Ozonolysis of Indigo: An ab initio study

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ABSTRACT

The theoretical investigation (studies) on calculations of indigo's electronic structure have been performed with the the high-level theoretical method, Gaussian03, all geometries have been fully optimized with MP2 method using a 6-31G** basis set. These calculations shown that low reactivity can be attributed to its highly stability. The intramolecular hydrogen bridges between amino and carbonyl took the nucleophilic and electrophilic attacks position. This intramolecular interaction was analyzed following the Bader's atoms in molecules theory. In the dimer formation, hydrogen bridges between amino and carbonyl, became intermolecular. Calculations for HOMO and LUMO orbitals indicated that the preferential attack positions are carbons 1 and 6, energy values of indigo·····OH interactions confirm that carbon 1 is the likeliest.

Keywords: Indigo, Theoretical study, atoms in molecules

1 INTRODUCTION

Indigo is the blue dye on denim, used by centuries, first on dresses in rural and industrial jobs later it was used on informal clothing. Nowadays, the annual production of denim is about 1080 millions of lineal meters, a little more than 16 turns around the planet, which means a consumption of 30 thousands tons of colorant. Fabric is dyed in vats with a heated solution of the *leuco* – form of indigo, which it is deposited inside the cotton fibers [1] and then is oxidized by air to obtain the blue form. The exhausted liquors, estimated in 35 millions of cubic meters per year, contain enough colorant to dyeing effluents intensely. It is not sure that indigo is toxic [2] (Ranking et al, 1992), but we know that this compound (its components) affect respiratory processes of animals and plants by the thinness of the residual colloidal powder and by its color and the aesthetics of landscapes.

It is very important to find treatment processes for the industrial textile effluents. Discoloration of indigo doesn't mean mineralization [3] (Peralta – Zamora et al, 1999) or partial degradation [4] (Vautier et al, 2001). Decomposition of the colorant may produce aromatic compounds whereof toxicity is bigger than indigo itself, whose insolubility (2ppm in water) preventing its bioactivity and bioavailability. Several methods of degradation have been proposed: electrochemical reduction [5,6] (Betchtold et al, 1996; Roessier et al, 2002); ozonation as general method for textile industries [3,7,8] (Peralta - Zamora et al, 1999; Aplin and Waite, 2000; Sevimli and Sarikaya, 2002); microbiological degradation with lignolytic fungi [9] (Balan and Monteiro, 2001) and enzymatic processes [3] (Peralta – Zamora et al, 1999), Fenton's, photo – Fenton's and electro – Fenton's processes [7,10] (Aplin and Waite, 2000; Flox et al, 2006); photocatalytic degradation [3,4,11] (Peralta – Zamora et al, 1999; Vautier et al, 2001; Prieto et al, 2005) and, recently, electrochemical oxidation with boron doped diamond (BDD) electrode [12] (Butrón et al, 2007). Photo degradation over indigo was made in solid state, irradiating the mixture of TiO2 photo catalyst and dye, observing the discoloration. Electrochemical oxidation with BDD (boron doped diamond) electrode was called "electroincineration" perhaps because no residuals were found after the treatment.

The molecule of indigo is very stable, millenary in fact. Perhaps it is the most used natural organic dye from all times. The clothes of Egyptian mummies, with more than four thousand years, were dyed with this colorant. Indigo is obtained as glucoside from several plants corresponding to the *indogofera* species and others as *glasto* or "cake weed" (*Isatis tinctorea*). In Central America there are samples of fabrics and colored walls dyed with this color, called "mayan blue" in the region [13]. The natural compound have been substituted with a synthetic one, since the last years of XIX century, after the reaction developed by Heuman and Lederer.

This work is concern about the stability of indigo molecule, studied trough electronic structure, the attack centers and proper oxidant agents, and other properties obtained by theoretical calculations.

2 METHODOLOGY

The theoretical investigation of the electronic structure calculations of the indigo was performed by the system of programs Gaussian03 [14]. Restricted Hartree - Fock theory (RHF) was used for closed shell systems and unrestricted Hartree - Fock theory (UHF) for open shell systems (radicals). The correlation energy corrections are introduced with Moller-Plesset perturbation theory up to second order (MP2). All geometries have been fully optimized using a 6-31G** basis set. Energy results from spin-projected MP2 calculations are used (PMP2) at the radicals. The frequency calculations have been performed at Hartee-Fock level. The topology of the charge density has been studied using the Bader's atoms in molecules theory with the AIMALL program at the MP2 level to identify critical points in the intramolecular and intermolecular interactions[15].

3 RESULTS AND DISCUSSION

Structural studies

Structure of indigo molecule obtained by calculations shown planarity in the expected stable trans form. Stability is related with intramolecular hydrogen bonds between ketone and imine groups. In spite of the calculated distance of 2.29 A, apparently large, this is lower than the sum of Van der Waals radii, 2.7 A. Calculations of indigo – indigo system, with both two molecules in the same plane, showed that intramolecular hydrogen bridges are transformed into intermolecular ones. The picture of dimer shows interaction between hydrogen in 4 – 7 and 7' – 4' positions, but planarity is maintained.

