STRUCTURAL AND ELECTRICAL STUDY OF 4-CHLOROPHENYL-N-4-FLUOROPHENYL-ANILINE.

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ABSTRACT: Computational calculation of aniline is a broad spectrum. In this current study structural information of $C_{18}H_{12}NFCl_2$ and electrical properties are estimated through computational methods. Quantum calculations reveal that the 120.6 electron volt (eV) first energy gap and 168.1 eV second energy band gap. Carbon and Hydrogen NMR prediction and Infar Red (IR) spectrogram provided the information about suture which is tabulated. The calculated ionization energy 142.16 , electron affinity 21.47 hardness 60.34, chemical potential -81.82 and Electronegativity 81.81, softness 0.016, electrophilicity index 55.46. Large energy gap shows high hardness and become less polarizable because of its hardness. The mixture of suitable ground and excited state wave functions is an outcome of polarizability. The title molecule is identifying as poor electrical conductor.

Keywords: aminobenzene, electron mobility, hardness, Insulator.

INTRODUCTION

The rapid demand of electronic gadget and development of high voltage technology also increases the demand of insulator as we know aniline precursors are used in polymer formation. Natural contamination on the surface of insulator makes gadget unfit (He *et al.,* 2019). An interaction between frontline molecular orbitals is shown by Woodward and Hoffmann by examining the interaction that could be accounted for both the region and stereo specificity. A vitality distinction concerning HOMO (i.e. highest occupied molecular orbit) and LUMO (i.e. lowest unoccupied molecular orbital) is assigned as the HOMO– LUMO gap energy. Frontier orbitals are designated as HOMO and LUMO (Hagberg *et al*., 2007). A HOMO level in organic semi-conductor is similar to valence band maximum in inorganic semi-conductors and quantum dots. Also a similar correspondence lies between the organic semi-conductors LUMO level and conduction band minimum inorganic semi-conductors (Bredas *et al*., 2014). Fundamentally the HOMO-LUMO gap energy is measured in terms of the energy variation between the two states. Also the exact calculation of LUMO lobe is helpful to envisage when an additional pi ligands occur in organometallic (Cheng *et al*., 2013).

DFT at B3LYP level and RHF level by employing 6-311++G∗∗ basis set have already been used to compute electrical properties as well as optical properties of pyrimethamine and sulfadoxine molecules in different states(Nouemo *et al*., 2015). The shrinkage effect of band gap depends upon carrier concentration of both light as well as heavy holes. Normally the carrier concentration through approximations is used to calculate analytical gain function (Osiński *et al*., 1982). An accurate calculation of HOMO-LUMO band gap energy not only predicts the colour produce by transition metals in solution but also predicts their stability and strength (Hasan *et al.*, 2017). The LUMO eigenvectors of the acceptors have ultimate effect on band gap calculation. Also, modification of the band gap by suitable substitution, plus the exact tuning and mesoscopic ordering are needed to be debated (Van Mullekom *et al*., 2001). The most reduced singlet → singlet turn permitted energized states are considered for the TD-DFT computations so as to study the properties of electronic change. HOMO– LUMO investigation is done so as to decide the manner in which the particle associates with different species (Choudhary *et al*., 2013). Various DFT dependent strategies can be used to investigate the structural and electronic properties of aniline. Optical geometry obtained by hybrid DFT produces better concurrence with the experimental results as compared to that are obtained by (Vaschetto *et el*., 1999). In order to overcome the difficulties and lacking of experimental data a topical rapid production of computational data is generated which grants the opportunity to match and extend the databases on materials properties. For optimization and molecular structure improved sources that assimilate both empirical and computational techniques open innovative prospects that may include uncovering of unsuspected compounds, metastable structures and correlations between several features (Curtarolo *et al*., 2012). Computational and tentative study for the improved structural parameters of molecules for p-nitroaniline, B3LYP/6-311G basis set are used to

