STABILITY AND AROMATICITY OF SOME CONJUGATED SYSTEMS BY QUANTUM ANALYSIS AT THE HÜCKEL LEVEL

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Abstract. Some physical and chemical properties of the hydrocarbons, of the acyclic and cyclic ions and of the heterocycles with nitrogen can be correlated with static reactivity parameters, described by the molecular orbitals method. The results of the calculations made using Hückel method are listed both as energy parameters and as parameters regarding π-electron density distribution. These indices point out the relative reactivity of planar compounds in a series and the sites in a molecule, where substitutions, additions, or other reactions occur. The characterization of the stability and the aromaticity of the investigated organic structures is undertaken in order to compare their chemical behaviour. Taking into account the calculations based on Hückel method and the literature data, aromatic and anti-aromatic compounds are compared to the non-aromatic planar systems. Also, the ranking of the aromatic ions according to their stability allows the correlation of their energy indices with the oxidizing and reducing character.

Key words: delocalization energy, aromaticity, wavenumber, hydrocarbons, Hückel method, chemical reactivity, free valence, electronic density.

INTRODUCTION

The planarity of the conjugated systems is a consequence of the type of sp^2 hybridization of the C and N atoms involved in the chemical bonds. Molecules become more stable by conjugation, which is an energy release process and the resulting energy is named the conjugation energy (E_{conj}). In the bond valence theory, conjugation energy is treated as resonance energy (E_{R}) and by the molecular orbital method (MOM) it is considered as delocation energy (E_{D}) [1].

Between the 1950s and 1960s, the applications of quantum chemistry on organic compounds were dominated by the use of the HMO method, which allowed the development of more advanced molecular orbital methods and, with the help of computers, contributed to the development of modern organic chemistry [28]. Professor Zeno Simon PhD was the first and the only researcher in Romania

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knowing and applying HMO method for organic compounds for many years. Professor PhD Zeno Simon developed this field in Romania and involved many other researchers that continued and diversified the applications of this method in organic chemistry.

The aim of this paper is to correlate some accessible results concerning quantum chemical computation with physicochemical properties of a few aliphatic and aromatic compounds. The investigated cyclic planar molecules with $(4n+2)\pi$ electrons present high stability, low magnetic susceptibility (diamagnetism), and a preference for substitution reactions instead of addition ones [5, 26, 31]. We apply Hückel molecular orbital method [11] to explain the reactivity of some hydrocarbons, acyclic ions, cyclic ions with an aromatic character and heterocycles with nitrogen respectively.

METHODS

Within this study we consider 15 organic compounds: ethylene (01), butadiene (02), cyclobutadiene (03), hexatriene (04), benzene (05), octatetraene (06), cyclooctatetraene (07), cyclopropenyl cation (08), cyclobutadiene dication (09), cycloheptatriene cation (10), allylic anion (11), cyclopentadiene anion (12), cyclooctatetraene dianion (13), pyridine (14) and pyrimidine (15). For these compounds we compute the energetic and structural indices and correlate them with their structure and chemical reactivity, especially the stability and aromaticity.

The general frame of molecular orbital theory [21, 22, 30] is based on a theorem of variational calculation which states that if, for a system described by the Hamiltonian operator $\hat{\mathbf{H}}$, we possess a set of approximate wave functions φ_1, φ_2, … φ_n for the first n levels, we can construct n linear combinations:

$$\phi_k = c_{k1}\varphi_1 + c_{k2}\varphi_2 + \ldots + c_{kn}\varphi_n\,;\quad k = 1, 2, \ldots, n \tag{1}$$

that approximate more exactly the first n energy levels of the system. These wave functions are obtained by minimising the mean values of an operator $\hat{\mathbf{F}}$ with respect to coefficients c_{kj}. The problem is reduced to solving the system of secular equations:

$$\begin{cases} c_{11}(F_{11} - \varepsilon) + c_{12}(F_{12} - S_{12}\varepsilon) + \ldots + c_{1n}(F_{1n} - S_{1n}\varepsilon) = 0 \\ \\ c_{n1}(F_{n1} - S_{n1}\varepsilon) + c_{n2}(F_{n2} - S_{n2}\varepsilon) + \ldots + c_{nn}(F_{nn} - S_{nn}\varepsilon) = 0 \end{cases} \tag{2a}$$

where, for the interaction between atoms p and q:

$$F_{pq} = \int \varphi_p^* \hat{\mathbf{F}} \varphi_q \mathrm{dV} \tag{2b}$$

$$S_{pq} = \int \varphi_p^* \varphi_q \, \mathrm{dV} \, . \tag{2c}$$

The S_{pq} integrals are also called overlap integrals. The system of secular equations (2a) can be solved only for n given ε_k values of parameters, which represent the approximate eigenvalues of the first n energy levels of the system.