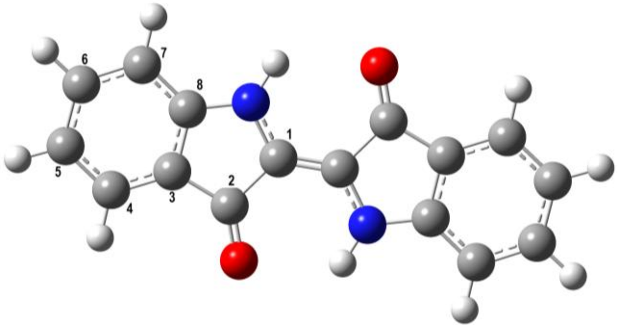


Figure 1. Structure of indigo molecule. Numbers arise from literature.

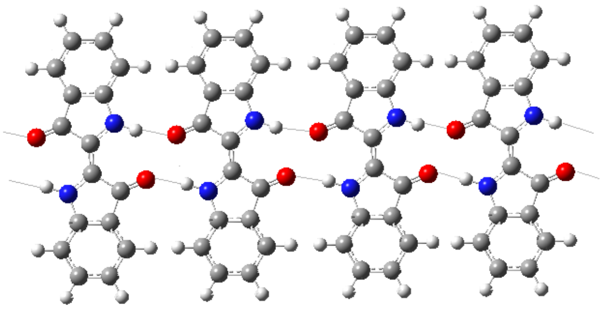


Figure 2. Indigo molecules arranged in a plane. Intramolecular hydrogen bonds become intermolecular. Note the interaction between hydrogen atoms in positions 4 and 7.

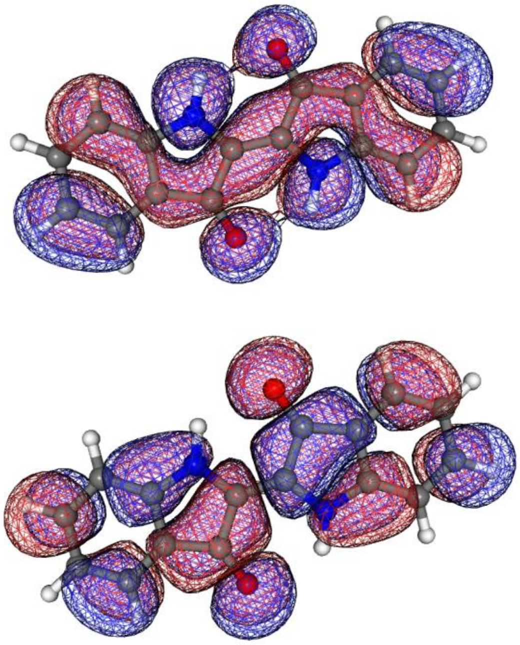


Figure 3. Frontier orbitals, HOMO (up) and LUMO (down).

The figure 3 shows the shape of the frontier orbitals for indigo. The red and blue colors represent the positive and negative phases. Both orbitals show bonding and antibonding character. The HOMO orbital presents bonding character along ten carbons the C1, C2, C3, C8, C7, C1´, C2´, C3´, C8´ and C7´, this allow the delocalization of electrons. This orbital also present antibonding with the carbons C4, C5 and C4´,C5´. The groups carbonyl and amino participate as antibonding, however this groups presents the same phase and their close up that can allow keto - enol tautomerism. It should be noted that the hydrogens over the carbons 6 and 6´ do not participate as bonding or antibonding. This means that these positions have a different reactivity than the rest of the molecule. In fact the introduction of substituents in the benzene ring have no pronounced effect in the color properties on the indigo dye, substitution of C6 hydrogen by bromine produce Tyrian purple, indigo carmine was obtained by substitution of C6 – C6' hydrogens by $NaSO_3$ groups.

The central C=C and the carbonyl group participate as antibonding in the LUMO orbital, like the five and six rings. In general it was assumed that the donor groups destabilize bonding and antibonding molecular orbitals whereas the inverse holds for acceptor groups [16] (Fleming, 1976). Excited molecular orbitals are acceptors.

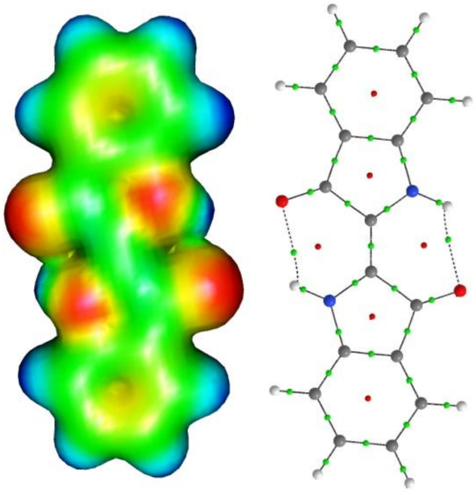


Figure 4. Density, critical points.

