

Studies Regarding the Nitrogen Atom Influence on the Aromaticity of Aza-Naphthalenes

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Abstract: Theoretical investigations regarding the aromatic character of naphthalene, quinoline and isoquinoline have been performed. Local aromaticity indices like HOMA, NICS, PDI and FLU have been computed, in order to establish the influence of the substitution of a CH group with an isovalent N atom. Also, the gas-phase enthalpies of deprotonation of naphthalene, quinoline and isoquinoline have been computed; results were compared with the experimental enthalpy of deprotonation of benzene.

Keywords: aromaticity, aza-substitution, *ab initio*

1. Introduction

During the last years, studies regarding the theoretical evaluation of the aromatic character have gained a continuous interest [1-3]. Most of the researches were focused on the aromaticity of polycyclic aromatic hydrocarbons, known as precursors of nanomaterials [4-6]. Also, a large number of studies have been oriented towards the investigation of the aromatic character of heterocyclic compounds [7-10].

Our previous studies dealt with the theoretical evaluation of the aromaticity of various mono- and multi-substituted heterobenzenes with elements of group 15 [11]. The influence of the heteroatoms was discussed as function of the geometric, magnetic and energetic properties of the compounds.

The present study aims to investigate the influence of the position of the N atom in bicyclic compounds. In this regard, aza-naphthalene derivatives (namely, quinoline and isoquinoline) were characterized by means of their geometric, magnetic and energetic properties. For comparison, the same computations were performed for naphthalene.

In order to investigate the effect of the N atom on the aromaticity of the quinolone and isoquinoline, the geometric index HOMA (Harmonic Oscillator Model of Aromaticity) [12,13] was employed. HOMA index was calculated with equation (1):

$$HOMA = 1 - \left[\frac{257.7}{n_{C-C}} (R_i - R_{opt})^2 - \frac{93.52}{n_{C-N}} (R_i - R_{opt})^2 \right] \quad (1)$$

HOMA values are included in the range [0,1], where 1 signifies the HOMA values for benzene (considered the etalon for the aromaticity studies).

Also, local reactivity indices (Fukui functions) [14] were calculated for each C atom of the cyclic compounds.

$$F_k^\alpha = \sum_{\mu \in k} |c_\mu^\alpha|^2 \quad (2)$$

(in this case α = HOMO orbital, with neglect of the overlap integral)

Electronic indices are widely used as descriptors of aromaticity. In the present paper, two electronic indices, FLU and PDI, computed within the "atoms-in-molecules" theory have been employed.

The aromatic fluctuation index (FLU) [15] represents an indicator of the electronic charge fluctuation between adjacent atoms in a ring [15]:

$$FLU(A \rightarrow B) = \frac{\delta(A,B)}{\sum_{B \neq A} \delta(A,B)} = \frac{\delta(A,B)}{2[N(A) - \Lambda(A)]} \quad (3)$$

Where: $\Lambda(A)$ – atomic localization indices

$N(A)$ – average population of atom A

$\delta(A,B)$ – delocalization indices

PDI [6,16] is obtained as the average of the delocalization indices of all para-relates atoms within a 6-membered ring. Larger PDI values are attributed to a strong aromatic character of the cycle.

$$\delta(A,B) = 4 \sum_1^{occ} \sum_j^{occ} S_{ij}(A) S_{ij}(B) \quad (4)$$

$$PDI = \frac{\delta(1,4) + \delta(2,5) + \delta(3,6)}{3}$$

As regards the magnetic criterion of aromaticity, NICS (Nucleus-Independent Chemical Shift) [17] index represents the absolute magnetic shielding computed at the center of each ring (NICS(0)) and at 1 Å above it (NICS(1)), respectively. Large negative NICS values mean a strong aromatic character, while the positive ones are the proof for non-aromaticity.

The investigated structures are presented in Figure 1:

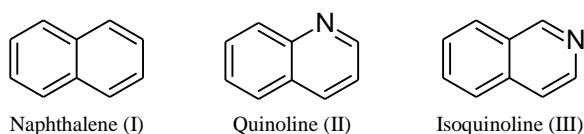


Figure 1. Compounds I-III investigated during the present study

2. Computational Details

The structures I-III were optimized at HF/6-31G(d,p) level of theory. No imaginary frequencies have been obtained, proving that the structures are real minima. PDI and FLU indices were computed with Multiwfn_3.3.4 software [18], while for all the other computations Gaussian 09W has been employed [19].

3. Results and Discussion

3.1. Geometric criterion

In order to investigate the effect of aza-substitution on the geometry of quinoline and isoquinoline, HOMA index was computed for each cycle. The results lead also to an estimation of the electron delocalization within the benzenoid rings and, thus, to an evaluation of their aromaticity.