Within the frame of molecular orbitals theory, the functions φ_q represent atomic orbitals (AO), while the more exact functions ϕ_k, which describe the motions of electrons around several atoms, signify molecular orbitals (MO). The HMO method may be characterised, against the general scheme of molecular orbital theory, by the following simplifying assumptions [14, 18]:

It deals only with π-electron system, σ-bonds are considered to mostly affect α and β parameters;

Each π-electron is considered separately, F_{pq} elements are taken independent of resulting charge distribution;

The matrix elements F_{pq} and S_{pq} corresponding to the system of equations (2a) are taken as:

$$F_{qq} = \alpha_q = \alpha + \delta_q \beta \tag{3a}$$

being proportional to ionisation potential of one electron in valence state of the atom q.

Here α_q is the so-called Coulomb energy for q atomic orbital, while β_{pq} is the exchange energy corresponding to the bond between the atomic orbitals p and q. Standard values α and β refer to the $2\mathrm{p_z}$ atomic orbital for carbon atom in benzene and to the π-bond in benzene, respectively, which in turn correspond to F_{CC} and $F_{\mathrm{C'C}}$ for a $2\mathrm{p_z}$ orbital of the carbon atom in sp^2 hybridized state.

$$F_{pq} \begin{cases} = 0 \text{ for non-neighbouring atoms.} \\ = \beta_{pq} = \eta_{pq}\beta \text{ i.e. proportional strength to bond between the } p \text{ and } q \text{ atoms} \end{cases} \tag{3b}$$

$$S_{pq} \begin{cases} = 0 \text{ for } p \neq q \text{ - i.e. so called zero differential overlap (z.d.o.) approximation} \\ = 1 \text{ for } p = q \end{cases} \tag{3c}$$

The integrals are negative but the value they are ascribed depends on the magnitude we want to compute. For exchange energy calculations, it is recommended to consider $\beta = (-16.5 \div -20)$ kcal·mol^{-1}, while for electronic transition calculations $\beta = -2 \div -2.5$ eV or $(-45 \div -60)$ kcal·mol^{-1} is also recommended. For the HMO method, the values of coulombic (δ_q) and exchange (η_{pq}) parameters are taken such as the obtained theoretical values to be correlated to the experimentally verified properties of the molecules [23, 30].

The energy ε_j of molecular orbitals of the acyclic planar systems made of sp^2 carbons is given by the following equation:

$$\varepsilon_j = \alpha + 2\beta \cos \frac{j\pi}{n+1} \tag{4}$$

in which n is the number of sp^2 carbons of the system and j is the number of molecular orbital.

In the case of the cyclic planar systems made only of sp^2 carbons, the energy ε_k of molecular orbitals is as follows:

$$\varepsilon_k = \alpha + 2\beta \cos \frac{2k\pi}{n} \tag{5}$$

in which n is the number of sp^2 carbons of the system and k represents the number of molecular orbitals. The later takes values of 0, ±1, ±2, … $+n/2$ for cycles with even number of atoms and values of 0, ±1, ±2, … $\pm(n-1)/2$ for cycles with odd number of atoms [1b, 13].

The energy of the highest occupied molecular orbital ($\varepsilon_{\mathrm{HOMO}}$) and of the lowest unoccupied molecular orbital ($\varepsilon_{\mathrm{LUMO}}$) are related to the reducing and oxidizing properties of the π systems, respectively [10, 16]. The difference ($\varepsilon_{\mathrm{HOMO}} - \varepsilon_{\mathrm{LUMO}}$) can be correlated with the first transition wave length (λ_1) of the electronic spectra (the maximum of the absorption band at the largest wave length) and also with the wave number $\nu'(\lambda^{-1})$.

The results of HMO calculations also conduct to the conjugation energy (E_{R}, E_{D}), that is the difference between the total energy:

$$E_\pi = \sum_i n_i \varepsilon_i \tag{6}$$

of the real molecule and that of a hypothetical system with localized double bonds.

Information with regard to the general stability of the system within the scale: non-aromatic, anti-aromatic, aromatic may be brought by the REPE (resonance energy per electron) $\left(E_{\mathrm{R}} / n_\pi\right)$ and $\overline{\pi}\left(E_{\mathrm{D}} / n_\pi\right)$ indices, where n_π is the number of π electrons in the conjugated system [25, 27]. The electron distribution parameters are [6, 7, 8, 29]:

– the electric charge of the π electrons of atom q (ρ_q)

$$\rho_q = \sum_i n_i c_{iq}^2 \tag{7}$$

$$\rho_q = \frac{\partial E_\pi}{\partial \alpha_q} \tag{8}$$

– the bond order (p_{pq} or π_{pq}) between atoms p and q

$$p_{pq} = \sum_i n_i c_{iq} c_{ip} \tag{9}$$

$$p_{pq} = \frac{1}{2}\frac{\partial E_\pi}{\partial \beta_{qp}} \tag{10}$$

– the free valence index (F_q)

$$F_q = \mathrm{C} - \sum_{p-\text{neighbours}} p_{qp} \tag{11}$$

The last summation is done over the atoms directly bonded to the q atom and for sp^2 hybridised carbon atom C = 1.732.

