



**PHYSICAL CHEMISTRY 2014**

12<sup>th</sup> International Conference  
on Fundamental and Applied Aspects of  
Physical Chemistry

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The Conference is dedicated to the  
25. Anniversary of the Society of Physical Chemists of Serbia

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September 22-26, 2014  
Belgrade, Serbia



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*Organized by  
The Society of Physical Chemists of  
Serbia*

*in co-operation  
with\_*

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## THEORETICAL STUDY OF SUBSTITUENT EFFECTS ON STRUCTURAL PROPERTIES OF ARYLAZO PYRIDONE DYES

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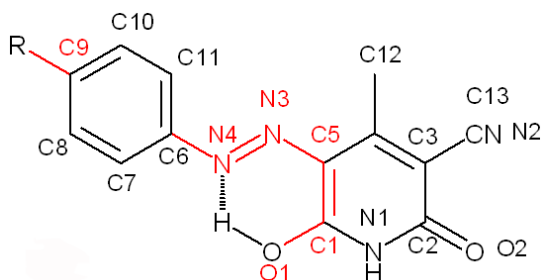
### ABSTRACT

Quantum chemical calculations performed by the density functional theory (DFT) were used to determine the structural parameters of arylazo pyridone dyes. The influence of electronic effects of substituent in diazo moiety of dyes on their structure properties was studied and quantified using Hammett equation. The correlation between dye bond length and Hammett substituent constants  $\sigma_p$  gave us possibility to locate the most sensitive bond to substituent effects.

### INTRODUCTION

The density functional theory is presently the most successful approach to compute the electronic structure of matter, in particular atoms, molecules, and the condensed phases. Using DFT method a great variety of molecular properties, such as molecular structures, vibrational frequencies, atomization and ionization energies, electric and magnetic properties, reaction paths, etc. could be predicted [1]. In this paper, the DFT method was used to determine structural parameters of substituted arylazo pyridone dyes (Scheme 1). The investigated dyes have the same benzene/pyridone skeleton, but different substituent group (R) in the benzene ring.

Arylazo pyridone dyes can exist as two tautomeric isomers, i.e. 6-hydroxy-2-pyridones (azo form) and



**Scheme 1.** Structure of arylazo pyridone dyes; R: OH, OCH<sub>3</sub>, CH<sub>3</sub>, H, Cl, Br, COOH, SO<sub>3</sub>H, CH<sub>3</sub>CO, CN, NO<sub>2</sub>



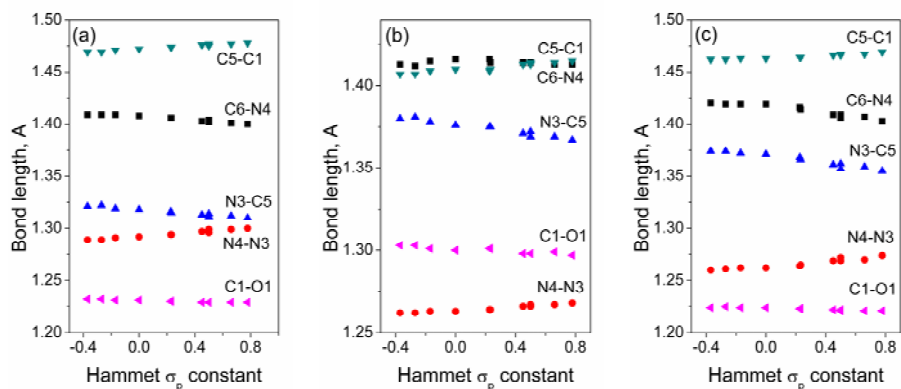
pyridine-2,6 diones (hydrazone form). In water beside azo-hydrazone equilibrium, the dyes can co-exist in acid-base equilibrium. The influence of electron-donating and electron-withdrawing substituents on structural parameters of the most stable forms of arylazo pyridone dyes (azo, hydrazone and anionic) was also studied and quantified by means of Hammett equation.

