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GROWTH, CHARACTERIZATION AND DFT CALCULATIONS ON 2-AMINO-6-METHYLPYRIDINIUM HYDROGEN GLUTARATE

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ABSTRACT
Single crystals of 2-amino-6-methyl pyridinium hydrogen glutarate (2A6MPHG) are grown using the slow evaporation technique. The structural determination was carried out by single crystal X-ray diffraction studies (SXRD) and it is found that 2A6MPHG belongs to the noncentrosymmetric space group $P2_12_12_1$. The functional groups were analyzed by the Fourier transform infrared analysis. The absorption spectrum of the 2A6MPHG crystal was studied by UV-VIS studies. The quantum chemical calculations were carried out for the title compound using density functional theory (DFT) analysis.
Keywords: Slow evaporation, SXRD, noncentrosymmetric, UV-VIS, DFT

INTRODUCTION

Nonlinear optical materials are at the forefront in emerging optoelectronic technologies because of their properties like refractive index, birefringence, transparency of the material, thermal stability along with the chemical stability [1-3]. More attention is drawn on organic nonlinear optical materials due to the possession of optical susceptibilities, the inherent ultrafast response times and for the lasers with high optical thresholds[4-6]. A notable amount of nonlinear optical activity is observed in organic molecules that normally possess π- electron conjugated moiety which is replaced by a donor group of electron on the one end and on the other an electron acceptor group which forms a conjugated structure "push-pull". The fundamental requirement for the NLO responses in materials is a noncentrosymmetric structure. The difficulties observed in inorganic materials in which the prerequisites of noncentrosymmetry and high susceptibilities must be accounted can be resolved in an organic compound by modifying the structure of organic chromophores by the appropriate chemical process in order to increase the molecular hyperpolarizability. Growing large and optical quality organic NLO single crystals becomes a natural difficulty and this is one of the major drawbacks. Due to this limitation, semi-organic materials were opted to owe to their high optical nonlinearity. The semi-organic materials contribute to designing crystals for photonic applications due to their flexibility. For engineering application the carboxylic acid having hydrogen bonding are preferred[7]. Pyridine and its substituted derivatives are often involved in hydrogen-bond interactions[8]. A very few complexes incorporating 2-amino-6-methyl pyridine have been crystallized and studied[9,10]. The title compound 2-amino-6-methyl pyridinium hydrogen glutarate was first synthesized by Sergiu Draguta et al.[11]

Based on our literature survey, there are no reports on the spectral and optical characterization of the 2A6MPHG crystal. In this paper, the growth and characterization of the 2A6MPHG crystal have been

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reported. Furthermore, density functional calculations such as optical geometry, frontier molecular orbitals and hyperpolarizability were carried out for the 2A6MPHG crystal.

EXPERIMENTAL

Material and Methods

The equimolar ratio of 2-amino-6-methylpyridine (Sigma 99%) and glutaric acid (Himedia 99%) are dissolved separately using methanol. Glutaric acid is added to 2-amino-6-methylpyridine and the white color precipitate was formed. Hot methanol was used to dissolve the precipitate and the solution was stirred well for about 5 hours. Whatman filter paper was used to filter the saturated solution. 2A6MPHG crystals (Fig.-1) were harvested after a time frame of 4 weeks.

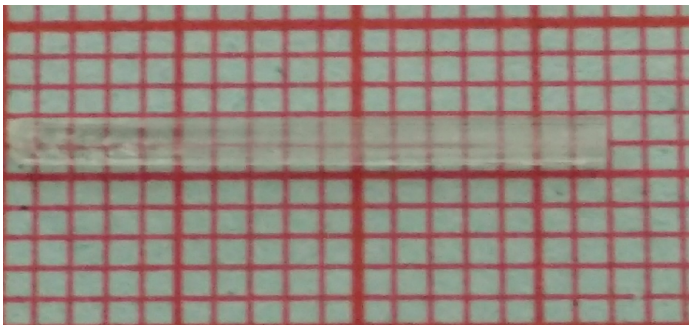

Fig.-1: Photograph of Grown 2A6MPHG Crystal

Characterization

2A6MPHG crystal was analyzed by a Bruker AX diffractometer with MoKα radiation (λ= 0.71073 Å). Perkin Elmer spectrophotometer was used to record FT-IR measurements in the wavelength range of 4000-400 cm^{-1} using a KBr pellet technique. The UV absorption spectrum of the 2A6MPHG crystal was studied in the range 200-800 nm by JASCO V-770 UV-Vis spectrophotometer. The computations were carried out using DFT analysis with B3LYP/6-31G (d,p) basis set[12].

