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Quantum chemical studies of cinnamic acid with anilines for electroptical activity

S. Deepthi[a], A. Jha[b], Ch. RaviShankar Kumar[a,*]

[a] Dept of Electronics and Physics Institute of Science, GITAM University, 530045, India
[b] Faculty, Dept of Chemistry Institute of Science, GITAM University, 530045, India

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ABSTRACT

The present day scientific scenario enhances the utilization of computational techniques to lighten the spectroscopic properties of molecules with intermolecular bonding. Experimental studies with FTIR and FT Raman were performed for inter molecular bonding with respective vibration modes in assigned regions. Computational B3LYP functional and MP2 method were employed for optimized structures visualized with molecular editor for cinnamic acid and its complexes (with family of anilines) for spectroscopic properties. A comparative study of the theoretical and experimental results was performed for fundamental modes. Spectroscopic studies related to their electronic structure and optical properties were attributed with excitation energy, absorption wavelength, dipole moment, frontier molecular orbitals, electrophilicity index for polarizability and first order hyperpolarizability. An analysis of molecular electrostatic potential and HOMO–LUMO contours reveal the electron distribution of cinnamic acid with family of anilines has influenced in enhanced electrooptical activity.

1. Introduction

Nonlinear electrooptics are the present day solutions for many body electronic properties of molecules due to the raised interest in the field of photonics [1–3]. There are many fields such as condensed matter physics, chemistry and medicine that find applications in nonlinear electrooptics and many other technical fields like computing, optical signal processing, acoustooptical devices. Many studies were performed for optical properties with their dependence structure, susceptibilities and synthesis [4–6]. Importance of nonlinear electrooptical properties (polarizability and first order hyperpolarizability) gained importance with quantum chemical methods though experimental cost of verifying these properties has become expensive. Computational calculation of the cinnamic acid and its complexes is performed with wave particle methods and electron density methods. Ab-intio methods and DFT methods are the two types of methods used to determine the electro-optical properties of cinnamic acid (CA) and its conjugates cinnamic acid with aniline (CAAN), nitro aniline (CANA), and chloroaniline (CACA). The theoretical prediction of these properties of molecules is extremely important to improve the electrooptical properties [6–8]. Cinnamic acid and its complexes with anilines pave way to determine several properties like energy difference, wavelength, dipole moment, quadruple moment, moment of inertia in addition with the enhanced electrooptical properties [9–12]. The intermolecular bonding nature of complexes is obtained through FTIR and FT RAMAN spectroscopy [13,14]. The molecular structures of CA and its complexes CACN, CANA and CACA were visualized with Avogadro molecular editor are illustrated in Fig. 1.

2. Materials and methods

Cinnamic acid and aniline derivatives were purchased from Sigma Aldrich and are used without further purification. The *p*-nitro aniline/*p*-chloro aniline/aniline (1 mmol) and concentrated HCl (4 mL) was stirred in ice bath maintaining the temperature below 0 to −5 °C. Cold solution of freshly prepared sodium nitrite (0.7 gms in 10 mL water) was then added drop wise with stirring at low temperature. The rate of addition was adjusted so that the temperature of the solutions remains below 5 °C. The solution was kept in an ice bath with stirring and used immediately in the next step. Cinnamic acid (1 mmol) was dissolved in 2 mL ethanol and cooled to 0–5 °C in an ice bath. This solution was then gradually added to the cooled diazonium salt solution, and the resulting mixture was stirred at 0–5 °C for 2–4 hrs and kept overnight in refrigerator. The resulting product was filtered, washed several times with cold water and dried. FTIR studies were carried with Thermo Nicolet 6700. FT Raman studies for all compounds were performed using BRUKER: RFS27. Basis set 6-31G(d) is chosen for MP2 and B3LYP functional method in determining spectroscopic properties with

* Corresponding author.
E-mail address: rskchaval@gmail.com (C.R. Kumar).

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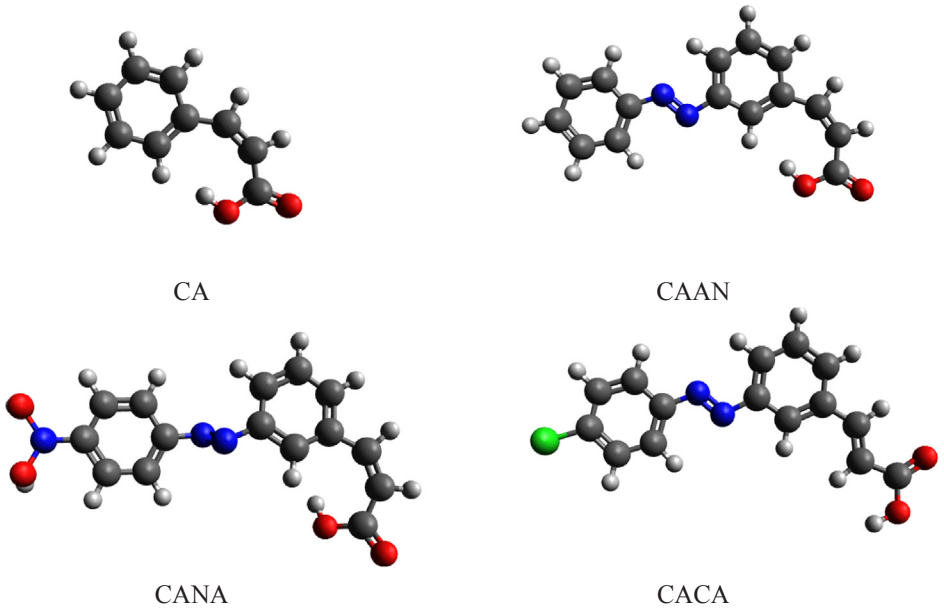

Fig. 1. Molecular structures of Cinnamic acid (CA) and complexes (CAAN, CANA, CACA).

