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Characterization and spectroscopic study of 4- (4-Nitro Benzene Azo)-3-amino benzoic acid compound by Gaussian 09 Program: A review

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ABSTRACT

Gaussian 09 program was used to follow up the theoretical calculations of 4-(4-nitro benzene azo)-3-amino benzoic acid in a method of Hartree-Fock to calculate IR, H-NMR and C-NMR spectrum, as used method ZINDO to calculate the electronic spectrum (UV), was adopted method (TD-SCF (self consistent field) /DFT (density functional theory)/ B3LYP to calculate the energies of orbital's (HOMO and LUMO) and found that the electron density centered at the carboxylic group COO and N=N group this means that the compound is capable of working as a ligand to synthesize many complexes, bond lengths and thermodynamic functions (ΔH^o, ΔG^o and ΔS^o) were calculated and found that the values of ΔH^o and ΔG^o to be negative, which refer to exothermic and spontaneous reaction.

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INTRODUCTION

Azo compounds are a critical class of chemical compounds receiving attention in research. They are extremely colored and are used as dyes and pigments for an extended time (Shama, S. A. et al., 2014 and Christie, R. M., 2015) Azo dyes contain at least of 1 nitrogen-nitrogen covalent bond (N=N); whereas di azo and tri azo dyes contain 2 and 3 N=N covalent bonds, respectively. The azo groups are generally connected to benzene and naphthalene rings, however also can be attached to aromatic hetero cycles or enolizable aliphatic groups. These side groups are necessary for imparting the color of the dye (Abd-Alredha, R. Al-Rubaie et al., 2012). Synthesis of most azo dyes involves diazotization of a primary aromatic amine, followed by coupling with one or additional nucleophiles (Otutu, J. O., 2013). In fact about half of the dyes in industrial use today are azo dyes, which are mostly prepared from diazonium salts, Azo compounds are the oldest and largest class of industrial synthesized organic dyes due to their versatile application in various fields, such as dyeing textile fiber, biomedical studies, advanced application in organic synthesis and high technology areas such as laser, liquid crystalline displays, electro-optical devices and ink-jet printers. Azo dyes which consist of at least a conjugated azo (– N=N–) chromophore (Olayinka, O. Ajani. Et al., 2013) Many azo-compounds have been applied as chromogenic reagents for the determination of several metal ions. The use of such reagents was found to depend essentially on their UV–Vis spectral properties. Many articles have been published concerning the spectral characteristics of azo compounds, which dealt with spectral-structure correlations as well as the effects of the medium on the band position (Dilek, Ç. Et al., 2014). azo dye compounds are known for their medicinal importance and are also known to be involved in a number of biological reactions such as inhibition of DNA, RNA and protein synthesis, carcinogenesis and nitrogen fixation. In a broader sense, the azo dyes constitute the largest diverse group of all the synthetic colorants (Al-Sheikh, M. et al., 2014). There is not much information available on the effect of these dyes on the

physiology of the gut micro flora or the kinetics of reduction in different environments (Ewelina, WT.; Łukasz, G., 2012). The main source of azo dyes in human organism is food. Groundwater can be a secondary source of contamination as 3 thousand tons of organic dyes are released into the surface water in the United States each year. Because of such a considerable hazard, many research groups have recently focused on the area of biodegradation of these dyes. It has been demonstrated that several microorganisms like lignolytic fungi or bacteria are able, under certain environmental conditions, to transform azo dyes to non-colored products or even to completely mineralize them. Lignolytic fungi, using lignin and manganese peroxidases or laccases, decolorize azo dyes (Nagham, M. Aljamali., 2015). In this paper we depend on the computational chemistry to follow the compound 4- (4-nitro benzene azo)-3-amino benzoic acid, which have structure as figure 1.