RESULTS AND DISCUSSION

Optimized Geometry of 2A6MPHG

XRD study reveals that the synthesized 2A6MPHG exhibits an orthorhombic crystal structure with the noncentrosymmetric space group $P2_12_12_1$. The cell parameters that are measured by XRD are found to be a = 5.2263 Å, b = 11.07 Å, c = 23.53 Å, α=β=γ= 90º and the unit cell volume is 1165 $Å^3$, which agrees with the earlier work[11]. The crystal structure of 2A6MPHG is formed by 2-amino-6-methyl pyridinium cation and hydrogen glutarate anion connected by hydrogen bonds. The ORTEP (Fig.2a) reveals that the 2-amino-6-methyl pyridine cation and the glutarate anion are linked by N-H…O hydrogen interactions, which exhibit the noncentrosymmetric structure with enhanced NLO properties. The optimized geometry was obtained by DFT analysis and is shown in figure 2b. From the calculated values (Table 1), it is found that the bond length N1-H7 is 1.681 Å which confirms the intermolecular hydrogen bonding interactions. The bond length observed for N2-H8 is 1.011Å and for N2-H9 is 1.008 Å. The increase in bond length is due to the hydrogen bonding interactions. In 2-amino-6-methyl pyridinium cation, the bond angles of C1-C2-C3 is 118.1°, C1-C2-H1 is 120.3°, C2-C3-C4 is 120° and a wide bond angle of 124° is obtained for C5-N1-H7 at the protonated nitrogen atom. The increase in bond angle in hydrogen glutarate C7-O1-H7 (112.2°) is due to N-H…O interactions. This confirms the intermolecular interactions between 2-amino-6-methyl pyridinium and hydrogen glutarate.

FT-IR Studies

The FT-IR spectrum of 2A6MPHG is depicted in Fig.-3. The absorption band appeared at 3307 cm^{-1} is attributed to NH stretching vibrations of pyridinium moiety. Aromatic C-H stretching vibrations are observed at 3024 cm^{-1}. The bands appeared at 2785 cm^{-1} and 2690 cm^{-1} are the characteristic of OH stretching vibrations of hydrogen glutarate anion. NH bending vibrations are observed at 1637 cm^{-1} and the C-C stretching vibrations are observed at 1562 cm^{-1}. The band observed at 1359 cm^{-1}, 1305 cm^{-1} and

1242 cm^{-1} are due to C-N stretching vibrations. The bands at 1043 cm^{-1} and 806 cm^{-1} are attributed to CH in-plane and out of plane bending vibrations. The band at 993 cm^{-1} corresponds to OH bending mode vibration and CH rocking is observed at band 758 cm^{-1}.