RESULTS AND DISCUSSION

The values of energy indices obtained by the HMO method are given in Table 1 for the acyclic and cyclic hydrocarbons and in Figures 1 and 2 for the carbocations and carbanions respectively.

It should be noticed that the electron occupation of molecular orbitals (ϕ) is similar as for the atomic orbitals (φ), according to the rules of Hund and Pauli [1c]. Energy indices calculations for hydrocarbons, carbocations and carbanions using the HMO method are based on relations (4), (5) and (6).

We apply for pyridine (14) and pyrimidine (15) the algorithm to compute the energy indices by performing the following steps:

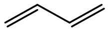
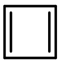
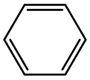
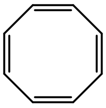
Indication of Streitwieser parameters [30] to perform calculations using the HMO method:

$$\alpha_\mathrm{C} = \alpha;\ \beta_\mathrm{CC} = \beta;\ \alpha_\mathrm{N} = \alpha + 0.5\beta;\ \beta_\mathrm{CN} = \beta. \tag{12}$$

Establishment of secular determinants and their cancellation in order to obtain solutions for the two nitrogen heterocycles, using the relations (1), (2 a, b, c), (3 a, b, c). Defining $(\alpha - \varepsilon)/\beta = k$ we intend to solve the polynomial equations generated by the two determinants for pyridine and pyrimidine.

Table 1

Energy indices computed by HMO method for cyclic and acyclic planar systems

Planar systems	n_π	ε_j	ε_k	E_π (β)	$\bar{\pi} = \frac{E_D}{n_\pi}$ (β)	ν'(λ^{-1}) (cm^{-1})
$C{=}C$ (01)	2	$\varepsilon_1 = \alpha + \beta$ $\varepsilon_2 = \alpha - \beta$		2.0000	0.0000	38486
 (02)	4	$\varepsilon_1 = \alpha + 1.6180\beta$ $\varepsilon_2 = \alpha + 0.6180\beta$ $\varepsilon_3 = \alpha - 0.6180\beta$ $\varepsilon_4 = \alpha - 1.6180\beta$		4.4720	0.1180	23784
 (03)	4		$\varepsilon_0 = \alpha + 2\beta$ $\varepsilon_1 = \varepsilon_{-1} = \alpha$ $\varepsilon_2 = \alpha - 2\beta$	4.0000	0.0000	38486
 (04)	6	$\varepsilon_1 = \alpha + 1.7974\beta$ $\varepsilon_2 = \alpha + 1.2494\beta$ $\varepsilon_3 = \alpha + 0.4214\beta$ $\varepsilon_4 = \alpha - 0.4214\beta$ $\varepsilon_5 = \alpha - 1.2494\beta$ $\varepsilon_6 = \alpha - 1.7974\beta$		6.9364	0.1560	16218
 (05)	6		$\varepsilon_0 = \alpha + 2\beta$ $\varepsilon_1 = \varepsilon_{-1} = \alpha + \beta$ $\varepsilon_2 = \varepsilon_{-2} = \alpha - \beta$ $\varepsilon_3 = \alpha - 2\beta$	8.0000	0.3333	38486
 (06)	8	$\varepsilon_1 = \alpha + 1.8792\beta$ $\varepsilon_2 = \alpha + 1.5320\beta$ $\varepsilon_3 = \alpha + \beta$ $\varepsilon_4 = \alpha + 0.3472\beta$ $\varepsilon_5 = \alpha - 0.3472\beta$ $\varepsilon_6 = \alpha - \beta$ $\varepsilon_7 = \alpha - 1.5320\beta$ $\varepsilon_8 = \alpha - 1.8792\beta$		9.5168	0.1896	13362
 (07)	8		$\varepsilon_0 = \alpha + 2\beta$ $\varepsilon_1 = \varepsilon_{-1} = \alpha + 1.4142\beta$ $\varepsilon_2 = \varepsilon_{-2} = \alpha$ $\varepsilon_3 = \varepsilon_{-3} = \alpha + 1.4142\beta$ $\varepsilon_4 = \alpha - 2\beta$	9.6568	0.2071	27213

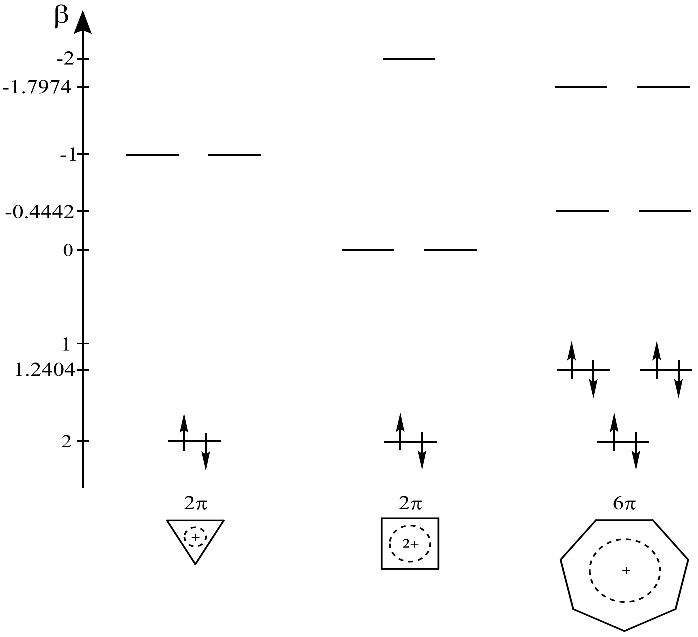


Fig. 1. The molecular orbitals in the $C_3H_3^+$ (08), $C_4H_4^{2+}$ (09), $C_7H_7^+$ (10).

