

# Spectral, Thermal, Optical, Dielectric and DFT Studies on 4-Dimethylaminopyridinium-Chloro-P-Nitrobenzoate Single Crystals

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## Abstract

A novel organic nonlinear optical 4-dimethylaminopyridinium *o*-chloro-p-nitrobenzoate (4DCN) single crystal was grown by slow evaporation solution growth technique. The crystal system and lattice parameters of the grown crystal were confirmed by single crystal X-ray diffraction. Different modes functional groups present in the title compound were confirmed by Fourier transform infrared (FT-IR) spectroscopic studies. UV-Vis-NIR spectra have been recorded to explore its optical transmission. First hyper polarizability and Mulliken charge analysis were also done for the sample.

**Keywords:** Crystal structure, spectroscopic, DFT

## 1. Introduction

In past few decades, organic nonlinear optical (NLO) single crystals have been prominently investigated due to their potential properties such as second and third harmonic generation (SHG; THG), piezoelectricity, pyroelectricity and ferroelectricity. Significant interest in designing a new NLO materials with enhanced second harmonic conversion efficiencies [1–5] as they are employed for wide range of applications such as laser frequency conversion, electro-optic modulation (EOM), frequency mixing, optical information processing, Terahertz (THz) wave generation and communication devices [6–12]. An organic molecule should have high second order hyperpolarizability ( $\beta$ ) to exhibit large NLO properties. The hyperpolarizability can be enhanced by increasing intramolecular charge transfer interaction by extending  $\pi$ -conjugated system [13]. The increase in conjugation length decreases the energy gap and narrows down the optical transparency window. To avoid this situation the principal way consists in the true changes of the state dipole moments of the particular molecular complexes and the long-range matrix [14]. So appropriately varying the particular molecule with respect to the surrounding matrix one can achieve the changes in the desirable directions. The molecular complexes in which extensive charge transfer interaction occurs between the donor and the acceptor molecules are also expected to have high NLO properties. Worldwide, Timofeeva of New Mexico Highlands University, Gunter of ETH Zurich, Kityk of Czestochowa University of Technology of Poland, Petrosyan of Molecule Structure Research Center of Armenia, Brahadeeswaran of crystal research lab, Anna University, India, Ramasamy of center for crystal growth of SSN college of Engineering, India to name but a few, have made

significant contribution for the designing and development of efficient materials for NLO applications [15-18].

Novel materials with enhanced nonlinear optical properties in third harmonic generation make thrust and maintain to get significant interest to the researchers as they motivated them to concentrate on growth and characterization of single crystals. To study the third order NLO properties of organic molecular crystals are comparably less with the photonic crystals in the field of second order NLO applications. The huge expectation has been generated among the research community for developing nonlinear optical materials for third harmonic generation materials. The materials employed in the generation of third harmonic generation frequency applications is encouraged due to its wide spread applications in sensor protection, optical switching based on nonlinear properties of the material like nonlinear refraction, nonlinear absorption and third order nonlinear susceptibility [19-20].

In this direction, we explored 4DCN is a new member in this distinct group. In the present manuscript we present our results on synthesis, crystal structure, growth, X ray diffraction, FTIR, UV-Vis and Z-scan of 4DCN. The studies mentioned here are, to the best of our knowledge, reported for the first time in literature.

## 2. Experimental

### 2.1. Materials Synthesis

The Pure specimens of 4-dimethylaminopyridine and o-chloro p-nitro benzoic acid was used without any further purification. The starting material synthesized by taking 4-dimethylaminopyridine and o-chloro p-nitrobenzoic acid with equimolar ratio (1:1). The required amounts of the reactants were calculated according to the reaction given below (Scheme 1). The solutions of 4-dimethylaminopyridine and o-chloro p-nitrobenzoic acid were separately prepared by dissolving their calculated amounts in methanol solvent. The o-chloro p-nitro benzoic acidsolution was then added dropwise to the 4-dimethylaminopyridine solution slowly by continuous stirring, which then turned into a yellow coloured precipitate. The yellow powder of 4DCN was separated by drying the resultant precipitate, at 35 °C. The synthesized salt was further purified by successive recrystallization processes using methanol as a solvent

