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Synthesis and Nonlinear Optical Absorption Properties of 2-Chloro-4’methoxy Benzoin Compounds

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Abstract:
A novel 2-chloro-4'methoxy benzoin (2C4MB) is synthesized via benzoin condensation and its structure is established using an X-ray diffraction technique. The Z-scan approach was used to explore the non-linear optical absorption (NOA) properties in solution. Under nanosecond pulse irradiation, the 2C4MB molecule demonstrated reverse saturable absorption (RSA).

Key words: Organic compounds, Crystal growth, Z-scan, Dielectric studies.

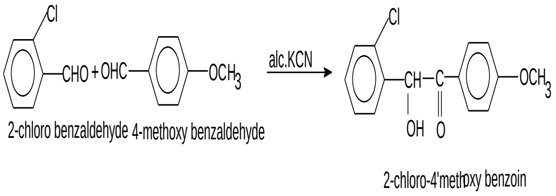
1. Introduction

With the rapid development of optical communication, the innovative materials with large and ultrafast nonlinear optical responses are needed for building the ultrafast optical switching and processing devices. Conjugated organic nonlinear optical (NLO) materials have attracted attention in recent years because to their second or third-order hyperpolorizability as compared to inorganic NLO materials [1]. Many studies are being conducted in attempt to synthesize novel organic materials with substantial second-order optical nonlinearities in order to meet current technological requirements [2]. They offer a plethora of possible uses, including as telecommunications, optical computing, optical data storage, and so on. The conjugated molecules are made up of a skeleton that contains conjugated - electrons; the conjugated bridge is connected to two end groups that have electron donor (D) and electron acceptor (A) characteristics. The electron acceptor group is responsible for the withdrawal of electronic charge from the donor through the conjugated bridge. As a consequence, the skeleton's π-electrons become polarized, which results in the formation of a significant molecular dipole moment. This moment defines a charge transfer axis that is roughly coincident with the chain axis of the conjugated system. These molecules are referred to as push-pull molecules [3,4]. The fundamental method of employing electron-donor and electron-acceptor substituents to polarize the -electron system of organic materials has been instrumental in the development of NLO chromophores with high molecular nonlinearity, strong thermal stability, increased solubility, and processability [5,6]. The formation of nonlinearity in large systems has been the subject of a significant amount of research in recent years, as has the relationship between nonlinear optical (NLO) responses and electronic structure and molecular geometry. The goal of this research is to design and construct NLO materials that have a significant amount of molecular hyperpolarizability at the molecular level [7,8].

Among other organic compounds, benzoin compounds are very important, many of the benzoins and its derivatives are reported to show interesting NLO properties [9, 10]. With the earlier reported work on the synthesis of 4-methoxy benzoin [11], 2-Chloro-4'methoxy benzoin (2C4MB) is introduced as a novel prospective candidate for third order NLO applications. The chemical structure of 2-chloro-4'methoxy benzoin, which has one electron donor (methoxy) and one electron acceptor (chloro) moiety, results in a push-pull configuration, which is a well-known method of improving optical nonlinearities [12]. 2C4MB was synthesized using benzoin condensation and produced as a single crystal via solvent evaporation. Its three-dimensional structure was also revealed by single crystal X-ray diffraction research. X-ray powder diffraction, nuclear magnetic resonance (NMR), and Fourier transform infrared (FTIR) were used to analyze the formed 2C4MB crystal. UV-vis spectroscopy was used to study the crystal's transmission in the visible and ultraviolet regions. TG-DTA curves were used to determine the crystal's thermal stability.

2. Experimental

The chemical 2C4MB was created through benzoin condensation using 4 g of KCN dissolved in 75 cc of water in a one-litre flask. The flask was filled with 6.8 g [0.05 mole] of 4-methoxy benzaldeyde, 7 g [0.05 mole] of 2-chloro benzaldeyde, and 75 cc of 95% ethanol. At boiling temperature, the mixture was reduced to a solution and refluxed for one and a half hours. Steam was then run through the solution, removing all of the alcohol and virtually all of the unreacted aldehyde. The product's condensed water was decanted and set aside for crystallisation. The product was then rinsed with cold alcohol after being pressed as free of oily material as feasible using a suction funnel. Approximately 14 g [yield was 60%] of crude product was obtained in this manner. The raw mixture was dissolved in hot alcohol and allowed to gently crystallize [Scheme 1]. The 2-chloro-4'-methoxy benzoin crystallized as colorless hexagonal crystals suitable for X-ray diffraction [16], [5]. The compound's melting point was discovered to be 84 C. The yield of pure 2-chloro-4'methoxy benzoin is between 60 and 70% [13].