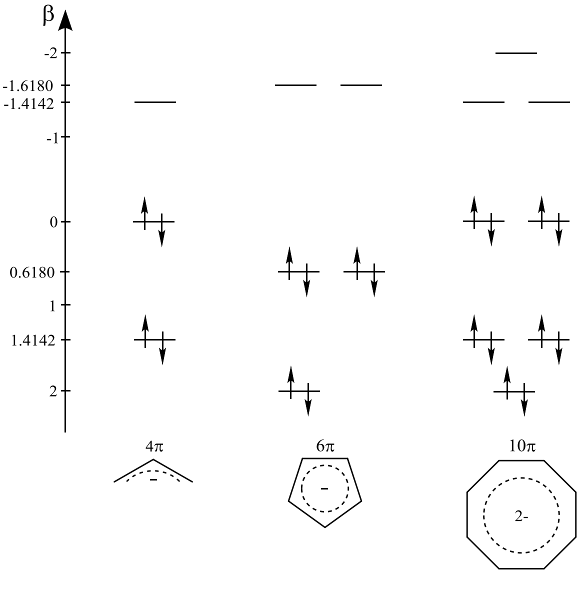


Fig. 2. Molecular orbitals in the carbanions: $C_3H_5^-$ (11), $C_5H_5^-$ (12), $C_8H_8^{2-}$ (13).

For pyridine we have:

$$\begin{vmatrix} (\alpha+0.5\beta)-\varepsilon & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-\varepsilon & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-\varepsilon & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-\varepsilon & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-\varepsilon & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-\varepsilon \end{vmatrix} = 0 \qquad (13)$$

$$\begin{vmatrix} k+0.5 & 1 & 0 & 0 & 0 & 1 \\ 1 & k & 1 & 0 & 0 & 0 \\ 0 & 1 & k & 1 & 0 & 0 \\ 0 & 0 & 1 & k & 1 & 0 \\ 0 & 0 & 0 & 1 & k & 1 \\ 1 & 0 & 0 & 0 & 1 & k \end{vmatrix} = 0 \qquad (14)$$

For pyrimidine we have:

$$\begin{vmatrix} (\alpha+0.5\beta)-\varepsilon & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-\varepsilon & \beta & 0 & 0 & 0 \\ 0 & \beta & (\alpha+0.5\beta)-\varepsilon & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-\varepsilon & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-\varepsilon & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-\varepsilon \end{vmatrix} = 0 \qquad (15)$$

$$\begin{vmatrix} k+0.5 & 1 & 0 & 0 & 0 & 1 \\ 1 & k & 1 & 0 & 0 & 0 \\ 0 & 1 & k+0.5 & 1 & 0 & 0 \\ 0 & 0 & 1 & k & 1 & 0 \\ 0 & 0 & 0 & 1 & k & 1 \\ 1 & 0 & 0 & 0 & 1 & k \end{vmatrix} = 0 \qquad (16)$$

In order to obtain the values of k and ε_i of the molecular orbitals corresponding to the two molecules, the symmetry properties were used. These properties contributed to the reduction of the degree of the secular determinants, thus facilitating their solving [12, 28]. Calculation of contributions of atomic orbitals to molecular orbitals (ϕ_i) takes into account that each k value corresponds to the secular system of associated equations, in conjunction with the normalization condition

$$c_{k1}^2 + c_{k2}^2 + c_{k3}^2 + c_{k4}^2 + c_{k5}^2 + c_{k6}^2 = 1 \tag{17}$$

with $k = 1, 2, 3, 4, 5, 6$.

The energetic indices computed for the two heterocycles with nitrogen (pyridine and pyrimidine) are revealed in Tables 2, 3 and 4, respectively.

Based on the results presented in Table 2 and the relationship (6), calculations can be made for the other energy indices of pyridine and pyrimidine. To support the determination of the E_{D} values of the two nitrogen heterocycles, the energies of the localized π bonds are used [4]. Calculations made for the bonds $\overset{\alpha}{\mathrm{C}}\overset{\beta}{—}\overset{\alpha}{\mathrm{C}}$ and $\overset{\alpha}{\mathrm{C}}\overset{\beta}{—}\overset{\alpha+0.5\beta}{\mathrm{N}}$ conduct to the energies of the π bonds localized by ($2\alpha + 2\beta$) and ($2\alpha + 2.5\beta$) respectively. Computed values of the $E_{\pi\ \mathrm{total}}$, $E_{\pi\ \mathrm{localized}}$, E_{D} and λ_1 for the two heterocycles with nitrogen are emphasized in Tables 3 and 4.

