Computational studies of Distinct Anilines for Electrooptical properties

Marla Prasanti¹, Anjali Jha² and Ch Ravi Shankar Kumar*¹

¹Dept. of Physics, Institute of Science, GITAM University, Visakhapatnam, India
²Dept. of Chemistry, Institute of Science, GITAM University, Visakhapatnam, India

E-mail:-rskchaval@gmail.com

Abstract. Significant studies of anilines reported biological activities like oxidation, polymerization, arylation, alklylation, protonation, conformation for photophysical and electrochemical properties using experimental and computational studies like CNDO, MINDO,PCILO that arise due to charge transfer interaction. These interactions still provide enough scope with analysis using electron density method to determine physical, chemical and electrooptical properties. The present work attributes family of anilines-aniline(AN), p-chloroaniline(CAN) and p-nitroaniline(NAN) with experimental studies like FTIR and FT Raman and Computational studies with GaussView4.1 package using B3LYP–basis set 6-311++(d,p) for electrooptical properties. Interpretation of experimental spectra of FTIR and FT Raman confirm the wave numbers are in specified range corresponding to functional group and fingerprint regions. It is observed that intensity of the wave numbers in Raman spectra are reduced in comparison with infrared spectra. Molecular structures are visualized with molecular editor Avogadro for molecular properties. Computational studies are performed for optimized structures wherein the computed infrared spectra and Raman spectra are in agreement with experimental spectra. Studies of charge transfer interactions determine properties like dipole moment, $\mu$Homo, $\mu$Lumo, energy gap, electrophilicity index, polarization and first order hyperpolarizability. A feature of work is NAN possess greater tendency in charge transfer interaction with reduced energy gap, high polarizability and first order Hyperpolarizability that enable to form complex for optical materials and devices.

1. Introduction

Many organic compounds possess significant features in both qualitative and quantitative aspects and in particular special classes of compounds are anilines that exist in powder and liquid form. These anilines gained functional importance during synthesis with various classes of materials as guests for various biological, physical and chemical properties. Anilines are weak donors with increase in concentration has disastrous effects in biological phenomena influencing remarkable effects on anti bacterial, anti fungal and anti inflammatory activities [1]. Remarkable properties were attributed with molecular mechanism due to charge transfer interaction for physical properties like nonlinear optical phenomena[2], local polarizability[3] and thermal properties[4].Chemical properties like radical addition[5], reaction times[6], bond properties[7] and electrochemical process for crystalline nature[8].Great many properties were influenced with experimental studies and computational studies either with anilines[9-10], substituted
anilines[11-12], derivatives of anilines[13-15], dopants[16-17], covalent linked anilines[18-19] and geometry structure[20]. However yet significant contribution of anilines continued still for its influence gained importance due to charge transfer interaction responsible for electrooptical properties in particular with oxides[21], acceptors[22] and liquid crystalline materials[23-24] for polarizability and first order Hyperpolarizability. These interactions arise with position of anilines linked with respective atoms for changes in molecular properties, transit of electrons between respective states, reaction mechanism for formation of complex. In the present study among family of anilines, three distinct anilines- Aniline(AN), \( p\)-chloroaniline(CAN) and \( p\)-nitroaniline(NAN) were attributed with functional mechanism with respect to molecular structures in figure 1 responsible for electrooptical phenomena using electron density method (B3LYP) 6-311++(d,p) of Gaussian package.

![AN, CAN, NAN](image)

**Figure 1:** Molecular structures of AN, CAN and NAN

2. Materials and Methodology
Solid and liquid samples of distinct anilines AN, CAN, NAN were of 99% purity obtained from Sigma Aldrich and used as such without any purification. Bonding mechanism for these anilines were attributed from the recorded FTIR spectra using Thermo Nicolet 6700 instrument with KBr pellet technique in the region of 4000 cm\(^{-1}\) to 400 cm\(^{-1}\). Confirmations of respective characteristic bands are performed along with intensities in Raman spectra using BRUKER RFS 27 in the range of 50-4000 cm\(^{-1}\).