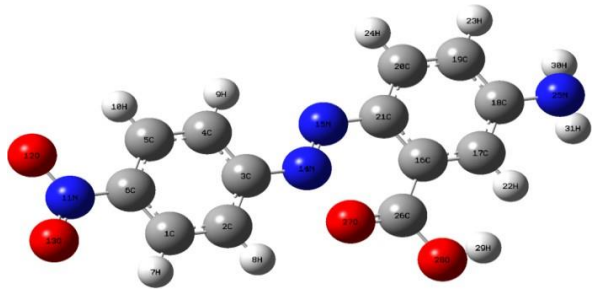

Figure 1: The Crystal Structure of 4- (4-nitro benzene azo)-3-amino benzoic acid

Computational Chemistry

The term computational chemistry is generally used when a mathematical method is sufficiently well developed that it can be automated for implementation on a computer. Very few aspects of chemistry can be computed exactly, but almost every aspect of chemistry has been described in a qualitative or approximately quantitative computational scheme. In short, a theoretical model or method is a way to model a system using a specific set of approximations. These approximations are combined with a calculation algorithm and are applied to atomic orbitals, defined by the basis set, in order to compute molecular orbitals and energy. Gaussian 09 is powerful software that can perform a multitude of calculations on a given molecule, which contains 4 main methods: semi-empirical, Ab initio, density functional (DFT) and molecular mechanics. The selection of theoretical model depends on the size of the system and on the level of approximation (David, Y., 2001). We used the DFT method, that is becoming more and more popular because the results obtained are comparable to the ones obtained using Ab initio methods, DFT differs from methods based on HF (Hartree – Fock) calculations, which is fundamental to much of electronic structure theory. It is the basis of molecular orbital (MO) theory, which posits that each electron's motion can be described by a single-particle function (orbital) that does not depend explicitly on the instantaneous motions of the other electrons (Sherrill, C. David., 2000). In this review we tend to use Gaussian 09 program to calculate IR, UV, H-NMR and C-NMR spectrum, HOMO and LUMO energies, bond lengths. The following data were calculated for every molecule in the Gaussian09 program and the following data were calculated for the compound of 4- (4-nitro benzene azo)-3-amino benzoic acid:

RESULTS AND DISCUSION

The molecule 4- (4-nitro benzene azo)-3-amino benzoic acid was prepared previously by characterized by electronic spectra using the theoretical calculations with Gaussian 09 in a method (TD-SCF-DFT) / B3LYP, where two peaks appeared the first peak (333-372)nm and were assigned to (n-π^*) transition and the second peak (430-439)nm , which assigned to (π- π^*) transition. Figure 2 shows the theoretical electronic spectra of the compound. As we followed the compound based on the vibrational spectra (IR), which appeared the peak (3389)cm^{-1} that was assigned to the stretching vibration of υ (OH) group, (1670) cm^{-1} assigned to asymmetric vibration υ_{as} (COO), (1563)cm^{-1} assigned to strong vibration υ_s (COO) and the peak (1448)cm^{-1} assigned to υ (-N=N-), figure 3 shows the theoretical vibrational spectra (IR) of the compound:

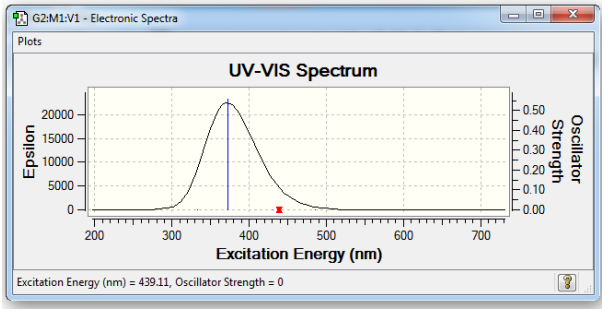

Figure 2: The Theoretical Electronic Spectra of 4- (4-nitro benzene azo)-3-amino benzoic acid

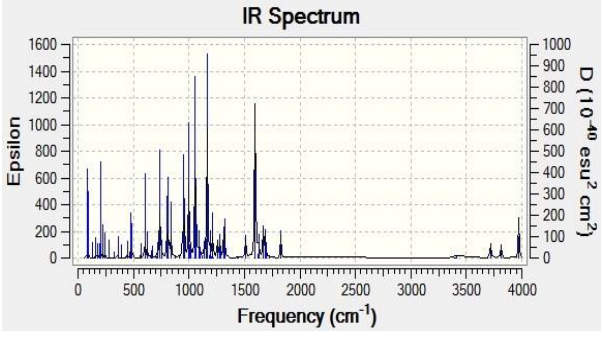

Figure 3: The Theoretical Vibrational Spectra (IR) of 4- (4-nitro benzene azo)-3-amino benzoic acid

As well as the compound was characterized by H-NMR and C-NMR with theoretical method as in the table 1, figures 4 and 5.