probe HOMO–LUMO energy level gap of 2.94 eV which indicates a strong approval for the manufacturing of photovoltaic devices(El-Mansy *et al*., 2013).
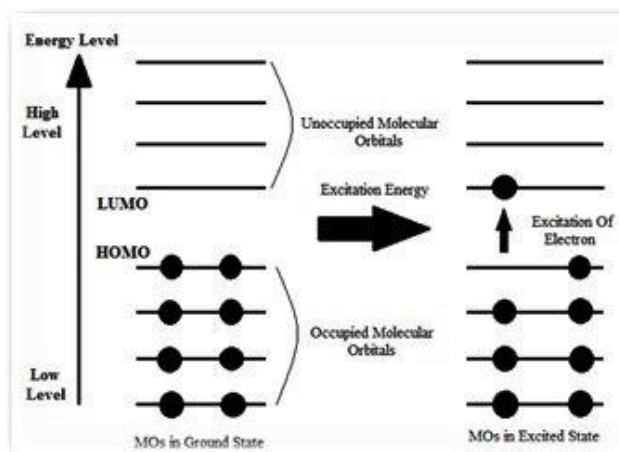

Fig.1. HOMO and LUMO of a particle. Each circle states to an electron in an orbital; when light of a suitably high repetition is utilised by an electron in the HOMO, it hops to the LUMO

Energy gap and electrical properties: The highest energy molecular orbital that may have any electron in it is called HOMO and above it next high energy orbital is called LUMO. Gap energy between HOMO and LUMO tells the nature of the wave-length absorbed by compound. In other words HOMO-LUMO gap can be calculated by measuring the absorbed wave-lengths by any compound in labs (Li *et al*., 2012). Most of the molecular orbitals do not have the same energy as well as not extremely symmetric for most of the molecules. Therefore Molecular orbital (MOs) consisting of a single orbit comprehends an increasing energy. All the electrons present in MOs are in the paired form because all closed shell stable molecules have even number of electrons (Li *et al*., 2012). For a variety of polycyclic aromatic hydrocarbons, the index of kinetic stability can be predicted by HOMO-LUMO gap which is divided by hypothetical polyene. If HOMO-LUMO gap is less than 1:00 it indicates that the HOMO is contributing to the decline in the topological resonance energy. It is simply concluded that if HOMO-LUMO gaps are less than1.30 the molecule will be more receptive. A significant number of the PAH particles with expansive contracted HOMO−LUMO gap are closed-shell substructures of non-metallic one-dimensional benzenoid polymers (Aihara *et al*., 1999).

HOMO-LUMO Interaction: All the molecules have a HOMO and a LUMO. Sometimes HOMO is not only the highest in the molecule but is unusually higher, like the one which has been indicated in red colour on the near right side. Sometimes the LUMO is unusually low, like

the one indicated in red on the far right side (Zhang *et al*., 2010). HOMO and this LUMO have reasonable energy match between them; there can be substantial lowering in energy. If the repulsion from interaction is overcome of other OMOs with one another, a reaction happens. An unusually high HOMO is necessary for a reaction in one reaction partner and an unusually low LUMO in the other. It is to be noted that because of its unusually high HOMO (its LUMO is nothing special) in the case on the right Molecule A is reactive. Molecule B becomes reactive because of its unusually low LUMO (its HOMO is nothing special). We can recognize functional groups by predicting which molecules should have unusually high HOMOs and which should have unusually low LUMOs, and by predicting reactions takes place among different functional with others. We'll be in great shape if we learn to identify unusually high HOMOs and unusually low LUMOs (Pohl *et al*., 2004).
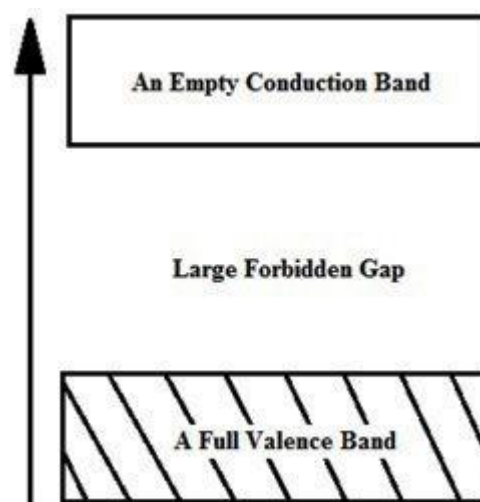

