2.06	3.21	5.27	2.06	3.67	1.61	0.62	-3.67	4.18

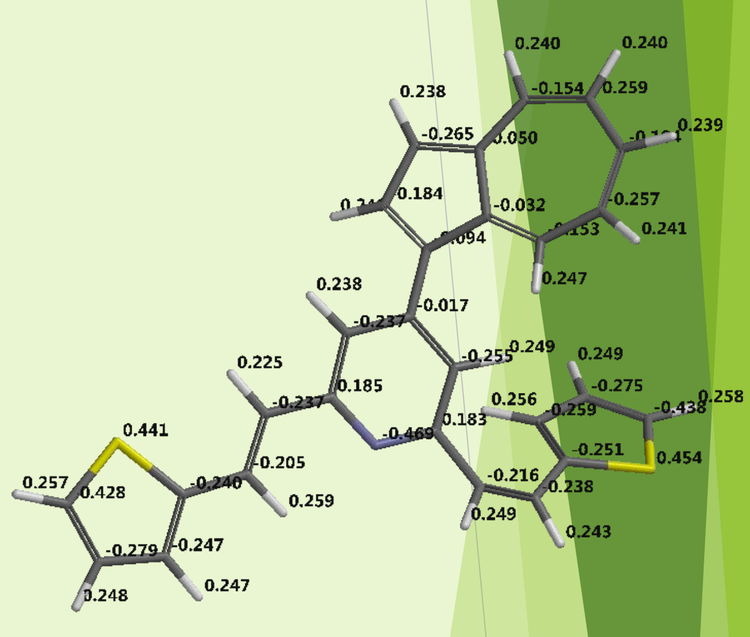
IP and *EA* can be furthermore correlated with the experimental oxidation and reduction potentials as previously shown for other compounds of electrochemical interest [4-6]. Kinetic stability (ΔE) and reactivity parameters (IP, EA, *x*, η, σ, μ, ω) *are* useful to evaluate complexing ability (toward heavy metals ions), and can be compared with similar results obtained for other structures to find the rational design of complexing ligands for modified electrodes.



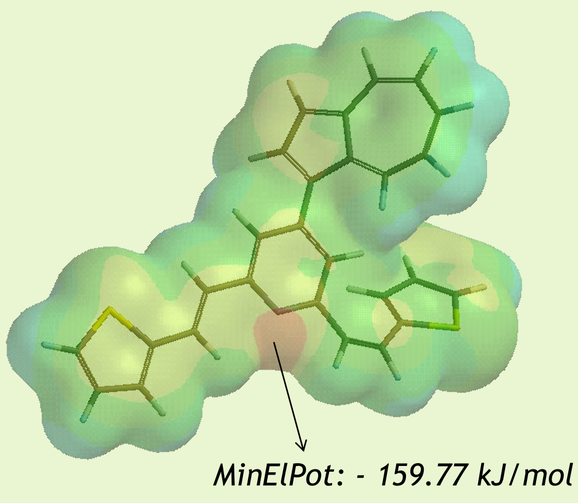
Frontier molecular orbitals energy levels and gap



Mulliken charges



Natural charges



Electrostatic potential map

CONCLUSIONS AND PERSPECTIVES

- ✓ **The reactivity analysis by computational means based on electron density properties, allowed the evaluation of a series of quantum parameters useful for electrochemical applications.**
- ✓ **Electrophilic and nucleophilic sites quantitatively approximated using DFT theory improve our strategy efforts in designing better ligands.**

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