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Article

STRUCTURE AND REACTIVITY OF SOME AROMATIC COMPOUNDS WITH ACIDIC AND BASIC CHARACTER

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ABSTRACT

Energetic and structural indices established with quantum-mechanics calculations by Hückel molecular orbital method (HMO) have been used to correlate the structure and reactivity of some diazotable and coupling compounds. The investigated molecules are used to obtain azo dyes.

Keywords: Amines, Dyes, Quantum chemical calculations, Structure, Reactivity of Aromatic Compounds

1. INTRODUCTION

The present investigation resides in our interests for aromatic compounds involved in substitution reactions [1]. The molecules selected for the study illustrate their role in diazotation and coupling processes as substrates and electrophilic reactants, respectively. Therefore, the aromaticity of some amines and their derivatives, also hydroxy arenes, can be correlated with both energetic and π electron density repartition indices, calculated by HMO method [2]. Some of the presented systems fit the general Ar-Y model (Y: $-OH$, $-NH_2$, $-NH_3^+$, $-NHR$, $-NR_2$), highly correlated with the electronic effects (σ and π) and substituent constants, too [3].

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In order to contribute to the knowledge of the structure-reactivity relationship in diazotization reaction, electronic spectra (200-800 nm) were recorded for sulfanilic acid, sulfanilamide and the corresponding hydrochlorides, for diazonium salts and hydrolysis products. Molecular orbital calculations using the HMO method were performed for the above mentioned molecules [4].

The diazonium salts were obtained through diazotization in acidic solution with sodium nitrite, the nitrous acid excess was destroyed with ammonium sulfamate. The concentrations and the preparation technique were those described in the specific literature [5].

Solid sulfanilic acid can also be treated with gaseous NOCl in order to obtain solid diazonium chloride with a 100% yield. The water produced within the reaction is removed *in situ* with the NOCl excess [6]. Diazonium salts as diazotization products, on the one hand, and electrophilic reactants in azo coupling processes, on the other hand, are also involved in thermal decomposition reactions [7]. The kinetics of thermal decompositions of diazonium salts of sulfanilic acid and sulfanilamide were monitored in solution by spectrophotometry. The following activation energies (E) and pre exponent (A) values were obtained for thermal decompositions of benzene diazonium salts: $E = 127.19$ kJ mol^{-1}, $A = 6.0 \cdot 10^{15}$ s^{-1} for the sulfanilic acid derivative, and $E = 124.20$ kJ mol^{-1}, $A = 4.0 \cdot 10^{15}$ s^{-1} for the sulfanilamide derivative [8]. For these quick reactions in which C-N bonds break, a value of $A > 10^{14}$ s^{-1} indicates that, within the activated complex, the interaction of π electrons between the nitrogen atoms and atoms of the molecule residue is weaken or even cancelled [9].

The correlation diagram of molecular orbitals and the correlation diagram of electronic states for the decomposition reaction of the benzene diazonium cation were established using Hückel molecular orbital calculations [10]. The activation energy of the thermal decomposition must be of purely thermodynamic nature, without a certain barrier, as the diazonium cation is more stable than the decomposition products [7]. The following activation enthalpies ($\Delta H^{\neq}$ / kJ mol^{-1}) and activation entropies ($\Delta S^{\neq}$ / J K^{-1} mol^{-1}) were obtained for thermal decompositions of benzenediazonium salts: for the sulfanilic acid derivative $\Delta H^{\neq} = 124.683$, $\Delta S^{\neq} = 48.116$ for the sulfanilamide derivative $\Delta H^{\neq} = 121.336$, $\Delta S^{\neq} = 44.350$ [8]. The activation enthalpies were quite high instead the corresponding activation entropies have high positive values.

The experimental data illustrate that stability of substituted diazonium ions, precipitated as diazonium fluoroborates, can be increased by complexation with crown ethers [11]. Diazonium cations are not strong electrophilic reactants due to delocalization of their positive change. Instead, a higher reactivity is encountered at those diazonium cations possessing electron attractive substituents in para positions [12]. The azo coupling process of these compounds may occur only with strong nucleophiles such as: phenolates, naphtholates, free aromatic amines, in which case it has an elevated selectivity [13]. Therefore, the azo coupling reactions occur almost unitary at positions with the highest electron density (ρ_q) of the coupling compounds [14]. The reactivity of coupling compounds, variously substituted at the same position, falls within the series $-\mathrm{O}^- > -\mathrm{NH}_2 > -\mathrm{OH}$, and the substitution orientation at multifunctional components is governed by pH through protolithic equilibriums in which hydroxyl and amino groups are engaged [15].