### 2.2. Crystal growth

The saturated solution of 4DCN was prepared at 30 °C and kept in a water bath, equipped with a Programmable Eurotherm Temperature Controller (Model: 3216; accuracy  $\pm 0.01$  °C). Prior to crystal growth, the bath temperature was initially raised to 5 °C above its saturation temperature and maintain the same for 12 h to dissolve any unwanted spurious nuclei present in the solution. Then the solution temperature was slowly lowered to 30 °C with a cooling rate of 0.3°C/h. After reached its saturation temperature the growth was performed by isothermal solvent evaporation method. The single crystals are obtained within 10 days.

## 3. Results and discussion

### 3.1. X-ray diffraction analysis

The single crystal X-ray diffraction data of the title compound were collected at 293 K with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.071073$  nm), and used Enraf-Nonius CAD-4 diffractometer with the  $\omega$ -2 $\theta$  scan mode. Cell refinement and data reduction were carried out using CAD-4 EXPRESS [21] and XCAD4 [22]. The structures were solved by direct methods procedure using SHELXS-97 [23] and refined by full-matrix least-squares on F<sup>2</sup> using SHELXL -97 program [23]. All non-hydrogen atoms

were anisotropically refined. The hydrogen atom positions were fixed at geometrically calculated distances to allow riding on the parent atoms to which they are attached. The molecular graphics were prepared by using the ORTEP. As grown single crystal of the compound were obtained from methanol solution. It belongs to triclinic system with space group P-1. The lattice parameters obtained are  $a = 7.3158(2)$ ,  $b = 12.7849(3)$ ,  $c = 16.6924(4)$ ,  $\alpha = 94.5610(10)$ ,  $\beta = 92.5040(10)$ ,  $\gamma = 101.1660(10)$  and the unit cell volume is 1524.08. Table .1 shows the crystal data and structure refinement for 4DCN. In the title compound, the 4-dimethylaminopyridinium appears in crystalline lattice as a single protonated cation and the o-chlorop-nitrobenzoate presents as deprotonated anion. The X-ray single crystal structure of the proton-transfer complex of 4-dimethylaminepyridine with o- chlorop- nitro benzoic acid shows the presence of mono protonated 4-dimethylaminopyridiniumcation gives intermolecular hydrogen bonding associations. The loss of proton in o-chlorop- nitro benzoic acid is confirmed by the lengthening of C-C bonds. In the o-chlorop-nitro benzoate anion the removal of the acid proton leads to shortening of C-O bond distance. The packing of molecules in lattice is determined by conventional and nonconventional C-H...O hydrogen bonds. The hydrogen bonded network of the compound clearly shows that the counter 4-diemthylaminopyridinium cation joined to the o-chlorop-nitrobenzoate anion via extensive hydrogen bonding. These hydrogen bonds are responsible for the stability of the compound. The ORTEP diagram and packing structure of the crystal is shown in figure1 and 2. The blue line in the figure represents the hydrogen bonds in the unit cell.