Scheme 1. Schematic representation of 2C4MB

3. Results and Discussion

3.1. Mass spectral analysis of 2C4MB

Mass spectroscopy was used to establish the compound's molecular weight and formula. Table 1 shows a list of the numerous fragmentations. The FAB mass spectrometer was used to estimate the molecular weight of the chemical, which reveals a weak signal [molecular ion peak] [Fig.1] at m/z 277, confirming the given molecular mass of the 2C4MB. The fragments record intense signals at m/z 261.97, 246,166, 133, 103, and 91, indicating the loss of the methyl group, methoxy, $-C_6H_4Cl$, $MeO-C_6H_4CO$, $-C_6H_5CO$, and Tropylium cation.

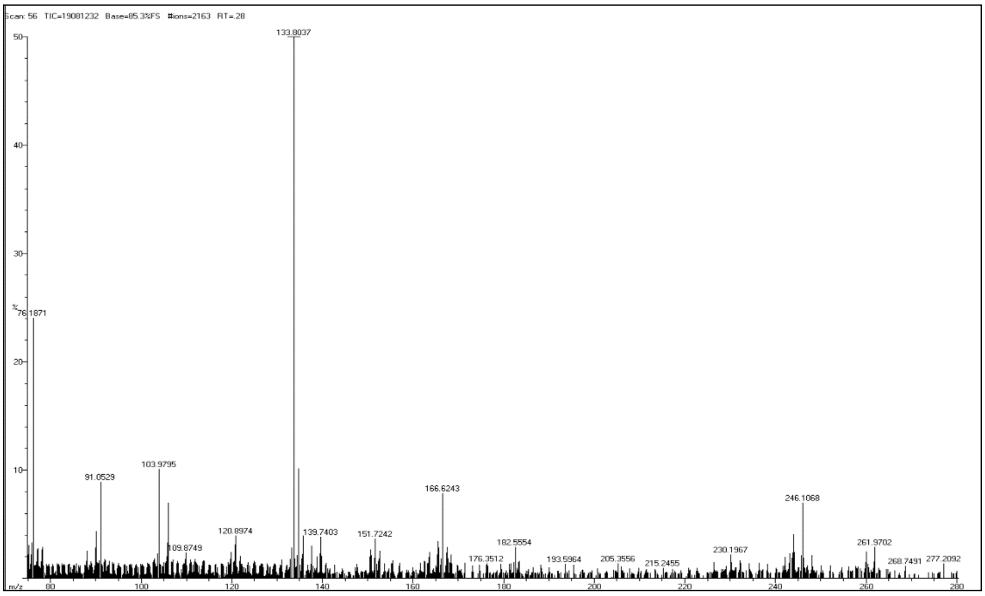


Figure 1. Mass spectra of 2C4MB

Table 1. Mass spectral fragmentation peaks for 2C4MB

261.9	M^+-CH_3
246	M^+-OCH_3
166	$M^+-C_6H_4Cl$
133	$MeO-C_6H_4CO$
103	[-C6H5-CO⁺]
91	Tropylium cation

3.2. FTIR spectral analysis of 2C4MB

[Fig 2] depicts the infrared spectrum of 2C4MB in solid KBr. The presence of intramolecular hydrogen bonding is shown by the appearance of a strong band at 1666 cm^{-1} corresponding to C=O stretching and a sharp band at 3475 cm^{-1} corresponding to a -OH stretching frequency [14]. and aromatic C-H stretching correlates to absorption at 3060 cm^{-1}. The aromatic C = C stretching frequency corresponds to absorption at 1569 cm^{-1} and 1602 cm^{-1}. The two faint absorptions at 979 cm^{-1} can be attributed to disubstituted benzene C-H deformation [Table 2].

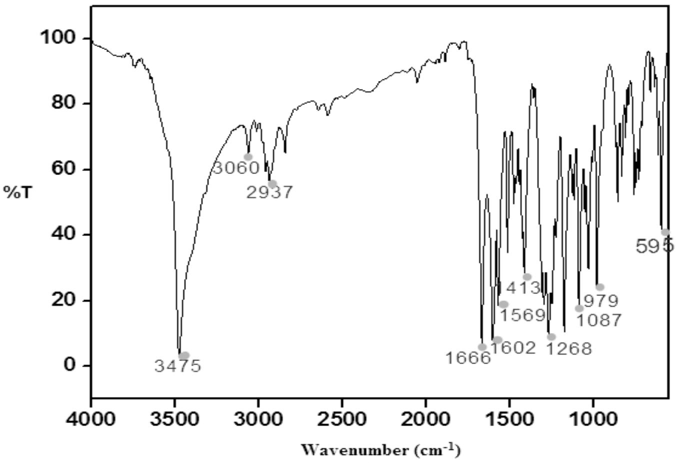


Figure 2. IR spectra of 2C4MB in solid KBr

Table 2. Vibrational assignments of the 2C4MB

FTIR for 2C4MB [wavenumber]]]cm^{-1}]	**Band assignments**
3475 cm^{-1}	-OH stretching
3060 cm^{-1}	Aromatic C-H stretching
2937 cm^{-1}[w]	Aliphatic C-H stretching
1666 cm^{-1}[vs]	Sym C=O stretching
1569,1602 cm^{-1}[vs]	Aromatic sym C=C stretching
1268 cm^{-1}[m]	C-OH in plane deformation
979 cm^{-1}[s]	-OH out of plane deformation
1087 cm^{-1} and 1030 cm^{-1}	Presence of Benzene ring deformation

w:weak; vw:very weak, m:medium, s:strong, vs:very strong.

