

VIBRATIONAL SPECTRAL STUDIES AND NON-LINEAR OPTICAL PROPERTIES OF 3-(METHYL PHENYL) PROPANE DINITRILE : A DENSITY FUNCTIONAL THEORY APPROACH

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Abstract-In this work, 3-(methyl phenyl)propane dinitrile molecule the vibrational spectral analysis was carried out by using Raman and Infrared spectroscopy in the range 400-4000cm⁻¹ and 50-3500cm⁻¹ respectively. The theoretical vibrational frequencies and optimized geometrical parameters have been calculated by using density functional theory using B3LYP function with the 6-311G(d,p) basis set by Gaussian 09 software package. The assignments of the vibrational frequency have been done by potential energy distribution (PED) analysis using VEDA4 Software. Homo-Lumo energy gap value suggests the possibility of charge transfer within the molecule. Stability of the molecule arising from hyper conjugative interactions leading to its non linear optical activity and charge delocalization were analysed using natural bond orbital techniques.

Keywords – FT-IR, FT-Raman, DFT, NBO, NLO

I. INTRODUCTION

Non linear optical (NLO) materials have recently attracted a lot of attention due to their potential use in the fields like laser technology, optical communication, optical data storage and optical signal processing [1–3]. In this respect organic nonlinear optical materials are found to have high nonlinear coefficient equated to those of inorganic materials [4,5]. The present work deals with vibrational spectral investigation of 3-(methyl phenyl)propane dinitrile using potential energy distribution analysis (PED) with the aid of density functional theory (DFT) calculations to study the optimized geometry, bonding features, nature of hydrogen bonding, frontier orbital energy and nonlinear optical property of the compound

II. EXPERIMENTAL

3-(methyl phenyl)propane dinitrile was purchased from Sigma-Aldrich Company with a stated purity of 99% and it was used without further purification. The FT-IR spectrum of the compound was recorded using the Perkin Elmer FT-IR spectrum in the range of 4000-400cm⁻¹. The spectrum was recorded with a scanning speed of 10cm⁻¹ min⁻¹ and the spectral resolution of 4.0cm⁻¹. The FT-Raman spectrum of compound was also recorded on the Bruker FRA 106/S instrument equipped with Nd:YAG laser source operating with 100mW power.

III. COMPUTATIONAL DETAILS

The quantum chemical calculation of 3-(methyl phenyl)propane dinitrile has been performed using Gaussian 09 program package [6] at the B3LYP level with standard 6-311G (d,p) basis set. This has been successfully applied in order to derive the optimized geometry and vibrational wave number of the normal modes.

IV. RESULT AND DISCUSSION

A. Optimized Geometry

The optimized geometry of 3-(methyl phenyl)propane dinitrile was obtained at B3LYP level. The theoretical and experimental values were compared and small deviation in some values were observed. The optimized structure of 3-(methyl phenyl)propane dinitrile is shown in figure.1

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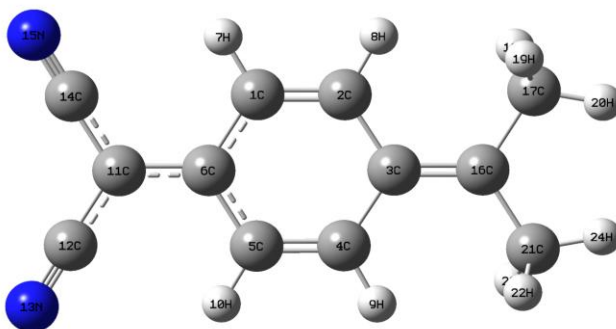


Figure1, shows the optimized structure of 3-(methyl phenyl)propane dinitrile

The calculated C-C (C_1-C_6) bond length is found to be 1.44Å and its experimental value is 1.429Å. The changes are observed due to the substitution of Dicyano methane group. In 3-(methyl phenyl)propane dinitrile the bond length of C_3-C_{16} is reduced very much when compared to experimental values. The reason is the presence of methylene group attached to C_{16} . The C-C-C bond angle of benzene ring is 120° and is said to be aromatic, but in this present work 3-(methyl phenyl)propane dinitrile show slight deviation in the C-C-C ($C_1-C_2-C_3=121.3$, $C_3-C_4-C_5=121.8$) bond angle because of this the aromatic character deviates due the substitution of methane and cyano group.

