Structural and Vibrational Analysis of DL-Norleucine Tartarate (DLNT) by DFT Methods

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Abstract

The Fourier Transform Infrared (FT-IR) of DL-Norleucine Tartarate (DLNT) has been recorded and analyzed. The structure of the compound was optimized by Density Functional Theory (DFT) B3LYP method with 6-31G* basis set using Gaussian 09 program package. A detailed interpretation of the infrared spectrum of DLNT was reported. The results were compared with the experimental values. The dipole moment and the first order hyperpolarizability values have been computed using DFT quantum mechanical calculations. The HOMO and LUMO energies were also calculated.

KEY WORDS: DL-Norleucine, hyperpolarizability, Density Functional Theory (DFT), FT-IR.

Introduction

Theory has been a vital element in the design of organic molecules for non linear optical applications for more than a decade. For ex., Marder et al.,[1] showed that bond length alternation is a useful structural guide for predicting the relative values of hyperpolarizabilities of a homologous series of molecules. Molecules with large optical non-linearities have become the focal point of current research in view of their potential applications in various photonic technologies, including all-optical switching and data processing.[2-7]

A variety of inorganic, organic and organometallic molecular systems have been studied for NLO activity [8]. Organic molecules that reveal extended pi conjugation, in particular, show improved second order NLO properties. Recent results [9] also recommend that molecular based macroscopic pi-electron systems possess many attractive NLO characteristics.

Prasad and Williams[10] explained that the certain classes of organic materials exhibit extremely larger NLO and electro optic effect. The design of most efficient organic materials for the non-linear effect is based on the molecular units containing highly delocalized pi-electron moieties and extra electron donor (D) & electron acceptor (A) group. The progress of pi-electron cloud from donor to acceptor makes the molecule to be extremely polarized. DL-Norleucine is both glucogenic and ketogenic amino acid. This is one of the amino acids having branched hydro carbon side chains. It is non polar and aliphatic in nature. On the basis of infra red spectroscopic study, the crystal of DL-Norleucine was assumed to belong a rather unusual type in which molecules two type of conformation [11,12].

In this present Communication, the synthesis, single crystal growth of DL-NorleucineTartarate (DLNT) from its aqueous solution by slow evaporation method has been reported. The title molecule is exposed to, DFT analysis, first order hyperpolarizability studies, vibrational studies and HOMO-LUMO analysis.

Materials and Methods

Synthesis

DL-NorleucineTartarate (DLNT) was synthesized by the incorporation of DL-Norleucine (Hi-media) and tartaric acid (Merck GR grade) in1:1stoichiometric ratio.

The calculated amounts of reactants in each of the reactions were thoroughly dissolved in double distilled water and stirred well for about 6h using a magnetic stirrer to ensure homogenous temperature and concentration over the entire volume of the solutions. The solution was filtered using a whatmann filter paper of pore size eleven µm, transformed to crystal growth vessels and crystallizations were allowed to take place by slow evaporation under room temperature .Transparent colourless DLNT were harvested in a period of 45 days by slow evaporation method and are shown in Fig.1.

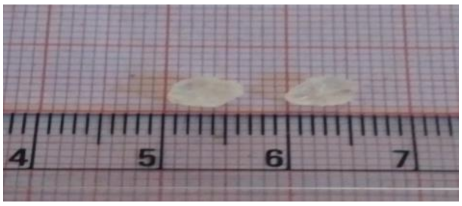

Fig. 1Photograph of DLNT crystals

Characterization

The FT-IR spectra were recorded in the range 400-4000cm^{-1} with a resolution of ± 4cm^{-1}and an accuracy of ± 0.01cm^{-1}on a BRUKER IFS 667 FT-IR SPETROMETER using KBr pellet technique .The various functional groups present in the grown crystals were identified and confirmed by recording the FT-IR spectrum.