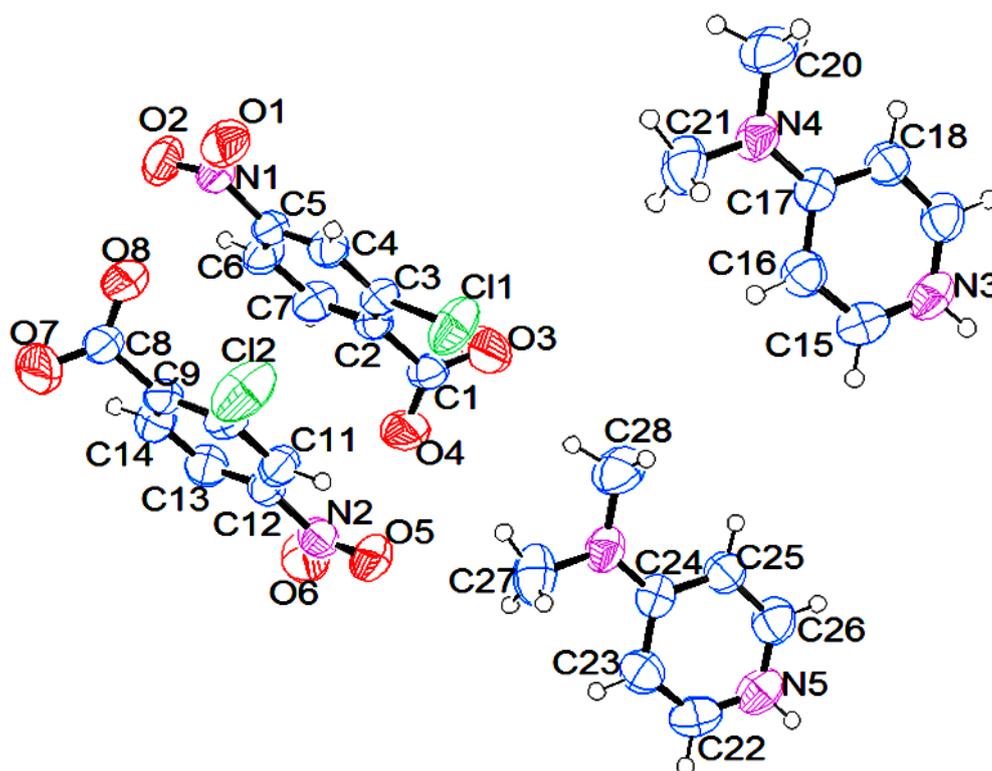
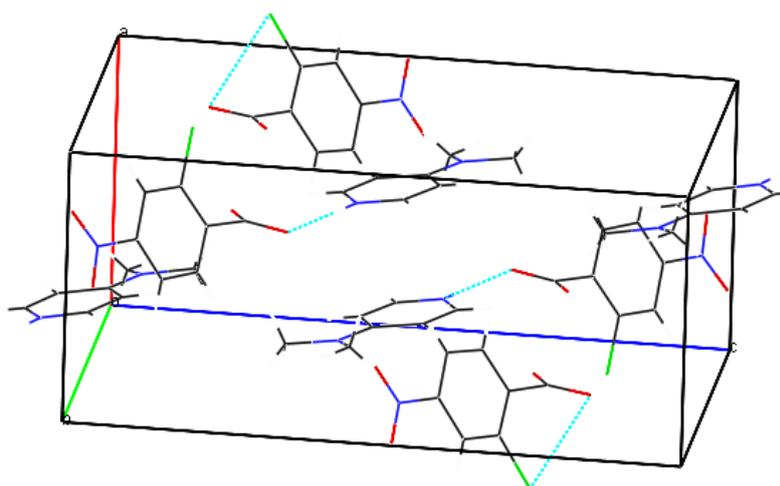


Figure 1. ORTEP diagram of 4DCN.