2.1 Computational Studies
Optimizations of respective molecular structures were visualized with molecular editor Avogadro. Electron density method(B3LYP) is implemented for study of charge transfer mechanism with hybrid function in ground state using basis set 6-311++(d,p) of Gaussian package.

3. Results and Discussions
3.1 Interpretation of IR and Raman Spectra
All the distinct anilines responsible for electrooptical phenomena were characterized with experimental studies like Infrared spectra and Raman spectra. Interpretation of Infrared spectra reveals that all the recorded wave numbers were in the assigned regions of respective functional and fingerprint regions. Recorded typical spectra of NAN is illustrated in figure 2 with respective characteristic bands are listed in table 1.
Table 1: Wave numbers of Distinct Anilines

| Name of the Compound | Characteristic groups |
|----------------------|-----------------------|
|                      | Stretching            | In Planebend         | Out Planebend         |
|                      | C-C | CN | NH | C-Cl | NO$_2$ | NO$_2$ | CC | CH | CN | NH | NO$_2$ | CH | NH | NO$_2$ |
| AN                   | 1496 | 1180 | - | - | - | - | 563 | 1273 | 484 | 1605 | - | 739 | - |
| CAN                  | 1493 | 1176 | 3377 | 633 | - | - | 501 | 1283 | 501 | 1614 | - | 825 | 825 | - |
| NAN                  | 1474 | 1108 | 3359 | - | 1300 | 1592 | 400 | 1300 | 494 | 1632 | 700 | 841 | 841 | 747 |

Interpretation of IR spectrum [25-26] reveals that all the characteristic regions are in the specified appreciable limits. Observations of CAN, with wave number 633 correspond to C-Cl stretch analogous to asymmetric (ASM), symmetric(SM), in-plane bend (IPB) and out plane bend (OPB) of NO$_2$ with assigned wavenumbers 1592, 1300,700 and 747cm$^{-1}$.CAN and NAN are anilines with para positions of chlorine and NO$_2$ influencing molecular properties responsible change in intensities and wavenumbers. Studies of intensities from infrared spectra with respect to anilines infer, characteristic bands like C-C, N-H exhibit even odd behavior in stretching and in plane bending, enhancement in C-N corresponding to stretch and inplane bend. Further with increase in intensities in N-H out plane bend and reduction in C-H of NAN with respect to anilines. Raman spectra contribute to change in wave numbers with intensities as illustrated in figure3. These studies reveal that the wave numbers are approximate with wavenumbers of infrared spectra with reduction in intensities responsible for these distinct anilines to participate as guests in formation of complex.
Experimental evidence of wavenumbers responsible as guests in formation of complex of distinct anilines corresponding to infrared and Raman spectra are illustrated in figure 4. All the assigned characteristic bands in infrared spectra are present in Raman spectra are visualized with bar diagram with respective colors associated with assigned functional and fingerprint regions as represented using Origin 8.0 in figure 4.
3.2 Computational Studies
All the molecular structures are visualized with optimization using molecular editor Avogadro illustrated in figure 5. Optimized structures are in ball and stick model with representative atoms stained as Carbon (grey), Hydrogen (white), Oxygen (red), Nitrogen (blue) and Chlorine (green).

![Figure 5: Optimized structures of AN, CAN, NAN](image)

Studies with molecular editor specify molecular properties in terms of number of atoms, number of bonds, degrees of freedom and molecular weight listed in table 2. Significant changes in molecular properties were observed in NAN in comparison to AN and CAN.

| Name of the compound | Number of atoms | Number of bonds | Degrees of freedom | Molecular weight (gm/mol.) |
|----------------------|-----------------|-----------------|--------------------|--------------------------|
| AN                   | 14              | 14              | 36                 | 93.126                   |
| CAN                  | 14              | 14              | 36                 | 127.572                  |
| NAN                  | 16              | 16              | 42                 | 138.124                  |