Computational methods

The quantum calculations were performed with Gaussian 09 program[13] using Density functional theory with b-31G* basis set. The molecular structure of DLNT molecule was optimized. The most stable, optimized structure of the molecule was predicted by the DFT/B3LYP method with b-31G* basis set, which is shown in figure2. The optimized structural parameters were then used for the vibrational frequency calculations to characterize all stationary points as minima. The results of GAUSS program[14] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy introduced by a least square optimization of the computed to the experimental data.

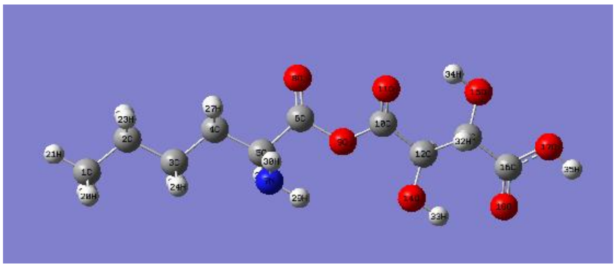

Figure2.Optimized geometry of DLNT

Results and Discussion

Hyperpolarizability Studies

First hyperpolarizability is a third rank tensor that can be described by a 3x3x3 matrix. It can be specified in the lower tetrahedral format. The output from GAUSSIAN 09 provides 10 components of this matrix as β_{xxx}, β_{xxy}, β_{xyy}, β_{yyy}, β_{xxz}, β_{xyz}, β_{yyz}, β_{xzz}, β_{yzz}, β_{zzz}, respectively. Many types of hyperpolarizabilities have been discussed in the literature denoted as β_{vec} (β vector), β_{ll} (β parallel), β_{tot} (β total). The components of β can be calculated using the following equation.

$$\beta_i = \beta_{iii} + 1/3 \sum_{i\neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji})$$

Using the x,y,z components of β, the magnitude of the first hyperpolarizability tensor can be calculated.

$$B_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

The complete equation for calculating the magnitude of β from GAUSSIAN 09 output is given as follows.

$$B_{tot} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$

Since the values of the first hyperpolarizability tensors of the output file of GAUSSIAN 09 are reported in atomic units (a.u.), the calculated values coverted into electrostatic units (1 a.u. = 8.6393x 10^{-33} esu).

The first order hyperpolarizability, total molecular dipole moment and HF values of DLNT are listed in the following tables 1 and 2. The connection between the electric dipole moments of an organic molecules having donor-acceptor substituent and first order hyperpolarizability is widely recognized in the literature.

Table1: Hyperpolarizability of DLNT Molecule

β_{xxx}	-165.1699
β_{yxx}	-44.4743
β_{xyy}	-60.4299
β_{yyy}	-26.3081
β_{zxx}	-11.0797
β_{XYZ}	12.2294
β_{zyy}	-60.4299
β_{zxx}	-11.0797
β_{yzz}	2.8274
β_{zzz}	1.1251
β_{tot}	$0.2576617283\times10^{-30}$esu

Table2: Calculated dipolemoment of DLNT

Dipole Moment	Exact Polarizability	Approximate Polarizability
X= -2.5222	177.125	187.186
Y= -3.2948	0.189	3.368
Z= 0.7199	124.078	207.642
Tot= 4.2113	0.752	0.387
	2.520	8.807
	98.378	155.648
HF Value	-972.6182182	

Vibrational Study

The FT-IR Spectrum of DLNT is shown in figure 3&4. The broad envelope between 3500 and 2500cm^{-1}includes absorption of stretching bands due to NH_3^+ ion of the amino acid . This region results from superimposed O-H and NH_3^+ stretching bands. The band at 2950cm^{-1} corresponds to broad C-H symmetric stretching[15]. The NH_3^+ asymmetric stretching mode is observed at 2666cm^{-1}. Multiple fine structure at the lower energy of the envelope indicates the strong hydrogen bonding interaction of NH_3^+ group with strong absorption of COO^- group at 1514cm^{-1}.The C-N vibrations produce a group of peaks between 1284 cm^{-1} and 958 cm^{-1}.Ring deformation bands are seen at 1411 cm^{-1} and 794 cm^{-1}[16] .The peak corresponding to 1118 cm^{-1},696 cm^{-1} brings C-O stretching, C-C bending .

