



## NMR and UV-Visible spectroscopic investigation on Methyl Amino Methyl Anthracene using computational calculations

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### Abstract

In this attempt of research work, the inducement of NLO property of the compound Methyl amino methyl anthracene(MAMA) has been analysed using computational calculations. The Gaussian hybrid computational calculations were carried out by HF and DFT (B3LYP and B3PW91) methods with 6-31+G(d,p) and 6-311++G(d,p) basis sets and the corresponding results were compared with experimental values. The change of chemical environment due to the addition of methyl amino methyl chain was studied. Moreover, <sup>13</sup>C NMR and <sup>1</sup>H NMR were calculated by using the gauge independent atomic orbital (GIAO) method with B3LYP methods and the 6-311++G(d,p) basis set and their spectra were simulated and the chemical shifts related to TMS were compared. A study on the electronic and optical properties; absorption wavelengths, excitation energy, dipole moment and frontier molecular orbital energies, were performed by HF and DFT methods. The calculated HOMO and LUMO energies (kubo gap) were displayed in the figures which show that the occurring of charge transformation within the molecule.

**Key words:** NLO property, organic molecule, tunable photonic applications, anthracene molecule, organic optical semiconductors (OOS), opto electronic activity.

### Introduction

Since the organic molecular synthesized materials having enriched crystal and semiconducting and NLO properties, they are popularly used in fabricating the opto-electronic and photonic devices [1]. The crystal materials made by the combination of optically active organic base molecules and optical catalytic ligand groups generally processing amplified NLO response, fast signal response time and tuneable photonic application [2-4]. The possibility of tuning the NLO properties such as fluorescence properties by the addition of active substitutional groups on anthracene molecule plays a significant role in order to construct Organic Optical Semiconductors (OOS) suitable for preparation of organic light-emitting diodes, organic crystal photovoltaics and organic thin film transistors [5-6]. Due to the opto-electronic properties (opto-electrical transducing capability mechanism), the anthracene molecules is basically used as a charge transfer materials called scintillators.

The Anthracene molecule is basically constructed by fusing three benzene rings known as polycyclic hydrocarbons condensed benzenoid structure, in which  $\sigma$  and  $\pi$  delocalized orbital's interaction system are formed to arrange organized nodal plane system causing the inducement of opto-electrical transducing mechanical platform. This arrangement is causing high fluorescence quantum yield for opto-electronic activity. The fluorescence anisotropy of anthracene crystals also depend on notable substitutional groups and compounds having



coordinate-covalent character. It is the great privilege of research workers to find the root cause of generating such desirable and tuneable opto-electronic properties by the addition of different ligand groups in anthracene molecule. After the thorough investigation made on literatures and primary sources, no work was not made to analyze the Anthracene on substitutional influence. In this work, the 9-(methyl amino methyl) anthracene molecule was investigated in terms of spectroscopic and theoretical tools to explore the optical, electrical and opto-electronic properties using experimental and theoretical molecular spectroscopy.

### Computational profile

The HF and DFT quantum chemical calculations of the 9-(Methylaminomethyl)anthracene were carried out using Gaussian 09 program package with 6-311++G(d,p) basis set. The calculated optimized parameters were presented in Table 1. The isotropic and anisotropic chemical shifts of  $^1\text{H}$  and  $^{13}\text{C}$  NMR are useful to explore the chemical environment of present compound were simulated in gas and solvent phase (DMSO, Methanol and Water) under GIAO guidance at B3LYP/6-311G++(d,p) level using the IEFPCM method.

The electronic absorption spectra obtained from Frontier molecular orbitals provides the estimation of band gap of the title molecular system were calculated at B3LYP/6-311++G(d,p) level which gives an detailed information of chemical reactions within the molecule. The interaction between bonding and anti-bonding (Rydberg orbitals) signified the divergence of molecular structure from the Lewis model and it was used to measure the delocalization. The HOMO-LUMO energies, absorption wavelengths and oscillator strengths are calculated using B3LYP method of time dependent DFT(TD-SCF), based on the optimized structure in gas phase and solvent (DMSO, Water and Methanol) phase.