Table 2

The own energies (ε_i) corresponding to k values and the molecular orbitals (ϕ_i) computed by the HMO method for pyridine and pyrimidine

Compound	k	ε_i	ϕ_i
C_5H_5N	–2.114	$\alpha + 2.1140\beta$	$\phi = 0.5260\varphi_1 + 0.4180\varphi_2 + 0.3570\varphi_3 + 0.3380\varphi_4 + 0.3570\varphi_5 + 0.4180\varphi_6$
	–1.159	$\alpha + 1.1590\beta$	$\phi = 0.5730\varphi_1 + 0.1950\varphi_2 - 0.3450\varphi_3 - 0.5960\varphi_4 - 0.3450\varphi_5 + 0.1950\varphi_6$
	–1.000	$\alpha + \beta$	$\phi = 0.5000(\varphi_2 + \varphi_3 - \varphi_5 - \varphi_6)$
	0.841	$\alpha - 0.8410\beta$	$\phi = 0.5460\varphi_1 - 0.3660\varphi_2 - 0.2370\varphi_3 + 0.5660\varphi_4 - 0.2370\varphi_5 - 0.3660\varphi_6$
	1.000	$\alpha - \beta$	$\phi = 0.5000(\varphi_2 - \varphi_3 + \varphi_5 - \varphi_6)$
	1.932	$\alpha - 1.9320\beta$	$\phi = 0.3050\varphi_1 - 0{,}3730\varphi_2 + 0.4160\varphi_3 - 0.4310\varphi_4 + 0.4160\varphi_5 - 0.3730\varphi_6$
$C_4H_4N_2$	–2.197	$\alpha + 2.1970\beta$	$\phi = 0.4680\varphi_1 + 0.4310\varphi_2 + 0.4680\varphi_3 + 0.3640\varphi_4 + 0.3310\varphi_5 + 0.3640\varphi_6$
	–1.280	$\alpha + 1.2800\beta$	$\phi = -0.5580\varphi_1 + 0.5580\varphi_3 + 0.4360\varphi_4 - 0.4360\varphi_6$
	–1.070	$\alpha + 1.0700\beta$	$\phi = 0.2670\varphi_1 + 0.4880\varphi_2 + 0.2670\varphi_3 - 0.3350\varphi_4 - 0.6260\varphi_5 - 0.3350\varphi_6$
	0.780	$\alpha - 0.7800\beta$	$\phi = 0.4320\varphi_1 - 0.4320\varphi_3 + 0.5600\varphi_4 - 0.5600\varphi_6$
	0.912	$\alpha - 0.9120\beta$	$\phi = -0.2990\varphi_1 + 0.6570\varphi_2 - 0.2990\varphi_3 - 0.2330\varphi_4 + 0.5130\varphi_5 - 0.2330\varphi_6$
	1.856	$\alpha - 1.8560\beta$	$\phi = -0.3450\varphi_1 + 0.3700\varphi_2 - 0.3450\varphi_3 + 0.4430\varphi_4 - 0.4780\varphi_5 + 0.4430\varphi_6$

Table 3

Computed values of $E_{\pi\ \mathrm{total}}$, $E_{\pi\ \mathrm{localized}}$, E_D and λ_1 for pyridine

Energetic indices	Pyridine
$E_{\pi\ \mathrm{total}}$	$2(\alpha+2.1140\beta)+2(\alpha+1.1590\beta)+2(\alpha+\beta)=6\alpha+8.5460\beta$
$E_{\pi\ \mathrm{localized}}$	$2(2\alpha+2\beta)+1(2\alpha+2.5\beta)=6\alpha+6.5\beta$
E_D	$(6\alpha+8.5460\beta)-(6\alpha+6.5\beta)=2.0460\beta$
λ_1	$\frac{1242}{2.39\left[(\alpha-0.8410\beta)-(\alpha+\beta)\right]}=282\text{ nm}$

Table 4

Computed values of $E_{\pi\ \mathrm{total}}$, $E_{\pi\ \mathrm{localized}}$, E_D and λ_1 for pyrimidine

Energetic indices	Pyrimidine
$E_{\pi\ \mathrm{total}}$	$2(\alpha+2.1970\beta)+2(\alpha+1.2800\beta)+2(\alpha+1.0700\beta)=6\alpha+9.0940\beta$
$E_{\pi\ \mathrm{localized}}$	$1(2\alpha+2\beta)+2(2\alpha+2.5\beta)=6\alpha+7\beta$
E_D	$(6\alpha+9.0940\beta)-(6\alpha+7\beta)=2.0940\beta$
λ_1	$\frac{1242}{2.39\left[(\alpha-0.7800\beta)-(\alpha+1.0700\beta)\right]}=281\text{ nm}$

Based on the data presented in the Figures 1 and 2 and in the Tables 1–4 and in correlation to specific literature data [4], we analyze and discuss the results obtained for the 15 investigated compounds in terms of their structure and stability.