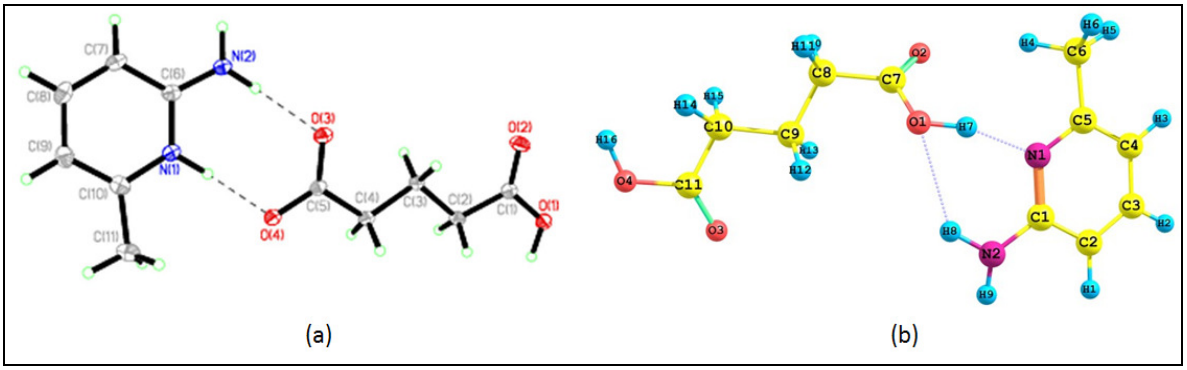

Fig.-2: (a) ORTEP and (b) Optimized Geometry of 2A6MPHG

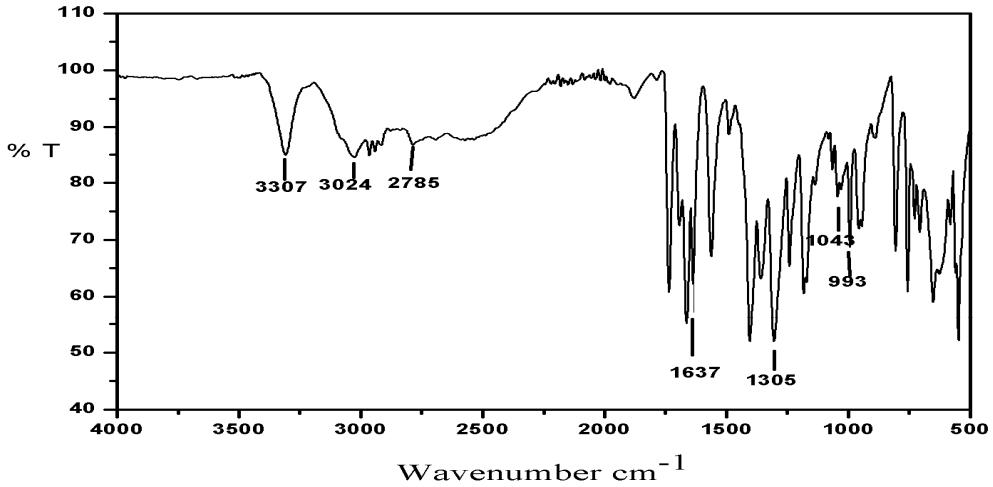

Fig.3. FT-IR spectrum of 2A6MPHG

Table-1: Bond Length and Bond Angle of 2-Amino-6-methyl pyridinium Hydrogen Glutarate

Bond Angle	Computational Data	Bond Angle	Computational Data
C1-C2	1.411	C2-C1-N1	121.7
C1-N1	1.346	C2-C1-N2	121.2
C1-N2	1.376	C1-C2-H1	120.3
C2-H1	1.085	C1-C2-C3	118.1
C2-C3	1.385	N1-C1-N2	117.0
C5-N1	1.352	C1-N1-C5	119.9
C6-H4	1.095	C1-N1-H7	115.5
C6-H5	1.093	C1-N2-H8	117.7
C6-H6	1.097	C1-N2-H9	118.3
H7-O1	1.023	C2-C3-H2	119.8
N2-H8	1.011	C2-C3-C4	120.0
N2-H9	1.008	C3-C4-H3	121.1
C7-C8	1.519	C5-N1-H7	124.0

C7-O1	1.338	H7-O1-C7	112.2
C7-O2	1.220	O1-H7-N1	164.0
C8-H10	1.094	H7-O1-H8	68.8
C8-H11	1.099	H8-N2-H9	116.0
O4-H16	0.968	N2-H8-O1	135.4
N1-H7	1.681	C8-C7-O1	112.7
H8-O1	2.361	C8-C7-O2	123.5

UV-Vis Absorption Studies

The UV absorption spectrum of 2A6MPHG revealed that a strong absorption peak occurred at 356 nm. Figure-4a depicts the UV absorption spectrum of 2A6MPHG. In pyridinium compound, the electron transfer from non-bonding (n) to anti-bonding (π*) orbital i.e., (n→π*) is evident from the absorption edge of the crystal around 356 nm[13].The absence of absorption in the entire visible region from 400 nm to 800 nm of the grown crystal makes the material suitable for the fabrication of optoelectronic devices.[14, 15]

HOMO- LUMO

The HOMO-LUMO energy gap describes the stability of a molecule in which the electron transfer characteristics were analysed[16, 17]. The HOMO-LUMO gap of 2A6MPHG (Figure 4b) was calculated by Gauss view 5.0. The HOMO and LUMO values are -6.253 eV and -1.099 eV, respectively. HOMO and LUMO are concentrated over the entire pyridinium molecule and the band gap was found to be 5.153 eV. The HOMO–LUMO energy gap elucidates the subsequent charge transfer interaction within the molecule.