Table 1 .Optimized bond length and bond angle

Bond Length / (Å)			Bond Angle / (°)		
MPD	Experimental Value	Calculated Value	MPD	Experimental Value	Calculated Value
C_3-C_{16}	1.398	1.377	$C_1-C_2-C_6$	121.1	121.3
C_6-C_{11}	1.392	1.391	$C_1-C_2-C_3$	121.2	121.2
C_1-C_6	1.392	1.391	$C_3-C_4-C_5$	120.9	121.5

B. Vibrational Spectral analysis

The vibrational spectral analysis of 3-(methyl phenyl)propane dinitrile molecule is performed based on the potential energy distribution analysis. The 8a mode of C-C stretching vibration are expected in the range 1570-1628 (6). In compound 1, 8a mode is observed in Raman as a strong band at 1599cm^{-1} . The corresponding calculated value is found to be 1614cm^{-1} . The $C\equiv N$ stretching vibration is expected in the range $2240-2220\text{cm}^{-1}$ [7]. The very strong band absorbed at 2222cm^{-1} (IR) and 2224cm^{-1} (Raman) are assigned to stretching mode. The corresponding calculated value found to be at 2260cm^{-1} .

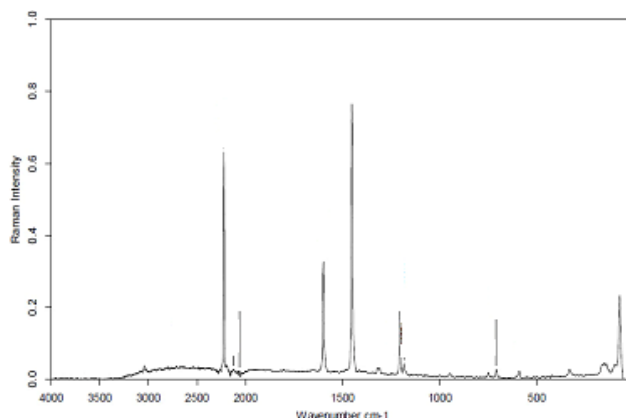


Fig.2 FT-RAMAN spectrum of 3-(methyl phenyl)propane dinitrile

C. NBO Analysis

The natural bond orbitals (NBO) calculations were performed using NBO 3.1 program [8] as implemented in the Gaussian 03 package at the DFT/B3LYP level in order to understand various second order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the intermolecular delocalization or hyperconjugation. It is an essential tool for the investigating charge transfer or conjugative interaction in molecular systems. The second order fock matrix was carried out to evaluate the donor – acceptor interactions in the NBO analysis. The stabilization energy contribution from the $\sigma(c_1-c_2) \rightarrow \sigma^*(c_1-c_6)$ (Table.2) interaction energy 14.6 . The most interaction energy in σ bond molecule $\sigma(C_6-C_{11})$ bond to antibonding $\sigma^*(C_{11}-C_{12})$ leads to stabilization energy of respectively.

Donar NBO(i)	E.D(e)	Acceptor NBO(j)	E.D(e)	E ⁽²⁾ KJ mol ⁻¹
$\sigma(c_1-c_2)$	1.98000 -0.75927	$\sigma^*(c_1-c_6)$	0.02700 0.47357	14.56032
$\sigma(c_6-c_{11})$	1.96077 -0.75722	$\sigma^*(c_{11}-c_{12})$	0.03716 0.49461	23.17936
$\sigma(c_4-c_5)$	1.98000 -0.75925	$\sigma^*(c_3-c_{16})$	0.02999 0.60401	9.87424

Table2.Second order perturbation theory

D. Non – Linear optical effects

The non-linear optical response of an isolated molecule in an electric field can be presented as a Tylor series expansion of the total dipolemoment, induced by the field.

$$\mu_{tot} = \mu_o + \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \dots$$

Where α is the linear polarizability, μ_o is the permanent dipolemoment and β_{ij} are the first hyper polarizability tensor components. The isotropic (or average) linear polarizability is defined as .

$$\beta_i + \beta_{iii} + \frac{1}{3} \sum (\beta_{ijj} + \beta_{jij} + \beta_{jji}), (i \neq j)$$

The first static hyper polarizability (β_0) and its related properties (β and α_0) have been calculated using B3LYP/ 6-311G(d,p) level based an finite field approach. The components of the first order hyperpolarizability from Gaussian '09 outputs are given below.

