

# A DFT Study on the Efficacy of Linking Agents (Sulfur and Nitrogen) to Connect Trans-azobenzene Sandwiched Between Two Gold Electrodes

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**Abstract:** Electronic structure calculations were performed to analyze the effectiveness of linking agents (sulfur and nitrogen) in connecting the trans-azobenzene sandwiched between two gold surfaces (Au-atoms). It was analyzed the dynamics of the load carrier and the electronic structure of the molecular backbone by applying an external electric field (EF), also a detailed structural, frontier orbital and natural bond orbital analysis (NBO) were performed. From the NBO analysis, it was possible to predict the path of charge flow in the molecular system. Electrostatic potential mapping allowed us to visualize the charge redistribution in the molecular system caused by the EF application. Our results indicate that when the nitrogen atom is used as a linking agent, the azo group of molecules may enhance their conductivity.

**Keywords:** DFT-field application, Moltronics-linking agent, Molecular orbitals, NBO.

## INTRODUCTION

**M**OLTRONICS provides a pathway for the development of the next generation of electronic devices, which are more powerful and compact in comparison to the previous ones. In this sense, the use of a single molecule as an electrical component was first envisioned by Mark Ratner and Aviram in 1974.<sup>[1]</sup> In late 1990's a lot of research works were conducted to explore the electrical behavior of molecular systems, due to the inability of the existing theories to explain the properties of systems at the molecular level (nano).<sup>[2–8]</sup> However, even currently, the analysis of the electronic properties at the molecular level implies many complicated issues, by which the theoretical investigations are useful in narrow down the associated problems. In this kind of molecular electronic systems, the

linking agent is the one which facilitates the bond formation between the metal and the organic molecule, because metal-molecule-metal junction is an important factor in determining the conductivity of the molecule.<sup>[9,10]</sup> Also, the molecular system may be influenced by an external electrical dipolar field (EF) causing changes in the molecular electronic structure in response to it. Generally, organic molecules are the most preferred to be used in moltronic devices due to their extended conjugation  $\pi$ , for easy electron transfer.<sup>[11–13]</sup> In this sense, azobenzene exhibits a simple molecular structure and the presence of lone pair of electrons in the azo group ( $-N=N-$ ) facilitates the electron transfer by highly extending the delocalization of  $\pi$  electrons.<sup>[14]</sup> In addition, azo groups have proved to exhibit photo isomerisation which makes them suitable for the fabrication of molecular switches.<sup>[15,16]</sup> Moreover,

azobenzene and its derivatives has attracted a lot of interest in various fields like non-linear optics, optical data storage, photochromic materials, dyes etc. Thus, the aim of this theoretical study is to investigate the effectiveness of linking agents (sulfur and nitrogen) in connecting the molecule (azobenzene) with the electrode (Au-atom). Since, the effectiveness of these linking agents is an important part in the design of new molecular wires and electronic devices.<sup>[17–19]</sup> During the present study the azobenzene is kept in its trans-conformation, which has a better conductance,<sup>[20]</sup> and a major thermodynamical stability in comparison to the cis-conformation.<sup>[21]</sup>

## COMPUTATIONAL DETAILS

All the calculations were performed at the DFT/B3LYP level of theory,<sup>[22,23]</sup> as implemented in Gaussian 09W software package.<sup>[24]</sup> Also, Au atoms were described through the LANL2DZ basis set,<sup>[25–27]</sup> in order to minimize the computational cost with the usage of effective core potential to perform valence electron calculations. To compare the effectiveness of the commonly used linking agent sulfur (S) with the nitrogen (N), the terminals of the optimized structure of trans-azobenzene is bonded to –SH group and –NH<sub>2</sub> groups yielding thiolated azobenzene (M-I) and azodianiline (M-II) respectively, then these structures were fully reoptimized. Also, it is important to mention that Au can couple covalently with M-I and M-II through S and N respectively by replacing H-atom.<sup>[17]</sup> Hence the H-atoms in –SH and –NH<sub>2</sub> groups were replaced by gold atoms to represent the metal electrode,<sup>[28]</sup> and named as extended molecule-I (EM-I) and extended molecule-II (EM-II) respectively for further calculations. In EM-II, since N-atom is used as a linking agent two Au-atoms per N-atom are bonded to build it a chemical stable structure.