Cyclobutadiene (compound 03) and its dimer cyclooctatetraene (07), both annulenes with $4n$ π electrons, have an anti-aromatic character. The last degenerated molecular orbitals of each of these two cyclic polyenes are considered to be occupied with only one electron, providing them the character of di-radical. Similarly, the nonaromatic compounds (01), (02), (04), (06) and (11) participate in the addition reactions, diene synthesis, are unstable in air and have low conjugation energies.

The compounds (05), (08)–(10), (12)–(15) have bonding molecular orbitals completely occupied (with two electrons each) forming closed blankets of $(4n+2)\pi$ electrons with aromatic stability according to the Hückel's law. These compounds also reflect high conjugation energies, non-olefinic character, and do not participate in addition reactions.

Using literature data concerning the standard enthalpy of formation ($\Delta H^0_{\mathrm{f,\,a}}$) [1d] to calculate the conjugation energies for annulenes (03), (05), (07), we noticed distinct values by comparison to those obtained using Hückel's method (Table 1).

Thus in relation to the non-aromatic acyclic polyenes (02), (04), (06), in this evaluation system, the conjugation energies correspond to the benzene: +20 kcal mol^{-1} (positive value, aromatic), to the cyclobutadiene –18 kcal·mol^{-1} (negative value, anti-aromatic) and to the cyclooctatetraene –2.8 kcal·mol^{-1} (weak anti-aromatic).

The ranking of the aromatic compounds according to their stability, and corresponding to the values $\bar{\pi}\left(E_{\text{D}} / n_{\pi}\right)$ calculated by the HMO method, is the following:

$$\left(\bar{\pi}(08)=\bar{\pi}(09)\right)>\bar{\pi}(10)>\bar{\pi}(12)>\bar{\pi}(15)>\bar{\pi}(14)>\bar{\pi}(05)>\bar{\pi}(13) \quad (18)$$

Probably for steric reasons, the compound (13) cannot adopt a planar configuration. Its conjugation energy is small, $\left(\bar{\pi}=0.1656\right)$, as for the non-aromatic hydrocarbons which are ranked by stability:

$$\bar{\pi}(06)>\bar{\pi}(04)>\bar{\pi}(02)>\bar{\pi}(01) \quad (19)$$

The results obtained using HMO and presented in Table 1 also sustain the correlation between the wavenumbers (ν') and the computed transition energies ($\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$), both for the acyclic and cyclic planar systems. Furthermore, the higher the number of double bonds of the conjugate system, the maximum absorption bands move to the visible.

Considering the compounds (05), (14) and (15), by analysing all data presented in Tables 1–4, we may conclude the following:

The values E_{D}/n_{π} sustain the lower stability of benzene by comparison to that of the heterocycles with nitrogen. The reactivity indices *HOMA* (Harmonic Oscillator Model of Aromaticity) [15, 24] place the three compounds in the same order of stability: benzene (*HOMA* = 0.988) < pyridine (*HOMA* = 0.995) < pyrimidine (*HOMA* = 0.999).

The computed values E_{R} for benzene and pyridine may be examples of correlations with literature data. Using β = 18 kcal·mol^{-1} there may be correlations such as: (i) for benzene 36 kcal·mol^{-1} = $[(6\alpha + 8\beta) - 3(2\alpha + 2\beta)]18$ [1b], and (ii) for pyridine 45 kcal·$\text{mol}^{-1} \cong [(6\alpha + 8{,}5460\beta) - 3(2\alpha + 2\beta)]18$ [2a].

The position of benzene in the hierarchy of stability of the three mononuclear aromatic compounds is evidenced by the fact that oxidation of phenylpyridine conducts to pyridine acids [2b], as well as by the fact that during the oxidation of benzopyrimidine the benzene nucleus is attacked leading to the pyrimidine-4,5-dicarboxylic acid [2c].

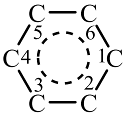
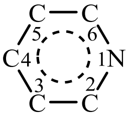
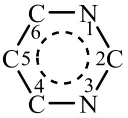
Using the coefficients of contribution of the orbital atomic wave functions (AO) to the molecular orbital wave functions (MO), we calculated as applications of the equations (7)–(11) the structural indices for the acyclic (01), (02) and the cyclic (05), (14), (15) planar systems, respectively. These data are revealed in Table 5.

These parameters, corresponding to the repartition of the (n_π) electrons, have implications in solving problems related to the chemical reactivity.

The charge density (ρ_q) informs about the behaviour of the atoms belonging to conjugate systems in ionic mechanisms.