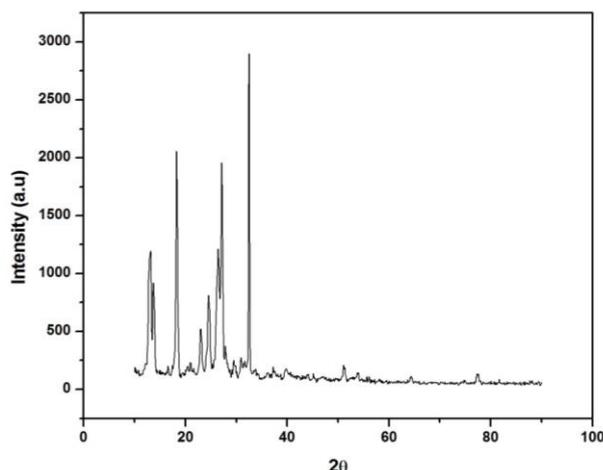
**Figure 2. Packing diagram of 4DCN.**

**Table 1. Crystal data and structure refinement for 4DCN.**

Empirical formula	C <sub>56</sub> H <sub>56</sub> C <sub>14</sub> N <sub>12</sub> O <sub>16</sub>
Formula weight	323.73
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	TRICLINIC, P -1
Unit cell dimensions	a = 7.3158(2) Å    alpha = 94.5610(10) deg. b = 12.7849(3) Å    beta = 92.5040(10) deg. c = 16.6924(4) Å    gamma = 101.1660(10) deg.
Volume	1524.08(7) Å <sup>3</sup>
Z	4
Absorption coefficient	0.272 mm <sup>-1</sup>
F(000)	672
Crystal size	0.20 x 0.15 x 0.10 mm <sup>3</sup>
Theta range for data collection	1.23 to 26.60 deg.
Limiting indices	-9<=h<=9, -16<=k<=15, -20<=l<=20
Reflections collected / unique	22801 / 6284 [R(int) = 0.027]
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6284 / 0 / 402
Goodness-of-fit on F <sup>2</sup>	0.943
Final R indices [I>2sigma(I)]	R1 = 0.0852, wR2 = 0.0639
R indices (all data)	R1 = 0.2177, wR2 = 0.1909
Extinction coefficient	0.0000(16)

Powder X-ray diffraction pattern for the grown crystals were carried out by using RICH SEIFERT diffractometer. Diffraction pattern data were collected on the diffractometer equipped with monochromatic CuK $\alpha$  radiation (1.540598Å) and detected by a scintillation counter. The recorded powder X-ray diffraction patterns for the compound in methanol solvent is shown in figure 3. The sharp and well defined Bragg peaks observed in the powder X-ray diffraction pattern confirm the crystalline phase of the compound. The peak intensities observed in powder X-ray diffraction pattern of the

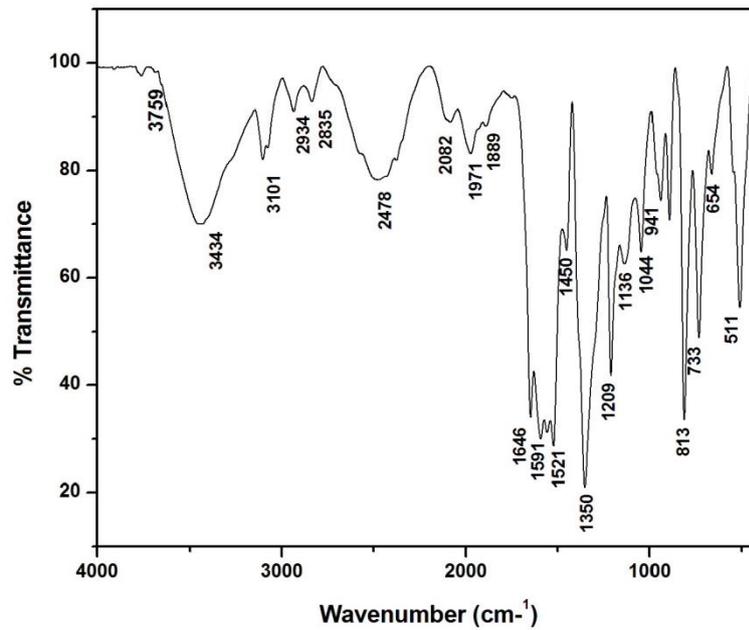
compound in methanol solvent shows high value and it indicates that the compound formed has high crystalline nature.