Fig.2. Schematic diagram of large energy band gap for insulators

MATERIALS AND METHODS

Generally, molecules comprising functional groups have certain properties that are similar to known drugs. Therefore, calculating the molecular property was significant parameter for oral drugs, and it was shown to be an important feature in drug discovery and development, also it was shown to be an important feature in material discovery and development. The molecular formula of 4-chloro-N-(4-chlorophenyl)-N-(4-fluorophenyl)-aniline molecule was $C_{18}H_{12}Cl_2FN$. The concern molecule contains a total 34 atoms. The molecule contains 34 atoms, there are three aromatic rings with the attachment of halogen family with each benzene ring, chlorine and fluorine is attached. Each halogen carrier benzene ring is attached with central nitrogen atom. Each aromatic ring contains four hydrogen

atoms in this way there are total twelve hydrogen atoms. Nine double bonds, no triple bond are present there are three rotatable bonds, as shown in fig 3. The molecular weight is 332.1 g/mol.
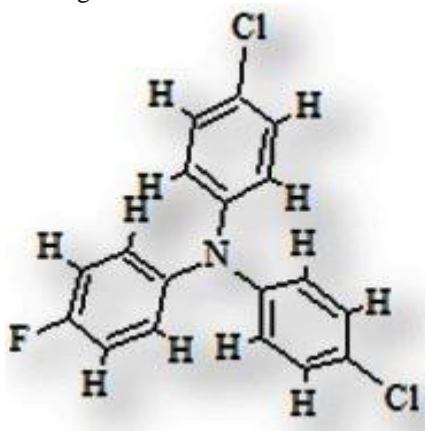

Fig.3. Arrangement of atoms of 4-chloro-N-(4-chloroph-N-(4-fluorophenyl)-aniline

Avogadro 1.2 was used to draw 3D molecular structure of title ANILINE. Universal force field is applied to optimize the geometry (Hanwell *et al.*, 2012). The IR spectroscopic analysis and opto-electrical properties were calculated by using GAMESS (Dykstra *et al.*, 2011; Gordon and Schmidt, 2005). Calculation was in basic set B3LYP (Becke3-Lee-Yang-Parr) and to utilize basis 6-31G*. Mestrelab research applications program was used for predicting NMR Carbon and Hydrogen (Cobas *et al.*, 2015). Gabedit 2.50 was used to interpret the results (Allouche *et al.*, 2011).

RESULTS AND DISCUSSIONS

The calculated energy gap between LUMO and HOMO is ΔE_1 (first energy gap) = HOMO-LUMO = -120.689eV which is much higher therefore it is poorly electrical conductor and more like an insulator. Similarly ΔE_2 (second energy gap) = HOMO-1 - LUMO+1= -168.149eV. In order to improve the performance of aniline secondary acceptors, analysts should reinforce assimilation in the distinctive range, upshift the LUMO energy level, and increase the electron movability. In order to measure the properties of a solar cell made by conjugated polymers by using fullerene derivatives a graph in direct relations plotted between oxidation potential and V_{oc} is calculated. A similar graph for the energy-conversion efficiency solar cell based on these relations can be plotted to calculate the band gap energy. (Scharber *et al.*, 2006).

All calculated values indicate that molecule is a poor conductor of electric current. Band gap is non-neglected parameter for optical material. In order to improve the performance of ANILINE secondary

acceptors; analysts should reinforce assimilation in the distinctive range, upshift the LUMO energy level, and increase the electron movability Hard organic molecules have a significant HOMO-LUMO energy gap.

The excitation energy is related to the mixing coefficient indirectly. Consequently hard molecules have less polarizablility. Hard acids and bases are endorsed by low polarizability, which is the most specific property of low polarizabilty. The value of χ determines whether a given molecule is a Lewis base or an acid. The mobility of electrons always directed from low χ to high χ (Pearson *et al.*, 1986).

Hard molecules are less reactive if electrons mobility or reshuffle is essential for the reaction. Hard organic molecules oppose changes in their charge number or sharing. Hardness of organic molecules varies from atom to atom whereas chemical potential (μ= -χ), remains the same everywhere within the molecule. Therefore in the application of chemical hardness, molecular orbital theory is beneficial. The reactions with Lewis acid or electrophile are evaluated by using HOMO whereas the reactions with Lewis base or nucleophile are evaluated by LUMO (Pearson *et al.*, 1986).