2. RESULTS AND DISCUSSIONS

Over time, performed calculations have shown that the HMO method correctly illustrates the variation of electronic density repartition and energy levels within a series of molecules, not too different from each other [2]. The method success is related to the use of parameters based on experimental results, fact that conducts to a significant compensation of errors arisen from applied simplifications [14]. Selecting the Streitwieser parameters (Table 1), the energetic and structural indices of conjugated systems possessing a certain number of electrons (n_π) have been calculated using computational techniques.

Table 1: The HMO parameters used in calculations (after Streitwieser) [16]

Group	h_x	*Bond*	$K_{Y\text{-}X}$
$-NH_2$	1.50	$Ar\text{-}NH_2$	0.80
$-\overset{+}{N}\equiv;\ \equiv N$	1.25	$Ar\text{-}N=$	1.00
$-OH$	2.00	$-\overset{+}{N}\equiv N$	1.00
$-N(CH_3)_2$	1.10	$Ar\text{-}OH$	0.80
$-NH_3^+$	0.50	$Ar\text{-}COOH$	0.90
$=O$	1.00	$-\underset{\vert}{C}=O$	1.00

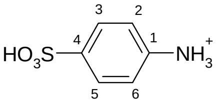
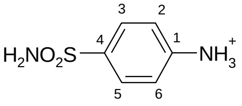
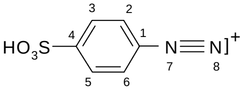
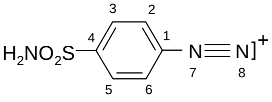
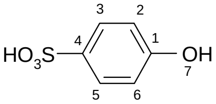
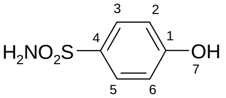
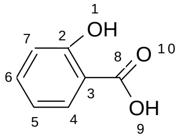
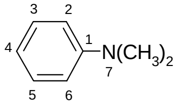
The presence of solubilizing ($-SO_3H$) and ($-SO_2NH_2$) groups does not interfere with the electronic state of the carbon atom to which they link. Moreover, these groups do not participate in conjugation with the aromatic ring [17,18].

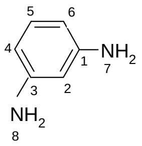
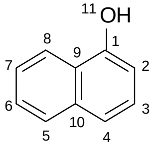
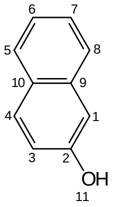
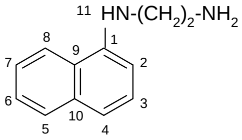
For a certain compound, the values of delocalization energy (DE), the highest occupied molecular orbital energy (ε_{HOMO}), the lowest unoccupied molecular orbital energy (ε_{LUMO}) facilitate the estimation of compound stability, and its reducing or oxidizing character. With regard to the absorption bands appearing in UV-VIS domain, the first band (λ_{max}) corresponds either to transition between ε_{LUMO} and ε_{HOMO} of the highest conjugated system or to transition from a non-participating atomic orbital to ε_{LUMO}. The $n\text{-}\pi^*$ transition needs a lower energy than the $\pi\text{-}\pi^*$ transition and thus it occurs at higher wavelengths [14,19].

Although, the HMO method does not adequately consider the electron repulsion, which opposes their agglomeration at a given atom, there is a certain consistency between parameters characterizing electron distribution and chemical reactivity of the corresponding atoms. Thus, the electronic densities (ρ_q) are correlated with atoms basicity, with their ability to participate in the electrophilic substitutions [2,14].

The values obtained by HMO method sustain the chemical reactivity interpretation given for the 12 investigated organic molecules (Table 2).

Table 2 Energetic indices calculated by HMO for the organic compounds used in diazotization and coupling reactions

Compound	n_π	$DE(\beta)$	ε_{LUMO}	ε_{HOMO}	λ (nm)
 (I)  (II)	6	2.0490	$\alpha - 0.8409 \cdot \beta$	$\alpha + \beta$	282
 (III)  (IV)	8	2.6073	$\alpha + 0.1786 \cdot \beta$	$\alpha + \beta$	633
 (V)  (VI)	8	4.1968	$\alpha - 0.999 \cdot \beta$	$\alpha + 0.8274 \cdot \beta$	284
 (VII)	12	5.1408	$\alpha - 0.5351 \cdot \beta$	$\alpha + 0.8386 \cdot \beta$	378
 (VIII)	8	3.7320	$\alpha - \beta$	$\alpha + 0.7437 \cdot \beta$	298

 (IX)	10	3.4650	$\alpha-1.0404\cdot\beta$	$\alpha+0.6824\cdot\beta$	302
 (X)	12	5.8872	$\alpha-0.6606\cdot\beta$	$\alpha+0.5382\cdot\beta$	434
 (XI)	12	5.8812	$\alpha-0.6332\cdot\beta$	$\alpha+0.5807\cdot\beta$	428
 (XII)	12	5.4264	$\alpha-0.6698\cdot\beta$	$\alpha+0.5022\cdot\beta$	444