Table 5

Structural indices (ρ_q, F_q, p_{qp}) of the investigated aliphatic and aromatic molecules computed using the HMO method

Planar system	ρ_q	F_q	p_{qp}
$H_2\overset{1}{C}{=}\overset{2}{C}H_2$	$\rho_1 = \rho_2 = 1.0000$	$F_1 = F_2 = 0.7320$	$p_{12} = 1.0000$
$H_2\overset{1}{C}{=}\overset{2}{C}H{-}\overset{3}{C}H{=}\overset{4}{C}H_2$	$\rho_1 = \rho_2 = \rho_3 =$ $= \rho_4 = 1.0000$	$F_1 = F_4 = 0.8375$ $F_2 = F_3 = 0.3903$	$p_{12} = p_{34} = 0.8944$ $p_{23} = 0.4472$
	$\rho_1 = \rho_2 = \ldots =$ $= \rho_6 = 1.0000$	$F_1 = \ldots = F_6 = 0.4000$	$p_{12} = p_{23} = \ldots =$ $= p_{61} = 0.6666$
	$\rho_2 = \rho_6 = 0.9260$ $\rho_3 = \rho_5 = 0.9928$ $\rho_4 = 0.9388$ $\rho_1 = 1.2080$	$F_2 = F_6 = 0.4040$ $F_3 = F_5 = 0.4140$ $F_4 = 0.4240$ $F_1 = 0.4040$	$p_{12} = p_{16} = 0.6640$ $p_{23} = p_{56} = 0.6640$ $p_{34} = p_{45} = 0.6540$
	$\rho_2 = 0.8460$ $\rho_4 = \rho_6 = 0.8680$ $\rho_5 = 1.0020$ $\rho_1 = \rho_3 = 1.2020$	$F_2 = 0.4040$ $F_4 = F_6 = 0.4260$ $F_5 = 0.4160$ $F_1 = F_3 = 0.4200$	$p_{12} = p_{23} = 0.6640$ $p_{16} = p_{34} = 0.6480$ $p_{45} = p_{56} = 0.6580$

The order of the p and q bond (p_{qp}), introduced in Hückel's approximation, correlates with the length and the energy of the bond. [8]. The higher the p_{qp}, the shorter is the bond and the higher is its dissociation energy.

The free valence index of the q atom (F_q) is the measure of the degree of reactivity of a position in a molecule [6]. In general, the addition reactions are preferably carried out on the atoms with the highest free valence index.

The results presented in Table 5 orient our discussions in the following directions:

(i) The chemical reactivity of ethene and butadiene, in correlation with the calculated structural indices and the reaction mechanisms, is correlated to their chemical properties;

(ii) One can see that the carbon atoms in ethene have relatively high free valence indices, so that the homolytic addition to the C=C bond has free atoms and radicals as intermediates. During this type of reactions, the alkene is transformed into a free radical that is then stabilized through one of the characteristic ways of free radicals.

(iii) Hydrogenation with metals and proton donors is not possible, considering the very weak reducing and oxidizing character of ethene. The addition of molecular hydrogen is made in the presence of transition metals such as Ni, Pd, Pt, Rh (heterogeneous catalysis) at normal or increased temperature and pressure [1e, 19a].

(iv) The bonds orders of butadiene ($p_{12} = p_{34}$) > p_{23} indicate the attaching degree of the double bonds but also the possibility of electrophilic additions of halogens, hydracids in 1,2 and 1,4 positions of diene.

(v) The radicalic additions of CCl_4 or Cl_3CBr in the presence of benzoyl peroxide and catalytic hydrogenation prefer the 1 and 4 positions in butadiene, with higher free valence indexes $(F_1 = F_4) > (F_2 = F_3)$.

(vi) The conjugated double bonds of butadiene are easily polarizable, thus offering it the capacity of being reduced with sodium or sodium amalgam as electron donors, and alcohol, water or acids as proton donors.

(vii) The enhanced reactivity of the carbons in positions 1 and 4 with higher free valence indexes is also attested by the diene synthesis [1f, 19b].

If $\rho_q = 1$ for all carbon atoms in hydrocarbons as ethene and benzene, in pyridine and pyrimidine, there is another picture. The calculations demonstrate that in nitrogen-containing heterocycles the π charge densities on atoms are usually different from the unit and are not the same for the distinct atoms of the molecule. For the two nitrogen-containing heterocycles, the results revealed in Table 4 are in agreement with the literature data [17] and illustrate the following remarks.

The attraction of the nitrogen atom in the pyridine on the six π electrons in the nucleus produces a decrease in the electron densities at positions 2, 4, 6 involved in nucleophilic substitutions. Electrophilic reactants preferentially attack positions 3, 5, but at a reduced rate compared to benzene. The behaviour of pyridine is related to the fact that chemical reactions occur in a strongly acidic medium, where it is found in the form of ammonium ion. The presence of an integer positive charge on the aromatic nucleus opposes the entry of a second positive charge, making the electrophilic substitution more difficult [2d].

In pyrimidine, the two nitrogen atoms influencing its aromatic sextet result in a marked drop in the electronic densities at positions 2, 4, 6, possible for nucleophilic attacks. Electrophilic substitution is difficult and occurs only in position 5 [2e].