Table 1: The Theoretical Values of H-NMR and C-NMR signals of the Compound

δ (ppm)	Type of C-H	δ (ppm)	Type of H
170.77	C-Carboxyl	7.66-8.37	Aromatic Proton
125.93-137	C-Benzene	9.5	H-Proton
		6	NH_2

Calculated the energies of orbitals (HOMO and LUMO) for the compound and showed that the excitation energy is 2.55eV and showed existence of an electronic density on the COO and N=N groups, which means it more award of electrons when it behavior as a ligand, Figures 6 showed the orbitals energies (HOMO and LUMO) of the compound:

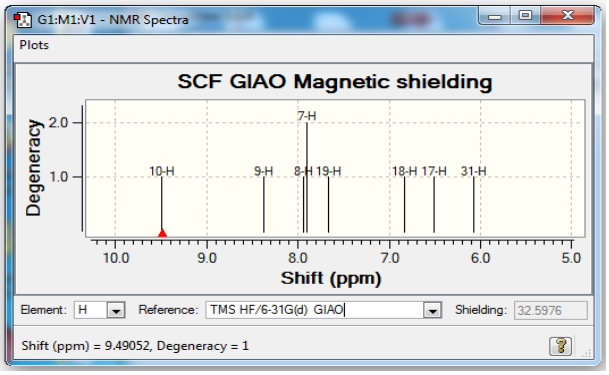

Figure 4: The Theoretical H-NMR Spectra of the Compound

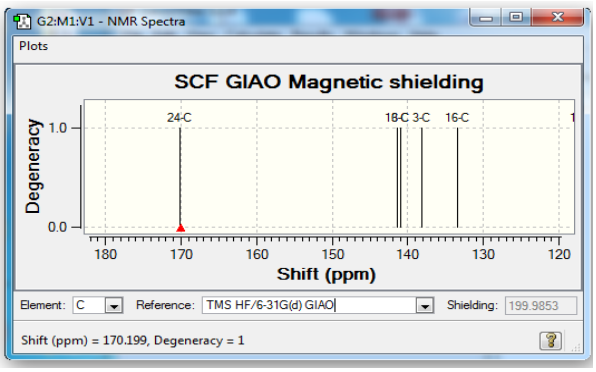

Figure 5: The Theoretical C-NMR Spectra of the Compound

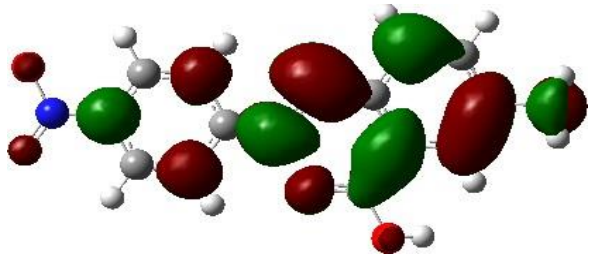

Figure 6: HOMO-LUMO Category of the Compound

Thermodynamic calculations (ΔH, ΔG and ΔS) were calculated for the compound using Hartree – Fock method as in the table 2 and has been found that the values of (ΔH and ΔG) are positive, which means that the reaction of 4 (4-nitro benzene azo)-3-amino benzoic acid synthesis was exothermic and spontaneous.

Table 2: The Theoretical Thermodynamic Calculations of the Compound

Δ_rH^o (cal / mole)	-66516
Δ_rG^o (cal / mole)	-73418
Δ_rS^o (cal / mole.K^{-1})	23.161

Table 3: The Bond Lengths of the Compound

Bond No.	Bond Lengths (A°)
$N_{11} - O_{12}$	1.36
$N_{11} - O_{13}$	1.196
$C_6 - N_{11}$	1.47
$C_5 - C_6$	1.401
$C_5 - H_{10}$	1.07
$N_{14} = N_{15}$	1.232
$C_{26} = O_{27}$	1.258
$C_{26} - O_{28}$	1.43
$C_{28} - H_{29}$	0.96
$N_{25} - H_{31}$	1.0

CONCLUSIONS

We concluded by studying the compound 4- (4-nitro benzene azo)-3-amino benzoic acid theoretically using Gaussian 09 program with different methods that the formation reaction of the compound is exothermic and spontaneous and it can works as a ligand to synthesize several complexes.

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