Table1. ($C_{18}H_{12}NFCl_2$) Aniline energy calculation.

S.No	Orbital	Energy (eV)
1	LUMO+4	-6.294
2	LUMO+3	-6.664
3	LUMO+2	-14.068
4	LUMO+1	-18.733
5	LUMO	-21.472
6	HOMO	-142.161
7	HOMO-1	-186.882
8	HOMO-2	-188.141
9	HOMO-3	-196.064
10	HOMO-4	-196.360

Table.2. Analine($C_{18}H_{12}NFCl_2$) electrical parameters calculations.

Calculated Reactivity Indicators	Symbolic Representation	Energy (eV)
Energy of HOMO	E_{HOMO}	-142.161
Energy of HOMO-1	E_{HOMO-1}	-186.882
Energy of LUMO	E_{LUMO}	-21.472
Energy of LUMO+1	E_{LUMO+1}	-18.733
I (ionization energy)	$-E_{HOMO}$	142.161
E_a (electron affinity)	$-E_{LUMO}$	21.472
η hardness	(I-A)/2	60.3445
μ (Chemical potential)	-(I+A)/2	-81.8165
S (softness)	1/η	0.01657
Ω (electrophilicity index)	$\mu^2/2\eta$	55.46
χ_m (Electronegativity)	½(I+E_a)	81.81

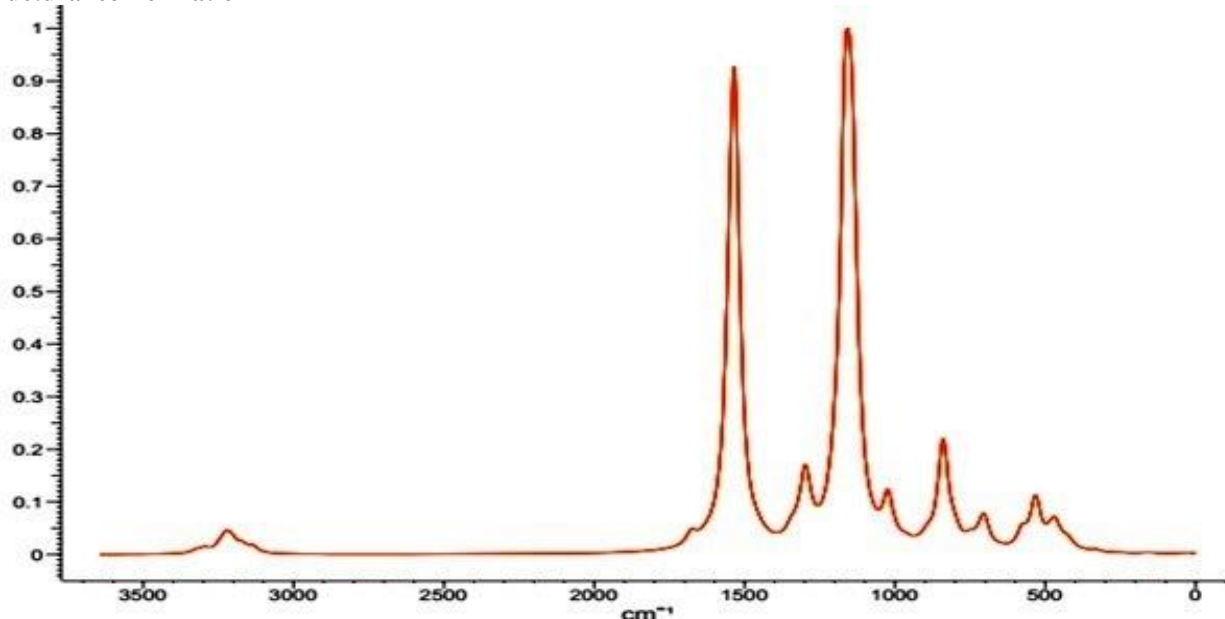**Structural conformation**

Fig.4. IR Spectrogram of 4-chloro-N-(4-chlorophenyl)-N-(4-fluorophenyl)-aniline

IR Theoretical Valuel: The spectrogram for IR value of title aniline lies in 0-3500 cm^{-1}. It is clearly interpreted from fig. 1. The following attachments are bonded with aromatic ring.