The free valencies (F_q) of the carbon atoms in the two nitrogen heterocycles are small compared to the calculated value for ethene ($F_C = 0.7320$) (Table 4). Thus, addition reactions (hemolytic attack) to pyridine and pyrimidine are difficult, as for benzene ($F_C = 0.4000$), requiring energy consumption to disturb the aromatic state and location of double bonds.

A large number of reactions for these compounds may involve addition as an initial step, but the term is limited if the product of the primary addition can be isolated [20].

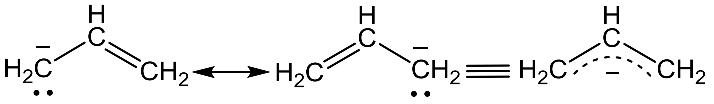
In pyridine and pyrimidine, the bonding orders are very close to the benzene bonding order ($p_{CC} = 0.6666$). In the studied molecules, the relation $\rho_N > \rho_C$, according to the electronegativity of these elements, changes in parallel to the basicity of these atoms [29b].

The aromatic ring, due to the π electrons cloud, has a basic character. The aromatic annulenes with $(4n+2)\pi$ electrons have affinity for electrophilic reactants (with electron deficiencies). Unlike planar acyclic systems that allow addition of electrophilic reactants, aromatic annulenes give substitution reactions with these reactants [1g].

Evidence that benzene is a weak base is that fixing of a proton (electrophile reactant) to the benzene level gives rise to a benzenonium ion (strong conjugated acid) [1h].

Pyridine ($pK_a = 5.29$) and pyrimidine ($pK_a = 1.3$) have basic and nucleophilic character because the electron pairs of heteroatoms are not involved in aromatic conjugation [2d]. Their low basic characters, ($\rho_N = 1.2080$) for pyridine and ($\rho_N = 1.2020$) for pyrimidine are due to the multiple bonds to which nitrogen atoms are attached as basic centres.

Since base ability (Lewis) also targets carbanions, we analyse this property in molecules (11) and (12). The high stability of the allyl carbanion (11) with $pK_a = 35$ is due to the conjugation represented by the boundary structures:



(20)

The stability of the anion of cyclopentadiene ($C_5H_5^-$) (12) with $pK_a = 15$ is explained by the involvement of an anionic electron pair in a six-electron aromatic system [19c].

Although the two analysed carbanions do not show ionization in aqueous media, they can form metalorganic complexes. The π complexes that can be formed are characterized by direct metal-carbon bonds, in which these anions have very strong base behaviour. Thus, as organic ligands they are σ-donors (σ-basics, σ-reducing) and π-acceptors on the π* orbitals (π-acids, π-oxidants). The metal that binds in complexes functions as the σ-acceptor (σ-acid, σ-oxidant) and π-donor (π-basic, π-reducing) [3, 9, 29c].

CONCLUSION

The values of the energetic indices calculated by the classical Hückel's theory are in good agreement with other data presented in the literature and with the experimental behaviour of the studied compounds.

The quantum mechanical calculations made by the HMO method have led to the energetic parameters for symmetric and asymmetric planar systems, their electron distribution parameters being correlated with the chemical reactivity of the atoms of these molecules. Thus, the higher the bond order (p_{qp}), the higher the reactive capacity of the bonds (multiple bond); the homolytic attack prefers the sublayer atoms with high free valence index (F_q) and the electrophile, unlike the nucleophile, prefers the atoms with high electronic charge density (ρ_q).

The results obtained by the HMO method are sustained by the selection of α_q and β_{pq}, as well as by the number of electrons (ν_q) and by the number of the atomic orbitals of each atom belonging to the conjugate systems.

The stable aromatic systems have $\varepsilon_{\mathrm{HOMO}}$ and $\varepsilon_{\mathrm{LUMO}}$ relatively much below and respectively over $\varepsilon = \alpha$. Analysis of the results obtained for the eight investigated aromatic molecules are presented in Tables 1 and 2 and in Figures 1 and 2; $C_4H_4^{2+}$ ($\varepsilon_{\mathrm{LUMO}} = \alpha$) should reduce easier and $C_8H_8^{2-}$ ($\varepsilon_{\mathrm{HOMO}} = \alpha$) should oxidize easier.

When comparing different molecules, such as ethene and benzene, free valence indices (0.7320 and 0.400 respectively) show that ethene gives much easier addition reactions than benzene, which is true. Having the same values of $\varepsilon_{\mathrm{HOMO}}$, $\varepsilon_{\mathrm{LUMO}}$, and ρ_C, the two molecules should behave in the same way to oxidation, reduction, nucleophilic and electrophilic substitutions, which is not true. The properties of ethene and benzene illustrate that these reactivity indices can only be used to compare molecules that are not very different.

The references made to the structure, as well as the conditions for the appearance of some properties of the acyclic and cyclic conjugate systems, that are incomprehensible by classical theories, have found explanations using energetic and structural indices calculated by the HMO method.

Difficulties encountered in interpreting the anti-aromatic properties of the cyclobutadiene and cyclooctatetraene must be related to the question of experimental determination of the conjugation energies, but also to their planarity which is probably sterically hindered.

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