### Results and discussion

#### Molecular geometry Deformation analysis

Though the present molecular system: 9-(Methylaminomethyl)anthracene belongs to  $C_{2v}$  point group of symmetry, the considerable non- centro symmetry gradient was observed. The molecule consists of 32 atoms where some of the group of atoms existed in different planes. This compound contains three hexagonal benzene rings fused with one another. The crystal appearance of the present compound was presented in the Figure 1. In this molecule, methyl amino methyl group was substituted in ninth position of anthracene ring as a chain. According to bond length distortion, it is well known that, the molecular geometrical symmetry was disturbed and thereby its physical properties were found to be changed as in the previous case [7]. Additionally, the chemical infection was observed in the form of alternation of chemical bond length in the ring by ethyl amino methyl chain. The change of core CC bond length was extended from the center ring to either part of hexagonal frame symmetrically therefore the physical property of the anthracene ring was ultimately modified regarding to the chain. Here, in the chain, the methyl group injected to the ethyl group via amino segment in which the electron cloud pulled from ethyl and methyl group and loaded to the anthracene ring. This chemical effect has stimulated immobile electron cloud with small amount of potential barrier which leading the semiconducting property in the compound. One can identify optically active materials from their crystal structures and also deduce the symmetry from optical measurements. The random crystallite orientation can lead to optical activity of the molecule [8].



According to Cartesian coordinate, the entire anthracene ring was placed along the x-axis and the ethyl amino and methyl group was placed along y and z axes. The structural deformation of the anthracene ring was evidenced from the stretching of bonds at the place of substitutional groups. The middle benzene ring was more distorted than the other two. The bond length C7-C24 is more elongated than others by 0.1141Å and the bond lengths C3-C7 and C7-C10 was increased by 0.0149Å and 0.0135Å respectively and there is a decrease in bond lengths in the bonds C2-H17, C1-H16, C11-H12 and C13-H21 due to the injection of substitutional groups. The bond angle at C3-C7-C10 decreased by 1.8358° and C3-C7-C24 increased by 0.34°. The bond angle at C7-C10-C11 is more and at C24-H25-H26 is least. The distance between the charge separation is also a deciding factor into the size of the dipole moment. The observed bond length variations indicates the dipole character of the molecule and also the charges are stabilised, which gives the evidence that the atoms in the molecule share the electrons unequally. This is caused by the substitutional pulling in the molecule. Hence the title molecule is NLO active.

### NMR profile

Nuclear Magnetic Resonance (NMR) spectroscopy is a versatile analytical technique for evaluating the chemical properties of an organic compound. The structure and purity confirmations can also be made by the use of NMR studies[9-11]. Also, it is possible to study the environment of all hydrocarbons occurring in the core as well as substitutional groups. The chemical information of the molecular components of the compound were obtained by means of the NMR spectral data which was calculated at B3LYP method with 6-311++G(d,p) level on the basis of GIAO method. The chemical shifts of the compound are reported in ppm relative to TMS for <sup>1</sup>H and <sup>13</sup>C NMR spectra which were presented in Table 2 and the corresponding spectra were shown in figure 2.

The NMR signals are divided into different domains of peaks with respect to the diamagnetic equivalence of carbon and hydrogen atoms. The isotropic chemical shifts in aromatic compounds are universally observed in the region of 100-160 ppm. The chemical shift at C7 was appeared to be 140 ppm that was very high in which the amino ethyl group was attached. The chemical shift of C3 and C10 were determined to be 127 ppm which is lesser than the chemical shift of C4 and C9 (131 and 130ppm). Similarly, the chemical shift of C5 and C15 were calculated to be 130ppm respectively whereas the chemical shift of C2, C11, C7 and C13 were found to be ranged from 126-127ppm respectively. From this observation of chemical shift in different core carbons, it was clear that, other than C7, the chemical shift of carbons of top moiety was lesser than the carbons of bottom moiety. This condition of chemical shift showed that, the chemical potential from the substitutional group was found to be directed to the center core of the anthracene ring which is transferred to adjoint rings via bottom moiety. The amino methyl chain produced two different chemical environment on the anthracene ring in which the electro chemical potential was depleted on the bottom moiety from the top moiety. Here, the chemical potential causing new properties in the compound was unidirectionally injected by the attached molecular groups in the ring. Such a charge depletion between the top and bottom moiety led the generation of optical and electronic path and thus the present compound in crystal form is able to have the semiconducting property.



### Frontier molecular analysis

The Frontier molecular orbital theory offer the information regarding light guiding and light amplifying mechanism of action in the molecular site. Usually, direct band gap for semiconducting mechanism is represented by the forbidden gap existed between HOMO and LUMO energy sequence. The semiconducting property in the organic crystals is setted up by orbital interaction lobes taking place in the degenerate orbital levels. The 3D diagram of the frontier molecular orbitals in IR and UV-Visible region for the title compound were displayed in figure 3 and 4.