Gaussian 03. There are no imaginary frequency modes in the optimized structure indicating the presence of minimum energy.

3. Results and Discussion

Vibration analysis of the CA and complexes is performed experimentally with two spectroscopic FTIR and FT RAMAN techniques. The spectra is interpreted with shift in the wave numbers and sharp peaks of spectra that confirm intermolecular bonding between three anilines (aniline, *p*-chloro aniline, *p*-nitroaniline) with cinnamic acid. An illustration in Fig. 2 signifies that these two techniques possess shifts in wave numbers approximately equal confirming the bonding nature of the complexes. All the complexes has characteristic feature of C-H, CDC (C double bond C), CO, NHOPB (NH out of plane bend) exhibit hypsochromic shift and C-H IPB (CH in plane bend) exhibit bathochromic shift indicating the aromatic nature with stability and intermolecular bonding.

Vibration studies were performed with B3LYP functional and MP2 method using 6-31G(d) basis set for cinnamic acid and its complexes with aniline, *p*-chloro aniline and *p*-Nitroaniline. Computational studies were performed signifies that there are no intermediate transitions. These studies reveal with shifts in wave numbers of functional and finger print regions confirming intermolecular bonding with stability. Wavenumbers of both B3LYP functional & MP2 methods are approximately equal in both functional and finger print regions as obtained in experimental method were illustrated in Fig. 3.

3.1. Quantum chemical studies- nonlinear electrooptical phenomena

Quantum chemical studies revels the nonlinear static optical properties (polarizability and first order hyperpolarizability) of the system of molecules have greatly influenced with their electronic structure [15,16] with accuracy for electrooptical activity. Spectroscopic analysis with experimental and theoretical methods confirms bonding nature, a prerequisite for electrooptical properties as listed in Table 1. Optimized structures of CA, CAAN, CANA, and CACA visualize bonding nature in all the complexes in ball and stick model using molecular editor Avogadro were illustrated in Fig. 4 and frontier molecular contours (FMO) in Fig. 5 with Gaussian 03 (B3LYP method). These contours responsible for HOMO and LUMO energies were computed with quantum chemical calculations [17–20] that results due to interaction of two atomic or molecular outermost orbital's of electrons. Colored contours in red are

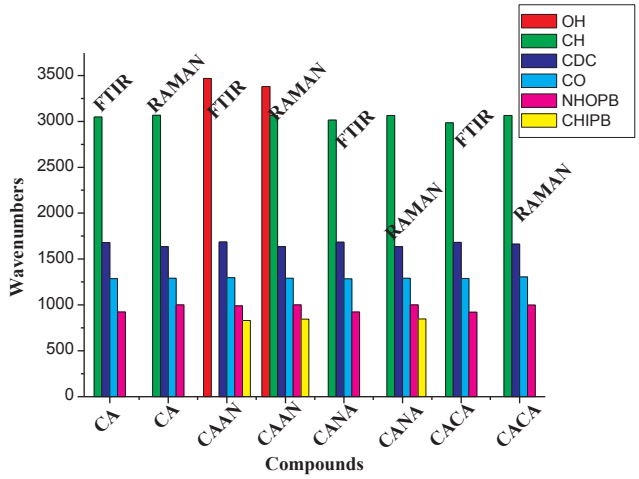

Fig. 2. Bonding studies with FTIR and FT Raman.

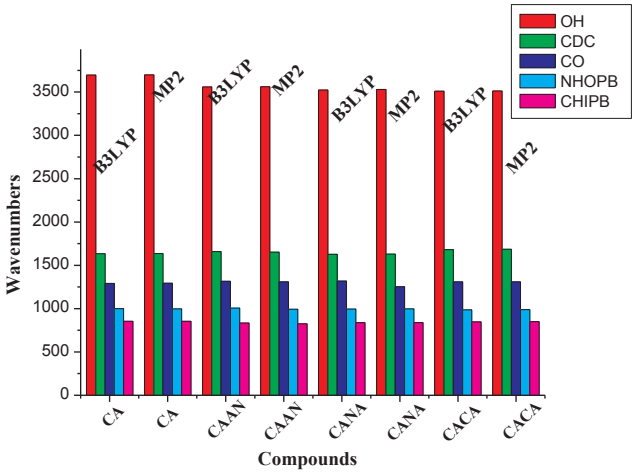

Fig. 3. Vibration studies with Quantum chemical methods.