**Figure 3. Powder XRD spectrum of 4DCN.**

### 3.2. FTIR Spectral analysis

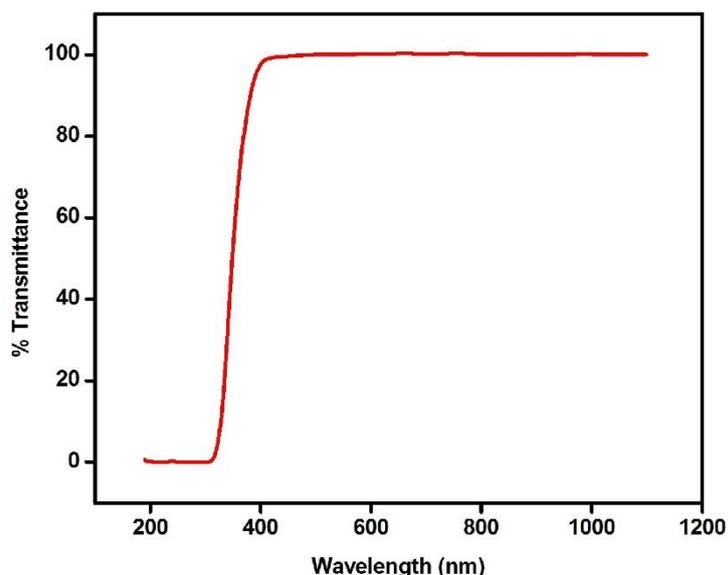
The FTIR spectrum of 4DCN was recorded using BRUKER IFS 66V model spectrophotometer, which is shown in figure 4. The vibrations of various functional groups present in the crystal is analyzed through spectrum. The OH stretching vibrational frequency is absorbed at  $3434\text{ cm}^{-1}$ . The absorption bands at  $3101\text{ cm}^{-1}$ ,  $2934\text{ cm}^{-1}$  and  $2835\text{ cm}^{-1}$  are assigned to CH stretching vibration. The NH stretching mode vibration is obtained at  $2478\text{ cm}^{-1}$ . The C=C stretching vibrational mode is absorbed at  $1971\text{ cm}^{-1}$ . In addition, the peaks at  $1646\text{ cm}^{-1}$  are assigned for the C=O stretching mode. The symmetric and asymmetric stretching modes of NO are revealed through the peaks at  $1591$  and  $1521\text{ cm}^{-1}$  respectively. The peak at  $1450\text{ cm}^{-1}$  is attributed to N=O stretching vibration. The CN stretching vibration is absorbed at  $1350\text{ cm}^{-1}$ . The peaks at  $1209$  and  $893\text{ cm}^{-1}$  are attributed to CH in-plan and out-plan bending vibration. The CH<sub>3</sub> bending vibrational frequency is absorbed at  $1136\text{ cm}^{-1}$ . The peak at  $1044\text{ cm}^{-1}$  is assigned for OH in-plane bending mode vibration. The peak at  $941\text{ cm}^{-1}$  is assigned to the vibration of NO stretching mode. The NH out plane bending vibrational frequency is absorbed at  $813\text{ cm}^{-1}$ . The absorption band at  $733\text{ cm}^{-1}$  are assigned to C-Cl stretching vibration. The O-N=O bending mode vibration is obtained at  $511\text{ cm}^{-1}$ . In addition, the peaks at  $664$  and  $411\text{ cm}^{-1}$  are attributed to in-plan and out-plan ring bending vibration. Hence, the coordination of pyridine and carboxylic compounds are confirmed by the presence of prominent functional groups in the FTIR spectrum.



**Figure 4. FTIR spectrum of 4DCN.**

### 3.3. UV-Vis-NIR spectral analysis

The grown crystals of 4DCN with thickness about 2 mm were subjected to UV-Vis-NIR spectral analysis in the wavelength range from 200 to 1200 nm, with the help of Varian Cary UV-Vis-NIR spectrophotometer. The UV-Vis-NIR spectral analysis is one of the important analyses to study linear optical characteristics of the crystal. Ultra violet and visible radiation causes the electron transitions from the ground to a high energy state in the material. UV absorption spectra arise from the transition of electrons within a molecule from a lower electronic energy state to higher energy state. When an atom or molecule absorbs the energy, electrons are promoted from their ground state to an excited state. The transmittance spectrum is depicted in the Figure5. From the spectrum, it is clear that UV cut-off wavelength of grown crystal is noted around 330 nm. The crystal is entirely transparent beyond cut-off wavelength up to 1200 nm. The transparent character of crystal is suitable and prerequisite for second and third harmonic generation of wavelength [24].