### EXPERIMENTAL

The investigated dyes were synthesized from the corresponding diazonium salts and 4-methyl-6-hydroxy-3-cyano-2-pyridone. A detailed procedure for dye synthesis and their structural characterization were given elsewhere [2-4]. All the DFT calculations have been carried out with the Gaussian 09, revision C.01 electronic structure program suite. The hybrid M06-2X density functional was used for geometry optimizations. An all-electron 6-31+G(d,p) basis set was used for all atoms. Analytical harmonic frequencies were calculated in order to ascertain that the optimized structures correspond to the minima on the potential energy surface.

### RESULTS AND DISCUSSION

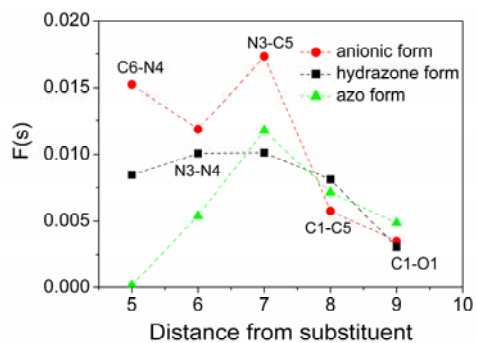
Geometry optimization for hydrazone, azo and anionic forms generated reliable minima structures as confirmed by the absence of imaginary force constant in vibrational analysis. Solvent was found to have negligible effects on the geometry of the investigated molecules. The results revealed that the pyridone and benzene fragments are completely planar with azo linkage in all forms. Concerning bond lengths, the attention was focused only to C6-N4, N3-N4, N3-C5, C1-C5, C1-O1 bonds and bond between benzene ring and substituent group, R-C9. The calculated bond lengths lie between the single and double bond, suggesting considerable electron-delocalization throughout the whole molecule.



**Figure 1.** Bond lengths versus Hammett  $\sigma_p$  constants for (a) hydrazone form (b) azo form (c) anionic form of arylazo pyridone dyes.

The single-double bond character of C1-O1 bond is confirmation that lone pair of electrons of oxygen participate in the pyridone resonance structure. Considering anionic form of dyes with electron-donating group, the negative charge on oxygen atom in pyridone ring decreases conjugation between substituent and benzene ring and therefore lengthens the R-C9 bond. Opposite, negative charge on oxygen atom in anionic form of electron-withdrawing substituents increase conjugation between benzene ring and its substituent, leading to shortening of R-C9 bond length.

In order to determine how much is particular bond affected by substituents, the calculated bond lengths were correlated with Hammett  $\sigma_p$  constants (Fig. 1). The good linearity is observed for all bond lengths indicating that investigated bond lengths are affected by substituent effect, thus confirming electron-delocalization through whole dye molecule. The sensitivity of particular bond to substituent effect was determined from the slope of regression lines for each bond. Results from Fig. 2 indicate that N3-C5 bond is the most sensitive to



**Figure 2.** The sensitivity,  $F(s)$  of the bond lengths to substituent electronic effects.

substituent electron effects, i.e. the substituents exert stronger effect on conjugation between N3-N4 bond and pyridone ring than on the conjugation between N3-N4 bond and benzene ring. Also, the conjugation is more affected by substituent effect in anionic form, than in azo and hydrazone form, which is probably a consequence of extra available electrons on oxygen atom in pyridone ring.

### CONCLUSION

The results from this study showed that bond lengths are influenced by the type of substituents, showing a good correlation with Hammett  $\sigma_p$  constants. Substituents exerted stronger effect on the conjugation between azo bond and pyridone ring than on the conjugation between azo bond and the benzene ring. The obtained results indicate the position of active reaction center, thus facilitating the determination of complex reaction pathways that involve investigated dyes. Bond length in anionic form of dyes is more sensitive to substituent effect than other two forms, due to extra available lone pair on oxygen atom.

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