TABLE 1. HOMA index, computed at HF/6-311G(d,p) level of theory

HOMA index	Naphthalene	Quinoline		Isoquinoline	
		all-C ring	N-containing ring	all-C ring	N-containing ring
	0,782	0,790	0,327	0,786	0,297

The results presented in Table 1 clearly show a decrease of local aromaticity together with the presence of the N atom within the 6-membered ring. Values of HOMA index for naphthalene are similar to the ones obtained for the all-carbon benzene ring of quinoline and isoquinoline, respectively.

TABLE 2. NICS(0) and NICS(1) indices, computed at HF/6-31G(d,p) level of theory

	Naphthalene	Quinoline		Isoquinoline	
		all-C ring	N-containing ring	all-C ring	N-containing ring
NICS(0)	-10,965	-10,952	-9,158	-11,849	-9,917
NICS(1)	-12,635	-12,567	-12,146	-13,459	-12,778

3.2. Magnetic criterion

One of the most widely used methods for investigating the aromatic character is the computation of NICS indices, the absolute magnetic shielding computed at the center of each ring. The results are presented in Table 2 and show only small differences among the 6-membered rings. All the obtained values are negative and suggest an enhanced aromaticity for all the cycles. Unlike the geometric index HOMA, the magnetic criterion shows no difference between the all-carbon and aza-rings.

3.3. Stability

It is well-known that the aromatic compounds are characterized by a high stability; in this regard, HOMO-LUMO gap is a reliable index for estimating the stability of a compound. Similar values of HL gap have been obtained for structures I-III, so the substitution of a CH group with an isovalent N atom does not have a significant influence on the stability of aza-naphthalenes.

3.4. Electronic indices of aromaticity

Two delocalization indices, PDI and FLU, have been computed. According to literature data [15,16], smaller values of FLU (FLU = 0 for benzene) and PDI values closer to 0,1 (PDI = 0,1 for benzene) suggest a strong aromatic character. The results presented in Table 4 show no significant differences among the all-carbon and aza-rings of naphthalene, quinoline and isoquinoline. In this regard, it can be said that the PDI index gives the same trend of aromaticity as the NICS index. Instead, the values obtained for the FLU index show a "decrease" in aromaticity of the cycles that contain one N atom.

3.5. Reactivity indices (condensed Fukui functions)

Condensed Fukui functions are one of widely used indices of reactivity. Within the present study, condensed Fukui functions were calculated for each C atom of the compounds I-III, in order to estimate the most reactive site for an electrophilic attack. The results are presented in Figure 2. The results are in good agreement with the experimental data; the N atom deactivates the cycle A and the electrophilic substitution occurs at the ring B. In the case of isoquinoline, the attack can also occur on ring A, in meta position towards the N atom.

TABLE 3. HOMO-LUMO gap (HF/6-31G(d,p))

Compounds	HOMO-LUMO gap (eV)
Naphthalene	10,60
Quinoline	10,82
Isoquinoline	9,75

TABLE 4. Delocalization indices PDI and FLU (HF/6-31G(d,p) level of theory)

Delocalization indices	Naphthalene	Quinoline		Isoquinoline	
		all-C ring	N-containing ring	all-C ring	N-containing ring
PDI	0,0736	0,0729	0,0734	0,0739	0,0742
FLU	0,0135	0,0148	0,0158	0,0134	0,0156

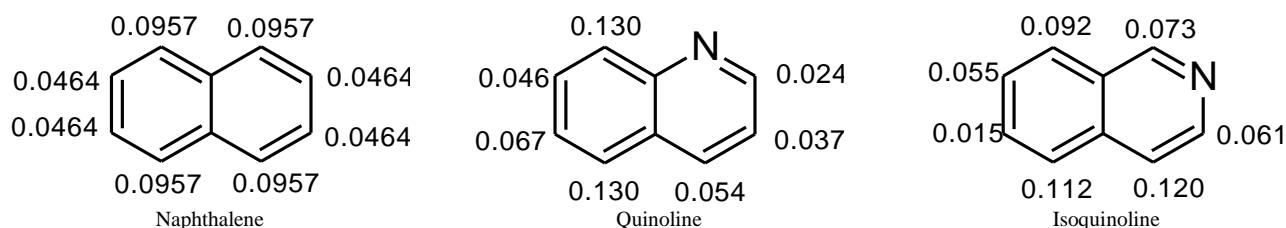


Figure 2. Condensed Fukui functions computed for an electrophilic attack (HF/6-31G(d,p))

4. Conclusions

A theoretical study regarding the influence of aza-substitution on the aromaticity of aza-naphthalenes has been performed. The local geometric index HOMA show a decrease of aromaticity for the rings that contain the N atom, while the magnetic index NICS show no significant differences for the aza-containing rings. The electronic index PDI correlates well with the magnetic index NICS, while FLU index predicts the same trend of aromaticity as the geometric HOMA index.

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Received: 05 December 2014

Accepted: 18 December 2014