**Figure 5. UV Transmittance spectrum of 4DCN**

### 3.4. Mulliken atomic charge

In applying quantum mechanical calculation to molecular system, the atomic charge is vital [25]. The impact of atomic charges decides the dipole moment, molecular polarization, electronic structure and many of Molecular Systems' properties. The calculation of mulliken atomic charge thus plays an important role in the application of quantum chemicals in the molecular system. The distribution of charges across the atoms suggests that donor and recipient pair molecules are formed. Figure 6 shows the mulliken charge distribution structure of the title compound. There are more negative charges in Carbon and Nitrogen atoms, while all hydrogen atoms have a positive charge. Furthermore, the C3 atom has a highest atomic negative (-1.443 e) charge in Mulliken atomic chargers. In the Mulliken population analysis, reaction behavioral analysis of the various chemicals of the electropillar and nuclear response systems is an effective way of interpreting and forecasting the electrical negative effects on the atoms in the molecule on the basis of a Mulliken population analysis.



participant to an acceptable assembly in a single bond connection path can lead to large variations of molecular dipole. The molecular polarization is to simultaneously strengthen the IR and Raman activity. Ab initio calculations in conjugated systems which predict exceptionally large Raman and the Infra-red intensity on equal normal modes [28, 29]. Analysis of the wave function shows that the absorption of the electron is the transition from the ground to the first molecular orbital. One-electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital is largely determined (LUMO).

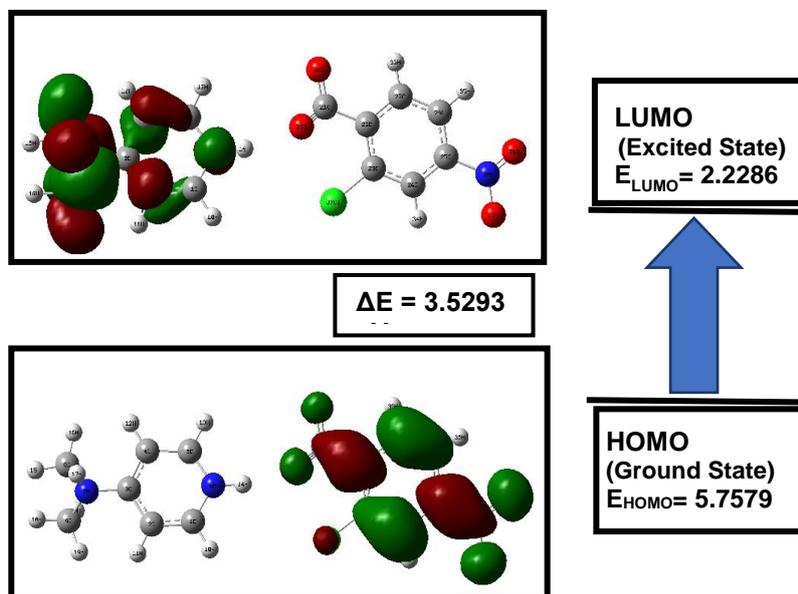


Figure 7. HOMO-LUMO Spectrum of 4DCN.

The energy gap between the HOMO and LUMO of 4DCN was calculated at the level of B3LYP/6-311++ (d, p) and shows that the energy gap of the molecule reflects the chemical activity. LUMO symbolizes the ability to obtain an electron as an electron receiver; HOMO symbolizes that the electron is donated. The calculation of the dimer HOMO - LUMO energy gap of titled compound is shown in fig. 7. Moreover, the lower energy gap of the HOMO and LUMO explains the possible transmission of charges in the fragment. The orbitals in the border region could show virtually degenerate energy levels

#### 4. Conclusion

The single crystals of 4-dimethylaminopyridinium and o-chlorop-nitrobenzoate was synthesized and grown in methanol solution at room temperature. The single crystal X-ray diffraction data of the title compound were collected. It belongs to triclinic crystal system with space group of P-1. The peak intensities observed in powder X-ray diffraction pattern of the compound in methanol solvent showed high value and it indicated that the compound formed had high crystalline nature. UV-Visible-NIR spectroscopy and HOMO, LUMO confirms the formation of the charge transfer complex. FT-IR spectral techniques establish the molecular structure of the complex adduct. First hyper polarizability and Mulliken charge analysis results were also done.

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