

## Estimation of Nitrogen Atomic Charges in N-Containing Aromatic Compounds and their Relevance in Hydrotreatment

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### Introduction

Atomic charges assignment plays an important role in most fields of Chemistry such as organic chemistry, photochemistry, materials science, catalysis, etc. In catalysis, and particularly in the petroleum treatment, the determination of atomic charges located at specific atoms like sulfur, nitrogen or metals in structural compounds containing in crude oils could help to understand better the mechanism of action of different catalysts and obtain correct descriptors that relate chemical reactivity of different compounds with catalyst active phase. This will help the development of more active and selective heterogeneous or homogeneous catalysts for specific atoms elimination imposed by severe ambient regulations in many countries.

There are several schemes to describe charges in specific atoms in a molecule; however, the charge is not a quantum mechanical observable. Therefore, there is no definitive procedure providing reliable and essentially exact values of atomic charges [1] and one is constrained to test and check the available methodologies aiming at establishing correlations between numerical calculated values for theoretical models and chemical reactivity or calculations for interactions. The main aim of this work is to obtain suitable descriptors relating chemical reactivity and localized charge at specific atoms. We used the observation of electrostatic potential surface as a help to identify qualitatively negative and positive spatial regions in molecules [2].

### Materials and Methods

To understand differences between both different nitrogen-containing aromatic compounds such as pyrrole and pyridine, and ring condensed derivatives present in crude oils we studied electronic properties calculated at B3LYP/6-311++G(d,p) level at Gaussian 03 package [3].

The interaction of nitrogen atom in both pyrrole and pyridine with an electronic deficient species, namely a positively charged proton [4], was estimated.

### Results and Discussion

HOMO surface reveals nitrogen nature in both systems: in pyrrole, nitrogen atom does not have electron density, the electron pair are delocalized in all ring system; whereas in pyridine electron density is localized on nitrogen atom. This is in agreement with the difference in nitrogen basicity of pyridine and pyrrole.

Table 1 describes the results obtained in this work. The comparative analysis of charges from Mulliken, NBO, AIM, and MK, confirms the basic character of compounds by MK scheme. Values of proton affinities of aromatic compound were compared with all atomic charges calculated at same level of theory to understand best correlation (Figure 1).

Table 1. Charge analysis for nitrogen atom in aromatic compounds

Compound	Mulliken	NBO	AIM	MK
Pyrrole	-0.107	-0.538	-1.1608	-0.1747
Indole	-0.088	-0.547	-1.1586	-0.4063
Carbazole	-0.027	-0.559	-1.1544	-0.6529
Pyridine	-0.073	-0.452	-1.0994	-0.6695
Quinoline	0.049	-0.444	-1.0961	-0.7255
Acridine	0.155	-0.476	-1.0955	-0.7904

### Significance

Our results have several implications on the hydrotreatment process of nitrogen aromatic compounds, as a base compound present in crude fuels

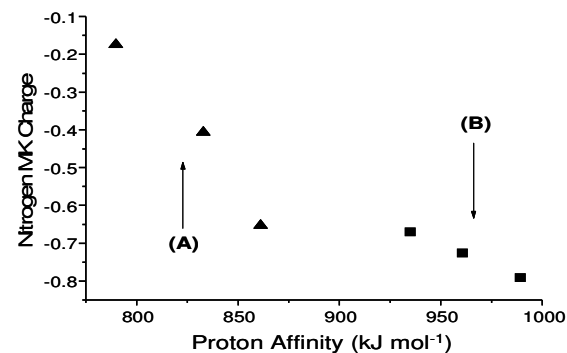


Figure 1. Correlation between nitrogen MK charges and proton affinities for non basic (A), and basic (B) nitrogen aromatic compounds.

### References

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