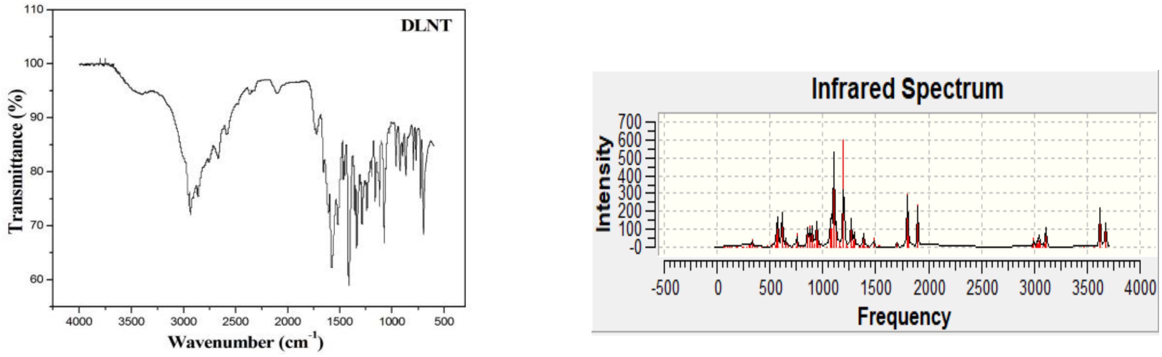

Fig. 3 Fig. 4

Figure 3 & 4 Experimental and Theoretical FT-IR Spectrum of DLNT

Wave number cm^{-1} (experimental)	**Wave number cm^{-1} (computational)**	**Assignments**
2950	3600	C-H stretching
2666	3050	NH_3^+asymmetric stretching
1514	1950	COO^- asymmetric stretching
1411	1400	Ring deformation
1284	1300	C-N vibrations
1118	1150	C-O stretching
958	980	C-N stretching
794	800	N-H deformation
696	700	C-C bending

Table.3 Vibrational assignments

The observed vibrational frequencies and their tentative assignments are listed in Table 3.It is found that theoretically obtain values are higher than experimentally obtained frequencies.This is because isolated DLNT molecule is used in theoretical calculation.

HOMO-LUMO Analysis

The interaction of two atomic (or) molecular orbitals produces two new orbitals. One of the new orbital is higher in energy than the original ones (the anti-bonding orbital) and one is lower (the bonding orbital). When one of the initial orbitals is filled with a pair of electrons (a Lewis base) and the other is empty (a Lewis acid), we can place the two electrons into the lower, energy of the two new orbitals. The "filled-empty" orbital interaction therefore is stabilizing. When we are dealing with interacting molecular orbitals, the two that interact are generally the highest energy occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the compound. These orbitals are a pair of orbitals, which allows them to interact most strongly. These orbitals are sometimes called the frontier orbitals, because they lie at the outermost boundaries of the electrons of compound. The intramolecular charge from the donor to acceptor group through a sing-double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR activity strong. The HOMO-LUMO energy gap of DLNT were calculated at B3LYP/6-31G (d,p) level, which reveals that the energy gap reflects the chemical activity of the molecule. The results of Homo-Lumo analysis for DLNT are

HOMO energy =-0.247a.u

LUMO energy =-0.048a.u

HOMO-LUMO energy gap =0.199a.u

The LUMO as an electron acceptor represents the ability to obtain an electron and HOMO represents ability to donate an electron. The strong charge transfer interaction through π-conjugated bridge results in substantial ground state donor-acceptor mixing and the appearance of a charge transfer band in the electron absorption spectrum.

Conclusion

The molecular geometry of the DLNT molecule in the ground state has been calculated by using DFT(B3LYP) method with 6-31G* basis set. The calculated dipole moment and the first order hyper Polarizability results indicate that molecule has a reasonably good nonlinear optical behaviour. Theoretical spectral frequencies are in good agreement with experimental data of FT-IR. The HOMO-LUMO energy gap helped in analyzing the chemical reactivity of the molecule.

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