• Aromatic Amines: 1286 cm^{-1} C-N medium stretching.

• Halogen group: The molecule contains two halogen members: Chlorine and Fluorine. Chlorine, which shows vibration at 700cm^{-1}. On the other hand, paramount fluorine peak at 1151cm^{-1}.

• Aromatic ring: Each aromatic ring contains di-substitute attachments i.e. nitrogen and chorine/ fluorine as narrated in fig 1. The presence of ring is confirmed at 1650 -1400cm^{-1}. At 1296cm/1 CH weak in plane H-bend. C-H stretching weak vibration 3200 cm^{-1}.

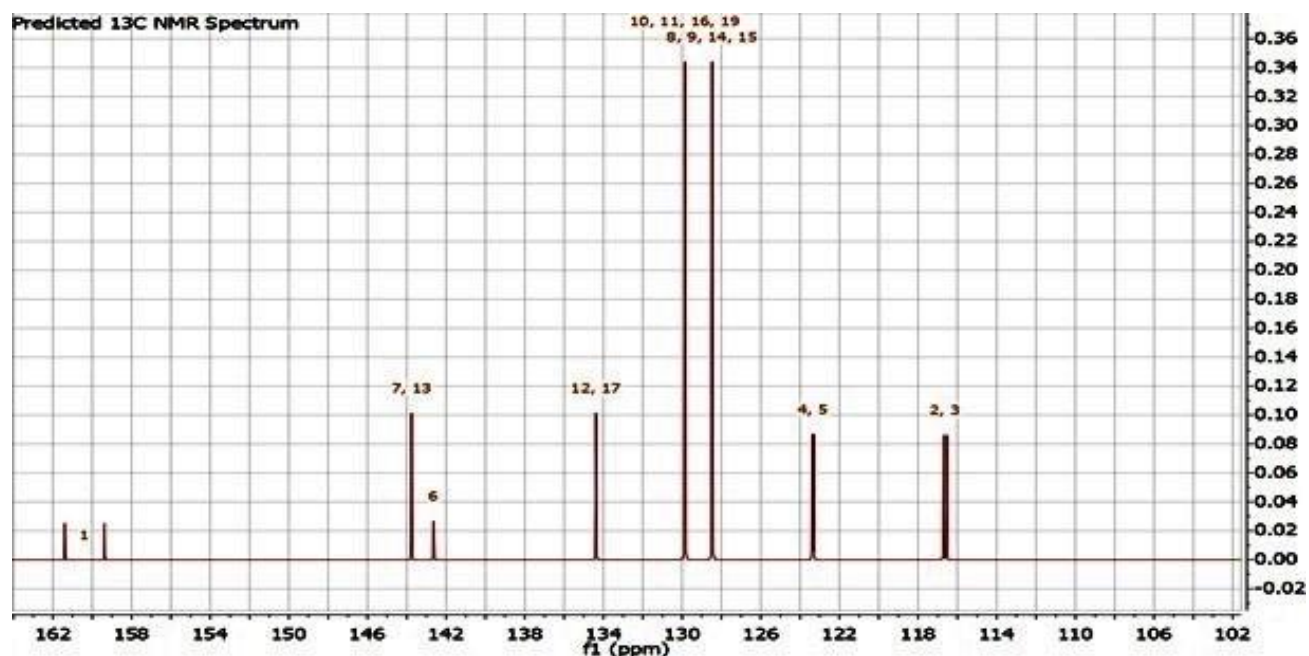**NMR C^{13} Predication:** On x-axis is in parts per million.

Fig.5. NMR C-13 predication of 4-chloro-N-(4-chlorophenyl)-N-(4-fluorophenyl)-aniline.

Table.3 Detail information of Carbon NMR.