Charge transfer interactions for studied using electron density method B3LYP [27] corresponding basis set 6-311++ (d,p) with Gaussian16. Studies with this method for respective molecular structures reveal infrared and Raman spectra confirming the evidence of experimental spectra. Studies with molecular orbitals are represented with FMO (Froter Molecular Orbitals) viz Highest Occupied Molecular Orbital (HOMO) in terms of ionization potential and electron affinities as Lowest Unoccupied Molecular Orbital (LUMO) [28-30]. HOMO is electron donor in green regions and electron acceptors correspond to LUMO in red regions as illustrated in figure 6 for the compounds with respective energies in eV. These contours are crowded with overlapped regions signifying greater tendency in electron transfer can be considered as guest in formation of complex responsible for charge transfer interactions with distinct anilines.
Studies of Electron density method focus on electronic properties table 3 responsible for provide charge transfer mechanism[31] in terms of dipole moment in debye(\(\rho\)), ionization potential\((\text{HOMO})\), electron affinity\((\text{LUMO})\), electronegativity\((\chi\))\text{[32]} in term of eV, chemical potential\((\mu\)) (related as \((\chi = -\mu)\)) and electrophilicity index\((\omega\))[32] in electron volts\(\text{(eV)}\). Electrooptical properties like polarization \((10^{-24}\text{esu})\) and first order Hyperpolarizability \((10^{-33}\text{esu})\) [33-34] for these optimized structures. Energy gap infer due to transition between energy levels, further with reduced gap results in reactive electrophilic sites of unstable molecules. The reactive nature of NAN influences dipole moment and related electronic properties like electronegativity, electrophilicity index and chemical potential. These enhanced electronic properties reveal changes in phase transition responsible for anisotropic nature of the molecule in terms of polarization and first order Hyperpolarizability. Interpretation of these studies infers reduced energy gap, and an enhancement in all electronic properties indicating the highly reactive nature of NAN among the distinct anilines. Anisotropy of polarization and first order Hyperpolarizability attribute the ordered behavior of molecules to orient along specified direction either with increase in temperature or with change in density of atoms responsible for charge transfer interaction.

| Name of the compound | \(E_{\text{HOMO}}\) | \(E_{\text{LUMO}}\) | \(\Delta E\) | \(\chi\) | \(\omega\) | \(\rho\) | \(\Delta\alpha\) | \(\beta\) |
|----------------------|----------------|----------------|--------|-------|-------|-------|----------|-------|
| AN                   | -5.574         | -0.351         | 5.222  | 2.963 | 1.681 | 1.836 | 27.327   | 286.016|
| CAN                  | -5.908         | -0.748         | 5.160  | 3.328 | 2.147 | 3.519 | 35.355   | 390.079|
| NAN                  | -6.544         | -2.420         | 4.123  | 4.482 | 4.873 | 7.834 | 42.452   | 978.780|

Electrostatic potential contours specify gradient of colors with red (electronegative) and yellow (electropositive) regions illustrated in Figure 7. Observation of these contours in phenyl ring specifies uniform distribution of electropositive behavior in AN and CAN corresponding to varied distribution in NAN. In the regions outside the phenyl ring influenced electropositive behavior in amino groups of distinct anilines and electronegative regions at nitro group of NAN. Outside of the phenyl ring the localized electronegative regions of AN and CAN corresponds to acceptors and distributed regions of NAN signifies greater participation as guests responsible for charge transfer interaction. A significant feature of these contours with distinct anilines is tendency NAN influenced due to nitro group than associated amino groups of AN and CAN as guests[35-36].
4. Conclusions
Distinct anilines were studied for wavenumber assignments and intensities of respective characteristic regions with spectroscopic methods FTIR and FT Raman spectra. Experimental studies from infrared spectra signified changes in wave numbers in assigned regions. There is a reduction of intensity in Raman spectra in comparison with infrared spectra signifying that these anilines ensure as guest in the formation of complex. Structures of distinct anilines were optimized with molecular editor Avogadro for visualization. FMO studies were performed with Gaussian16 basis set 6-311G+(d,p) for visualization of contours and determination of electrooptical properties. Studies of optimized molecular structure and properties responsible for electroptical activity were attributed with bandgap, dipole moment, electro negativity, electrophillicity index, polarization and first order Hyperpolarizability. A feature of the study among distinct anilines is greater participation of NAN can be considered as guest for formation of complex responsible for electrooptical activity.

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Figure 7: ESP Contours of AN, CAN and NAN
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