Figure 4 shows the electronic density of molecule. The extended density (in green color) is in agreement with the picture of HOMO – LUMO frontier orbitals. It is remarkable the intramolecular hydrogen bonds. Critical points, calculated with atoms in molecules theory, show the same pattern. Also occurs in the dymer structure (figure 5). In these patterns is possible to observe that intramolecular hydrogen bonds become intermolecular. It seems that there may exists repulsions between aromatic hydrogen, but the representation of critical points revealed interactions between them, increasing the chemical stability of the compound. Interactions can be analyzed by the internal orbitals (figure 6).

Chemical reactivity of indigo with ozone or HO• free radicals.

Approximations of O_3 to indigo isolated molecule do not give significant interaction. Ozone reacts with water in agreement with reactions [17] (Kogelschatz & Eliasson, 1995):

$$O_3 + H_2O \rightarrow HO_3^+ + HO^- \rightarrow 2\ HO_2\bullet$$

$$O_3 + HO_2\bullet \rightarrow HO\bullet + 2\ O_2$$

HO• interact with C1 and or C6 carbons. Interaction with C1 clearly produced bigger distortion than produced with C3 or C6. Interaction with C1 clearly distort indigo molecule as shown in figure 7, breaking the extension of conjugation and electronic density of molecule. Calculus of interaction energy between HO• and C1, C3 and C6 gave the stability of the formed adduct. In table 1 we observed that stability is reached when adduct is formed over C1 and C6 centers, but over C1 is better.

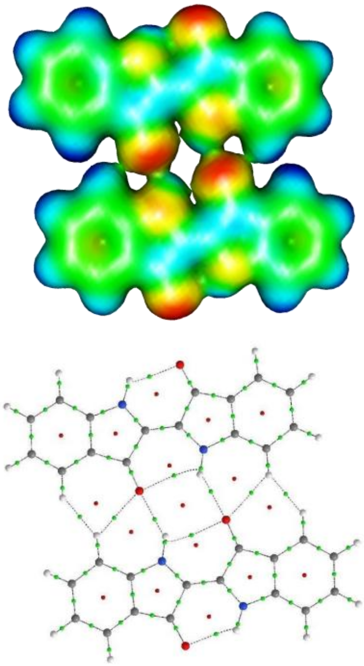


Figure 5. Density and Critical Points of the indigo Dimer

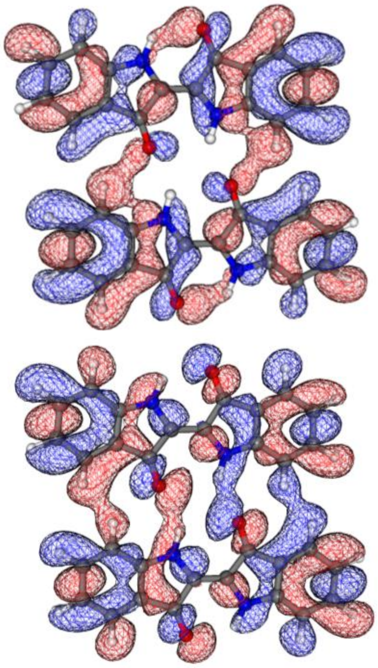
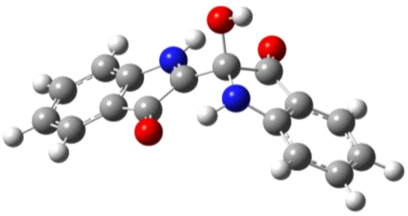
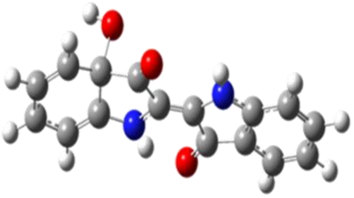


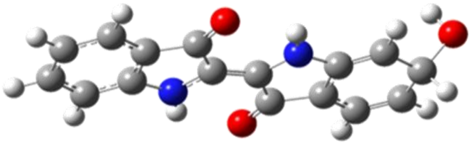
Figure 6. Internal orbitals of the dimer Density orbital of the Interaction of the carbonyl –H aromatic and H-H aromatic.



Carbon 1



Carbon3



Carbon 6

Figure 7. Interaction of HO• with Indigo on C1, C3 and C6

Table1. Energy of interaction between OH• and C1, C3 and C6 of indigo molecule.

	ΔE, kcal/mol
Indigo + HO• (with no – interaction)	0.0
Indigo + HO• over C1	– 32.8
Indigo + HO• over C3	+9.0
Indigo + HO• over C6	–9.0

4 CONCLUSIONS

Indigo is very stable due to the large conjugation inside the molecule and by intra and intermolecular hydrogen bridges. According to the critical point calculation from atoms in molecules theory and confirmed by the analysis of internal orbitals, the main interaction centers have high electron densities.

There were no interaction between ozone and indigo. All attempt of assembly this set, resulted repulsive. The very slow reaction obtained experimentally must be driven with free radicals HO•

Frontier orbitals HOMO and LUMO indicate that C1, C3 or C6 were the expected points for attack with free radicals HO•. Calculations of energy interaction between indigo ··· •OH set showed that C1 was the preferred attack point center.

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