Carbon atom	Peaks in ppm	Carbon atom	Peak in ppm	Carbon atom	Peak in ppm
1	1aaw60	7	143	13	143
2	116	8	128	14	128
3	116	9	128	15	128
4	123	10	129	16	129
5	123	11	129	17	134
6	142	12	134	18	129

The C-13 NMR is used to predict the carbon atoms in the molecule. The current molecule contains only 18 carbon atoms, each benzene ring contain six carbon atoms, carbon atoms no 8,9,14,15 NMR shift visible at 128ppm, carbon atoms no 10,11,16,19 NMR shift at 129 ppm. Carbon atom 4 and 5 show NMR shift at 120, carbon atom 12 and 17 show NMR shift at 134 ppm, carbon atom no 7,13 show NMR shift at 143. Alone peak of carbon 6 at 147 and carbon atom no 1 peak at 160 ppm as show in fig. 4 which is profound in tabular form. Carbon NMR predation in n-chloroform.
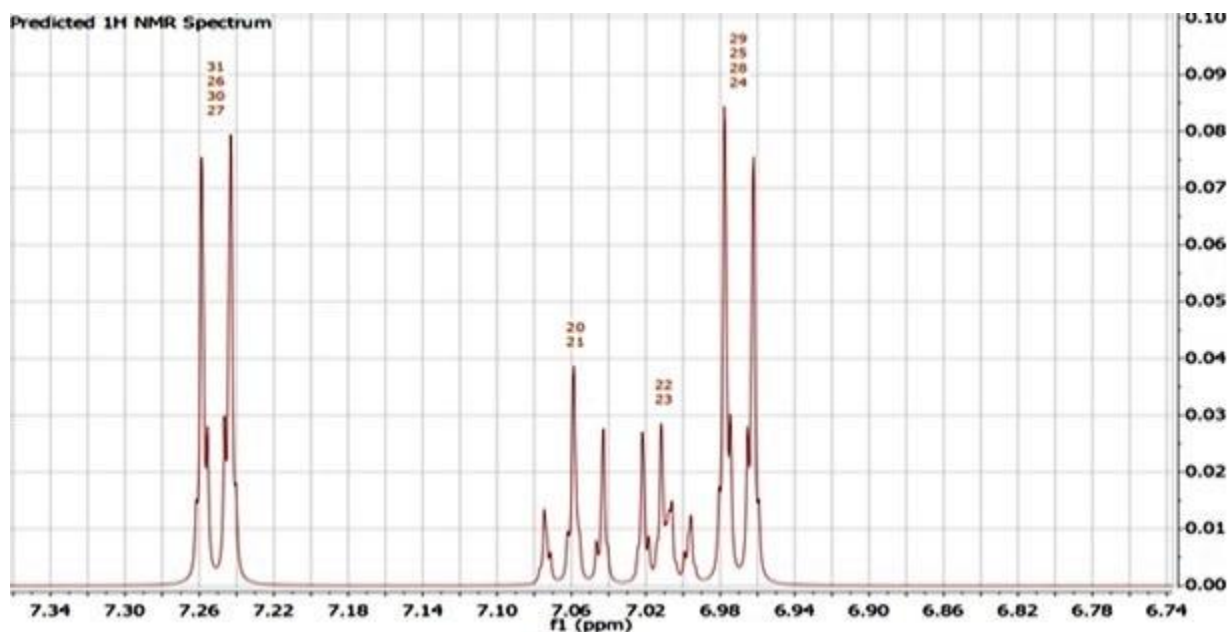
NMR H[1] Predication: On x-axis is in parts per million.

Fig.6. NMR H[1] Spectrogram4-chloro-N-(4-chlorophenyl)-N-(4-fluorophenyl)-aniline.

The analysis of H[1] NMR is more important than C[13] NMR in the current study to predict the structure. H-NMR shift for concern molecule lie 6.94-7.27 ppm. Hydrogen atoms no 22 and 23 show shift at 7.01 ppm, hydrogen atom no 20 and 21 show shift at 7.06 ppm. Hydrogen atoms no 21,26,30,27 shows shift at 7.25ppm. Rest of hydrogen atoms i.e 29,25,28 and 24 show NMR shift at 6.97 ppm. As shown in fig 6.

Conclusion: The field of computational spectroscopy is still in its infancy to highlight intrinsic properties of organic compound still need to be report. The success of this computational analysis opens a pathway to apply a correct algorithm, force field for the assignments of aniline family. Further it is strongly needed to calculate the polarization density, the magnitude of the displacement vector, the dielectric constant, the electric susceptibility for complete description of electrical and optical properties of title molecule.

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