

Spectral, Optical and Quantum Chemical Analysis of Morpholinium Cinnamate Single Crystal

R. Bhuvaneshwari¹, B. Subash¹, K. Sakthi Murugesan^{1,a)}

¹*Department of Physics, Presidency College, Chennai - 600 005, India*

^{a)}Email id: ksakthimurugesan2492@gmail.com

Abstract. An organic nonlinear optical (NLO) crystal, morpholinium cinnamate (MC) was grown by slow evaporation at room temperature. The crystalline perfection is analyzed through powder XRD analysis. NMR spectral analysis confirms the molecular structure of the compound. UV-vis spectrophotometer study revealed that the grown crystal had good optical transparency in the entire visible region with a wide optical band gap of 3.8 eV. The optimized structure, electronic properties, and frontier energy gap were analyzed by DFT (density functional theory). The lowering in the HOMO and LUMO energy gap explains the ultimate charge transfer interactions that take place within the morpholinium cinnamate molecules.

INTRODUCTION

The expectable construction of assemblies or networks through intermolecular interactions such as co-ordination bonds or hydrogen bonding in the entire crystal lattice of crystalline materials having desired physical chemical properties is the main objective of crystal engineering. It is a multidisciplinary area and it has implications for materials chemistry, supramolecular chemistry, molecular recognition and biology. The unlimited architectural flexibility of the organic molecules permits them to be tailored for designing and obtaining novel processible nonlinear optical (NLO) materials and their structures can be modified to get the desired NLO properties [1]. The organic materials normally possess higher third-order optical nonlinearity and it can be used in vast applications like amplitude modulation, phase modulation, switching and other signal processing devices [2]. Particularly, the organic compounds are more appropriate for the above applications because they have high nonlinear optical susceptibility compared to inorganic materials owing to delocalized electrons at π - π^* orbitals. Morpholine is a kind of secondary aliphatic amine. The design of neoteric nonlinear optical (NLO) materials is based on morpholine having an aliphatic ring which acts as an acceptor. Cinnamic acid is an organic compound. It is a white crystalline compound that is slightly soluble in water. Organic compounds are very attractive for many photonic applications including nonlinear optics, electroluminescence, photovoltaics, molecular electronics and opto-electronic technologies [3]. Morpholine forms salts with organic acids, and the crystal structures of a limited number of these with either aliphatic acids, (e.g. the acetate) or aromatic acids, (e.g. the 4-nitrobenzoate). The structure of morpholinium cinnamate was already reported by Graham Smith [4]. Herein we report the synthesis, growth, optical structural, optimized structure, frontier molecular orbital properties of grown single crystal.

EXPERIMENTAL DETAILS

Material Synthesis and Crystal Growth

Morpholinium cinnamate compound was synthesized by dissolving morpholine (Sigma Aldrich 8.72 ml) and cinnamic acid (Sigma Aldrich 5.4 g) in water (100 ml) as per the equimolar ratio. By the method of slow evaporation, the MC crystal was grown and its crystalline property was enhanced and purified in ambient condition. Further, the homogenous solution was obtained by stirring the solution for 6 hours without any disturbance and the

solution was filtered twice with filter paper (Whatmann) to remove impurities. It was tightly covered and kept in dust free environment. Good quality, non-hygroscopic and transparent crystal was taken from the solution with a span of 30 days. The dimension of the crystal is observed to be of $35 \times 20 \times 4$ mm³ and the as-grown crystal is shown in Fig.1 (inset).

RESULT AND DISCUSSION

Powder X-ray Diffraction Analysis

The MC crystal was employed to powder XRD analysis and the pattern was attained by BRUKER D8 advanced powder X-ray diffractometer with Cu K α 1 radiation was scanned completely with the range of 5 – 40 $^\circ$. The peaks were indexed with POWDER X software and the indexed pattern for MC crystal as depicted in Fig.1. The well-defined peaks at particular 2θ values illustrate the crystalline quality of the title crystal. MC exhibits in the triclinic crystal system and the unit cell dimension values are $a = 5.7365$ (7) \AA , $b = 9.7526$ (10) \AA , $c = 11.7760$ (11) \AA , $\alpha = 103.270$ (8) $^\circ$, $\beta = 93.468$ (9) $^\circ$, $\gamma = 105.493$ (10) $^\circ$ and volume $V = 612.69$ (12) \AA^3 . The calculated lattice parameters are in good agreement with that of the obtained single crystal data [4].