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

Where

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{yzz} + \beta_{yxx}$$

$$\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}$$

$$\alpha_o = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

The calculations of linear polarizability (α) and first order polarizability (β) from the Gaussian output have been explained in detail [25], and DFT has been extensively used as an effective method to investigate the organic NLO materials [26]. Since the values of the polarizabilities (α) and hyperpolarizability (β) are reported in atomic units (a.u), the calculated values have been converted into electrostatic units (E.S.A) [For α , 1au = 0.1482 x 10⁻²⁴ e.s.u; for β , 1au = 8.639x10⁻²³ E.su] [9].

The static polarizability and dipolemoment are calculated using Gaussian '09 program software is found to be 1.66x10⁻²³ esu and 5.67 Debye respectively . The calculated first order hyper polarizability is 3.5 times greater than that of urea [β of urea = 3.78 x 10⁻³ esu].The SHG efficiency of the title compound is found to be 1.2 times greater than that of Urea.

E. HOMO-LUMO analysis

The energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupiedmolecularorbital(LUMO) are computed at B3LYP/ 6-311G (d,p) level.

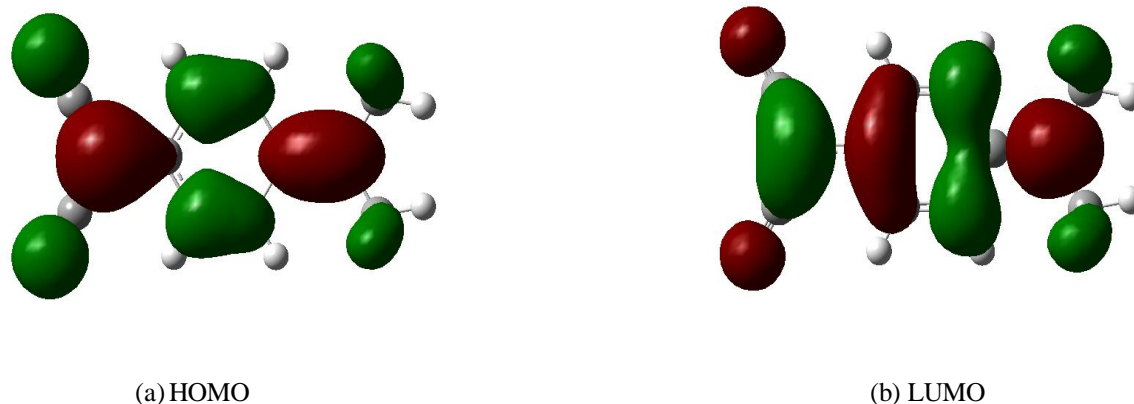


Figure 3.HOMO and LUMO plots of MPD

The HOMO-LUMO energy gap is -0.12312eV . The low value of the HOMO-LUMO energy gap confirms charge transfer within the molecule.

F. Second Harmonic Generation Test

The most widely used technique for conforming the SHG efficiency of NLO materials is Kurtz-Perry powder SHG method. The emission of green radiation from the sample confirms the second harmonic generation property. The obtained SHG efficiency of the title compound is found to be 4.8 times greater than that of urea

IV CONCLUSION

The ground state geometrical parameters of monometric structure were predicted by DFT calculations with a quite high accuracy when compared with a similar system which crystallographic structure was determined by X-ray analysis. The scaled vibrational frequencies Show a great agreement with recorded FT-IR and FT-Raman vibrational spectra. In addition the calculated first hyperpolarizability value of 3-(methyl phenyl)propane dinitrile 3.5 times larger than the magnitude of urea. Therefore the investigated compound can be a candidate of non linear optical materials.

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