Tabel 3. Electronic densities (ρ_q) calculated by HMO for the atoms of some coupling components of sulfanilic acid and sulfanilamide diazonium salts

Compound	ρ_1	ρ_2	ρ_3	ρ_4	ρ_5	ρ_6	ρ_7	ρ_8	ρ_9	ρ_{10}	ρ_{11}
V, VI	0.9547	1.0400	0.9980	**1.0292**	0.9980	1.0400	1.9400	-	-	-	-
VII	1.9306	0.9035	1.0572	0.9523	**1.0288**	0.9574	1.0417	0.6394	1.8953	1.5939	-
VIII	0.9538	1.0484	0.9977	**1.0367**	0.9977	1.0484	1.9172	-	-	-	-
IX	0.9521	1.0989	0.9521	**1.0835**	0.9953	**1.0835**	1.9173	1.9173	-	-	-
X	0.9442	1.0561	0.9958	**1.0407**	1.0071	0.9983	1.0095	0.9934	1.0210	0.9993	1.9346
XI	**1.0566**	0.9530	1.0259	0.9957	0.9983	1.0097	1.0000	1.0096	0.9984	1.0138	1.9399
XII	0.9418	1.0685	0.9952	**1.0514**	1.0092	0.9980	1.0127	0.9923	1.0248	0.9993	1.9076

- The hydrochlorides of sulfanilic acid and sulfanilamide (I), (II), and also their diazonium salts (III), (IV) present low values of delocalization energy (DE), as these compounds are double substituted in para positions with electron attractive groups. The hydrolysis products of sulfanilic acid and sulfanilamide diazonium salts (V), (VI), and also the salicylic acid (VII) are more aromatic than N,N-dimethyl aniline (VIII) and m-phenylene diamine (IX), in accordance with TOPAZ aromaticity [20]. Moreover, using the Hückel theory (HT) it can be seen that 1-naphthol (X) and 2-naphthol (XI) are more stable than 1-naphthyl ethylenediamine (XII), and the (V), (VI) compounds are more aromatic than (VIII) molecule.
- The ε_{LUMO} and ε_{HOMO} values indicate that (I), (II), (III), (IV) compounds are the most resistant to oxidation, and the (VIII), (IX) molecules are the most resistant to reduction. The (III), (IV) compounds should be stronger oxidizing agents, and the (XII) polynuclear amine should be stronger reducing agent.
- For the (I), (III), (V) compounds that are present in the acidic solution when sulfanilic acid diazotization occurs, and also the (II), (IV), (VI) compounds present in the medium when sulfanilamide is diazotized, the correlations between $\lambda_{calculated}$ and spectral measurements ($\lambda_{experimental}$) are satisfactory [4].
- Regarding the electronic densities calculated with HMO method for the atoms of (V) to (XII) molecules (Table 3), it should be mentioned that their relative values are more important than their absolute ones within this series of similar compounds, or for different atoms of the same substance.
- The atoms electronic densities follow the $\rho_O > \rho_N > \rho_C$ relationship being in good agreement with the known electronegativity tendency [21,22]. The usage of phenolates and naphtolates, strong nucleophiles, in azo coupling reactions is based on the fact that the oxygen atom in the $-O^-$ anion is less electronegative than in the -OH group due to its negative charge [14].
- The calculated values in Table 3 place the coupling components upon reactivity as follow:

(IX) > (VIII) > (V), (VI) > (VII); (XII) > (X); (XI) > (X), according to their experimental behavior.

- The diazonium cations (III), (IV) perform electrophilic attacks to the following atoms: C(4) of (V), (VI), (VIII), (IX), (X), (XII), C(5) of (VII) and C(1) of (XI) coupling components. It should be mentioned that the ($-SO_3H$) group of (V) molecule and the ($-SO_2NH_2$) group of (VI) molecule are removed through these reactions [12].
- Even though the C(2) atoms of (V), (VI), (VIII), (IX), (X), (XII) compounds and C(7) atom of (VII) molecule are positions with the highest electronic density, the electrophilic attacks do not occur at these atoms due to steric impediments.

The motivation of choosing these molecules is mainly linked to the azo dyes that can be synthesized from these (Table 4).

Table 4: Aromatic amines, hydroxy arenes and corresponding azo dyes [13]

Diazotable compounds	*Coupling compounds*	*Azoic dyes*
I	VIII	Methyl orange
	XI	*β*-naphthol orange
	X	*α*- naphthol orange
	VII	Chromatable acid yellow
II	IX	Red prontosil

4. CONCLUSIONS

The calculation of energetic indices by HMO method for the investigated conjugated systems enables their comparison regarding aromaticity and oxidizing/reducing character. The performed analysis underlines that as the bonds conjugated system extends the maximum absorption band moves towards visible domain. In this context, naphtolates are preferred as coupling components. We found a good agreement between structural indices and also between them and reactivity of atoms of series of similar compounds.

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