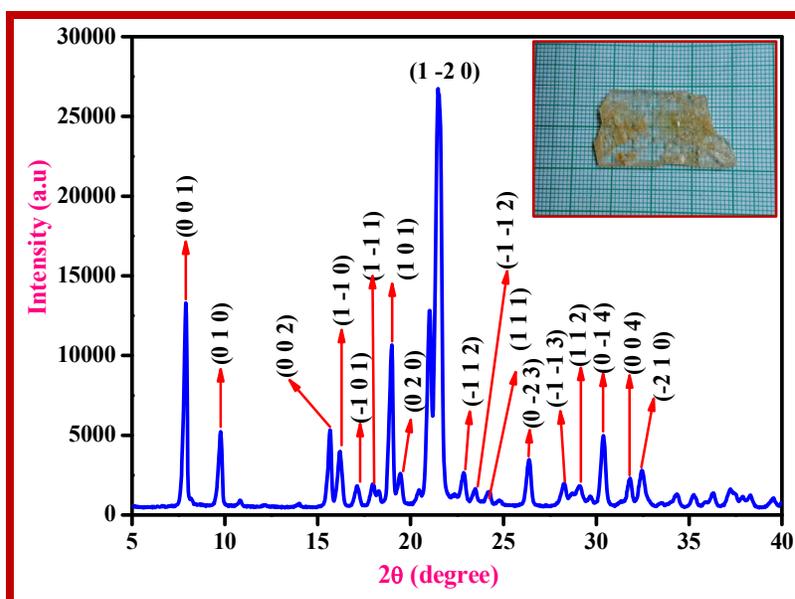


FIGURE 1. Powder X-ray diffraction pattern and as-grown (inset) of MC crystal

Spectral Analysis

NMR gives information about the number of magnetically distinct atoms of the type being present in the compound. When hydrogen nuclei are under studies, one can determine the number of each of the distinct types of hydrogen nuclei as well as obtain information regarding the nature of the immediate environment of each type. Similar information can be determined for the carbon nuclei. The carbon and proton NMR spectrum are shown in Fig. 2 (a & b). The ^{13}C NMR spectrum evidently shows the deprotonation of cinnamic acid at 175.624 ppm this may be ascertained to the presence of a fast proton exchange between the cinnamic acid and morpholine and this peak confirms the protonation of the title compound. The shift occurs at 43.082 ppm is due to the carbon of morpholinium moiety. The shift at 63.554 ppm is due to the meta position of morpholinium. The signal appears at 129.585, 128.944 and 124.070 ppm are assigned to the aromatic carbons of cinnamate. The signal is observed at 127.657, 135.115 and 140.805 are attributed to the aliphatic carbons of cinnamate. The doublet chemical shift at 7.4975 ppm which is assigned to the protons in NH_2 group attached to a carbon atom and this peak confirms the transfer of the proton (H) from cinnamic acid to morpholine. The aromatic protons of cinnamate are observed in the spectrum from 7.387 to 7.252 ppm. The aliphatic protons of cinnamate are observed at 7.483 and 6.410 ppm. The signal observed

DFT analysis

The electronic properties such as HOMO and LUMO energies were determined using the DFT approach. The HOMO (highest molecular orbital) and LUMO (lowest unoccupied molecular orbital) orbitals are referred as frontier molecular orbitals attributable to its large significance in determinative optic and electrical properties. HOMO is having the flexibility to donate an electron to the LUMO and LUMO is having the power to withdraw an electron from HOMO. The energy value of HOMO is directly connected to ionization potential that determines the chemical stability of a molecule and the LUMO energy is directly related to electron affinity. The plots of HOMO-LUMO are shown in Fig. 3(b). The green and red color indicates the negative and positive phases of MC compound. The higher energy value of HOMO (-6.162 eV) implies that the MC compound is chemically stable. The LUMO was predominately localized over the cinnamate anion with the energy value of -1.513 eV. The HOMO-LUMO energy difference is 4.649 eV and it suggested that strong intermolecular hydrogen bonding occurred between the cation and anion.

CONCLUSIONS

Good quality of single crystal morpholinium cinnamate was grown by the slow evaporation solution growth technique at room temperature. Powder XRD analysis reveals the crystalline quality of the sample. The molecular structure of the compound is confirmed by NMR analysis. Optical studies showed that the MC crystal has an extensive transmission range from 311- 900 nm with the cut-off wavelength 310 nm. From the HOMO-LUMO energy gap, the charge transfer interactions in the grown crystal shows the strong N-H...O, C-H...O and hydrogen bonding has been confirmed.

ACKNOWLEDGMENTS

The author R. Bhuvaneshwari would like to thank UGC, Government of India for providing the Senior Research Fellowship through Rajiv Gandhi National Fellowship scheme.

REFERENCES

1. K. Mohana Priyadarshini, A. Chandramohan, G. Anandha Babu, P. Ramasamy, *Solid State Sciences* **28**, 95-102 (2014).
2. S. Leela, R. Hema, Helen Stoeckli-Evans, K. Ramamurthi, G. Bhagavannarayana, *spectrochim. Acta A* **77**, 927-932 (2010).
3. R. Bhuvaneshwari, M. Divya Bharathi, G. Anbalagan, G. Chakkaravarthi, K. Sakthi Murugesan, *J. Mol. Struct.* **1173**, 188-195 (2018).
4. Graham Smith, *Acta Cryst E* **71**, o850–o851 (2015).