The title compound was composed of anthracene and the substitutional groups such as ethyl, amino and methyl. Here, the HOMO interacting system was appeared as  $\pi$  orbital interacting system and they were found to be at C1-C2, C5-C6, C11-C13 and C13-C15. Also,  $\delta$ -bond interactions found on C3-C7-C10 and C4-C8-C9 which shows the electronic charge transfer property. In LUMO, there were one  $\sigma$ -orbital found on C7,  $\pi$ -orbitals found on C8-H20, C1- C6 and C13-C14 and cascading orbitals were appeared in C2-C3-C4-C5 and C9-C10-C11-C15 on the benzene rings at the corners. Also, there were empty orbitals on the substitutional groups on both HOMO and LUMO. From this, it was observed that the benzene rings at the corners of the anthracene compound were acting as electron donors and the middle benzene ring was acting as the electron acceptor and this was the main cause for the compound to acquire the semiconducting property and the energy gap was found to be 3.1467eV.

Also it was observed that in HOMO+1, there were  $\sigma$ -orbitals on C2, H25, N27 and H31,  $\pi$ -orbitals found on C2-C3, C5-C6 and C10-C11 and cascading of orbital made on C7-C24-C26-C28-H30-H32 and it was given in figure. In LUMO-1, there were lobe formations found on the 2P orbitals of the atoms C1, C3, C4, C6, C9, C10, C13 and C14. From this interaction, it was perceived that electron transitions have taken between HOMO and LUMO, also stabilization of the molecule has been occurred and the electron clouds were shared. Due to the sharing of the electron clouds between the spatial orbitals, there is a mutual sharing of physical and chemical properties between anthracene and the substitutional groups. The fluctuated charge levels and the measurement of the band gap exhibits that the molecule has moderate electronic properties.

### Optical properties analysis:

The theoretical UV/Vis spectroscopic technique is basically applied for studying the crystallographic information and the structural insight amalgamation. It is also used to analyse the molecular formation to enable the semiconducting property [12-14]. The physical and chemical properties offered by molecular mechanism processed by the molecular combination in the material being analysed. According to the experimental result the UV visible absorption peak was located at 390nm which was represented by the characteristic wavelength of C-N bond and C=C, both were present at substitutional place and main frame. It was confirmed that the above both bonds were found to be C'T complex of the present compound. Simultaneously, in the theoretical result, the peak was observed at 399 nm which was unique and also represents the same C'T complex. It was the major peak found at 399 nm with the energy gap of 3.10 eV under the oscillator strength of 0.078 and the signal was belongs to  $n \rightarrow \sigma^*$  transition band R-band (German, radikalartig). According to the band location, the absorption band was assigned to UV Quartz region by which the present compound was confirmed to be semiconductor with active semiconducting property. Other two bands were observed with virtual intensity and has no



considerable effect on characteristics. In solvent phase, the same result was obtained and no further effect of solvent on compound was observed.

### Mulliken charge distribution analysis

Mulliken charge distribution gradient is an important molecular charge measurement which is used to analyse the chemical potential with respect to the charge orientation[15-17]. As 9-(Methyl amino methyl)-Anthracene composed of three benzene rings along with the injection of ethyl, amino and methyl groups in which the molecular charge levels were oriented depending upon the active and passive electron pulling of donor and acceptor of the same. Usually, the charges are alternatively filled in core carbons in order to compensate chemical equilibrium forces existed among the atoms. But here, the electronic orientation on core carbon was modified by electron withdrawing and electron donating groups injected over the anthracene ring. When a suitable ligand is added with the base compound, the desired charge distribution for the active optical response is made. When ethyl amino and methyl is substituted with anthracene the mulliken charge levels are redistributed. The mulliken charge assignment was presented in table 5 and the related diagram was displayed in figure 6.

In this case, the ligand group adjoined at the central part of anthracene ring due to which the electron gradient was distributed positively and thereby the semiconducting mechanism was initiated at the centre ring and was extended symmetrically on supported side. The methyl group was found to be donated electron cloud to the amine group where the electronic energy was forced to transmit to the CH<sub>2</sub> group which was indicated by negative color gradient on 24C. Simultaneously the electron clouds on core carbons of the central ring was slightly pulled by the same CH<sub>2</sub>. So, the electron cloud on the core carbons were patternized uniformly and the core carbons turn out to be protonic places. Such a uniform depletion of electronic and protonic content over the molecule stabilizing the non centro symmetrical property. Thus, the semiconducting mechanism induced on the molecular site and the material become electronically and optically active.

### Conclusion

The geometry of the present molecule was optimized in HF and DFT level of theories and the optimized parameters have been calculated and presented. The alternation of the bonds and bond angles with respect to substitutional groups are discussed. From the NMR chemical examination, it is very important to note that, the introduction of substitution groups as new substituent in a compound was increased the semiconducting property in moderate way. The Mulliken charge analysis has been carried out in order to explain the redistribution of charges and simultaneously, the change of physical and chemical properties are interpreted. From the observation, it was clear that, the molecule is very reactive for electrical and optical properties. As this compound optically active, the addition of ethyl amino methyl group was further improving the electronic and optical activity. So, the present compound can be used to prepare NLO crystals.



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