Here, it is important to comment that in the nanoscale regime, the contact (bond) made between the metal electrode and the molecule may alter the electronic structure of the last one.<sup>[7]</sup> Thus, in order to predict such effects Au atoms were connected to the molecule through the linking agent. Also, the EF was applied along the molecular axis of EM-I and EM-II, with the field strength varying from 0 to 0.26 V / Å in five steps as implemented in Gaussian 09W suite of program. Also, to reveal the existence of inter molecular interactions Natural Bond Orbital (NBO) calculations were carried out using NBO 3.1 program.<sup>[29]</sup> The molecular orbitals (MOs) and the electrostatic potential (ESP) mappings were plotted using GView05 program.<sup>[30]</sup> The density of states (DOS) was calculated employing GaussSum program.<sup>[31]</sup> The molecular descriptors such as hardness ( $\eta$ ) and softness ( $S$ ) were calculated through the equations (1) and (2), respectively,<sup>[32]</sup>

$$\text{Hardness: } \eta = \frac{(E_{\text{LUMO}} - E_{\text{HOMO}})}{2} \quad (1)$$

$$\text{Softness: } S = \frac{1}{2\eta} \quad (2)$$

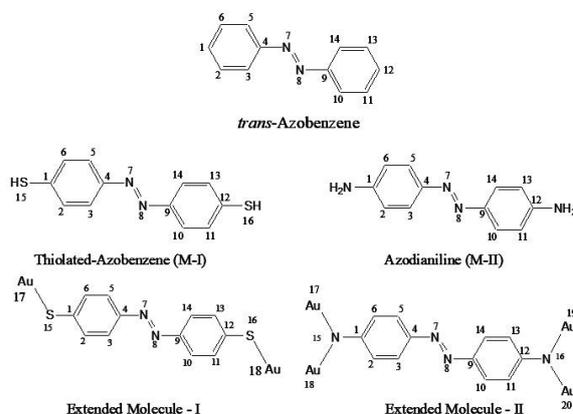
The values of these descriptors allow predicting the ease with which an electron may be transferred through the metal-molecular system.

## RESULTS AND DISCUSSION

### Structural Analysis

The conductivity of a molecule is expected to be high when it is in a planar configuration.<sup>[33]</sup> Hence, the trans-conformation of azobenzene was used for the entire study. The structure of the molecules was analyzed in order to find out the influence of the linking agents and Au atoms over the planarity of the molecule. The bond lengths of the optimized structures are reported in Table 1, and the atom numbering of the studied molecules are depicted in Figure 1.

The bond length of C2–C3, C3–C4, C–N and N=N bonds in azobenzene are 1.402 Å, 1.417 Å, 1.433 Å and 1.290 Å respectively, which are in close agreement with the values reported in the literature.<sup>[34,35]</sup> The inclusion of linking agents (sulfur and nitrogen atoms) and Au atoms slightly alter the bond lengths. Note that the parallel bonds to the molecular axis (C2–C3, C5–C6 and C4–N7) are shortened and the other bonds are elongated. The bond lengths variations are higher in EM-II in comparison to EM-I. The N=N bond length increases to 1.292 and 1.305 Å in EM-I and EM-II, respectively. On the other hand, the C–N bond length is shortened to 1.428 and 1.410 Å in EM-I and EM-II, respectively. The S–C and N–C bond length is elongated with the inclusion of Au atoms. The Au–S and Au–N bond lengths are 2.398 and 2.064 Å, respectively.



**Figure 1.** Structure and atom numbering of the set of molecules.