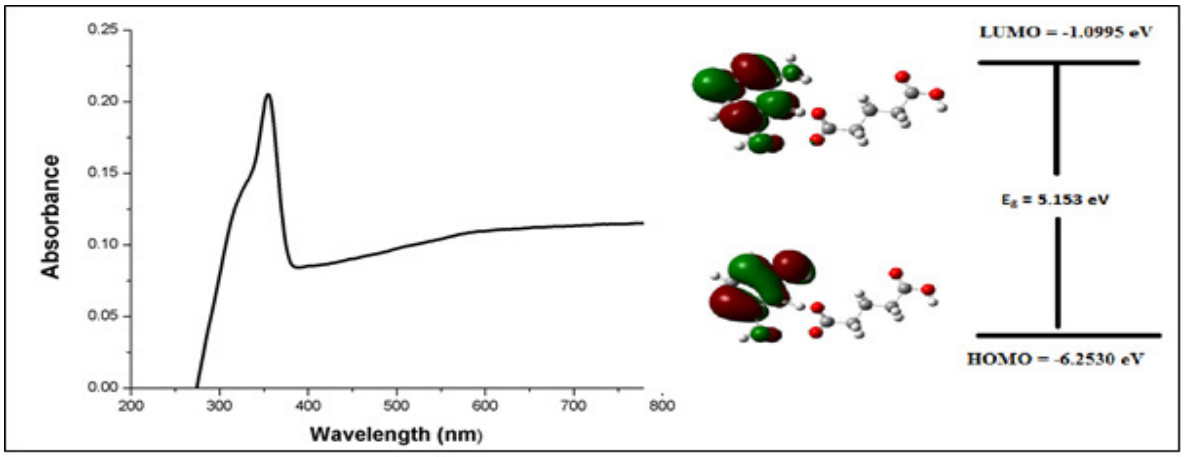

Fig.-4: (a) UV-Vis Spectrum and (b) HOMO LUMO Energy Gap of 2A6MPHG

Hyperpolarizability Calculations of 2A6MPHG

The optical properties of a molecule are analyzed by hyperpolarizability calculations which aids in designing materials for optoelectronic applications[18-21]. The polaraizability and hyperpolarizability of 2A6MPHG were calculated at the level of **B3LYP/6-31 G** (d,p) by the gaussian 09W package.

The polarizability is defined as:

$$\alpha_{tot} = \frac{\alpha_{xx}+\alpha_{yy}+\alpha_{zz}}{3} \quad (1)$$

Where α_{xx}, α_{yy} and α_{zz} are the diagonal components of the polarizability tensor.

First, hyperpolarizability is a third rank tensor that can be described by 3x3x3 matrix. By using the Kleinman symmetry[22], the 27 components are reduced to 10 components. The first hyperpolarizability tensor β is calculated by:

$$\beta tot=\sqrt{(\beta_{xxx}^2+\beta_{xyy}^2+\beta_{xzz}^2)+(\beta_{yyy}^2+\beta_{yzz}^2+\beta_{yxx}^2)+(\beta_{zzz}^2+\beta_{zxx}^2+\beta_{zyy}^2)} \quad (2)$$

The calculated value of the mean polarizability (α) and β_{tot} for the titled compound are 14.47 x 10^{-24} e.s.u and 12.23×10^{-31} e.s.u. Large β value indicates that the 2A6MPHG is an effective nonlinear optical crystal.

CONCLUSION

Semiorganic crystal of 2-amino-6-methyl pyridinium hydrogen glutarate (2A6MPHG) was grown by employing the slow evaporation process. The cell parameters and functional groups of 2A6MPHG crystal were confirmed by SXRD and FT-IR analyses. UV-visible transmission study shows an absorption peak at wavelength 356 nm. DFT computation was carried out to study the molecular structure. The HOMO-LUMO energy gap was found to be 5.153 eV and the first-order hyperpolarizability was determined as 12.23×10^{-31} e.s.u.

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