3.3. UV-Visible Analysis of 2C4MB

The optical absorption spectrum of the formed crystals in ethanol was measured from 200 to 800 nm and is presented in Fig. 3. According to the absorption spectrum, there is relatively little absorbance across the whole visible region. UV and visible light absorption includes electron enhancement in π → π* or n → π * transitions from the ground state to higher energy levels. π → π* transitions are responsible for a relatively mild absorption between 250 and 290 nm. The absorption near 300 nm implies a significant vibrational fine structure. The absence of substantial absorption in the UV-Visible spectrum area from 400 nm to 1000 nm indicates that the 2C4MB crystals are suitable for SHG applications [15]. This suggests that 2C4MB crystals could be used in the manufacture of optical devices.

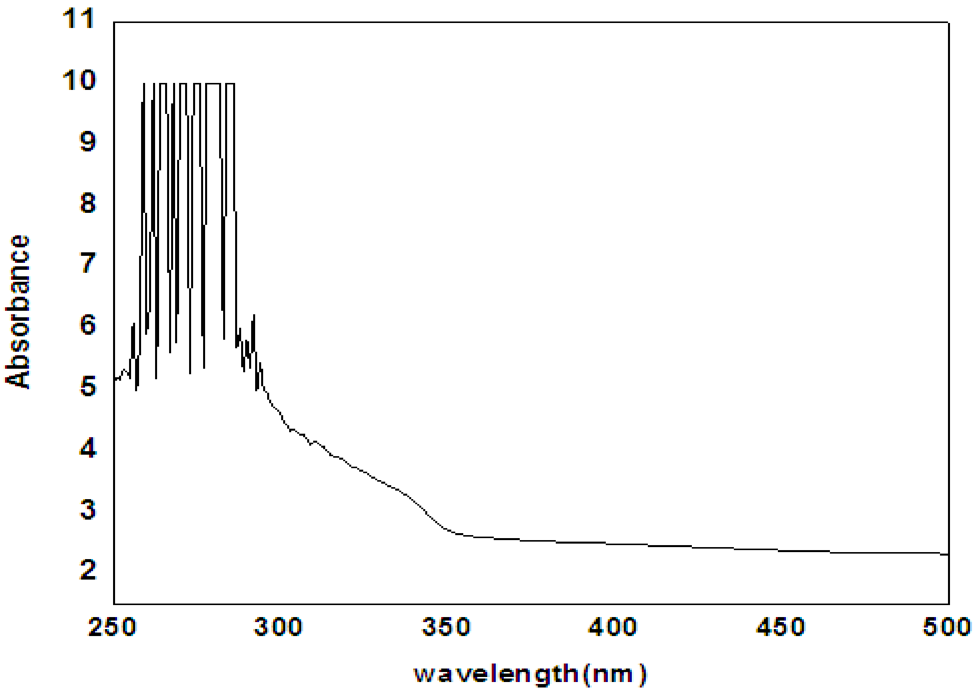


Figure 3. UV spectra of 2C4MB

3.4. X-Ray Diffraction

Following the completion of the single crystal study, it was determined that the crystal is a member of the triclinic system and belongs to the centrosymmetric space group, P1. The lattice parameters have been discovered to be as follows: a = 9.0100 Å, b = 9.3148 Å, c = 9.4557 Å, α = 103.968 (2)º, β = 90.767 (2)º, γ = 118.4680(10)º, and the volume of the unit cells has been found to be 669.28 Å3. Both a CHOH and a CO group are responsible for connecting the two phenyl rings that make up the molecular structure. In the case of two rings, the dihedral angle between them is -20.11(17) Å. At an angle of around 80 degrees, one of the benzene rings is tilted toward the other. The crystal has a –OCH3 group located at the C (2) position, which functions as an electron donor, and a –CO group located at the C (8)-O (2) position, which functions. Due to the fact that the torsional angle between the –CHOH group and the C=O group O (2)-C (8)-C (9)-O (3) is -20.11(17), it may be concluded that the two groups are desynchronized. The torsional angle that exists between the carbon atoms that make up the phenyl group, C (5)-C (8)-C (9)-C (10) is -75.30 (14).The fact that the two benzene rings are not coplanar is demonstrated by this. The dihedral angle that exists between the carbon atoms of the phenyl ring and the carbonyl carbon.

The fact that the benzene ring and the C=O are practically perpendicular to one other is demonstrated by the fact that the value of O (2)-C (8)-C (9)-C (10) is 103.29 (10). The bond angle between the C (7)-C (2)-C (3) compounds in 2C4MB is found to be 119.92 (12), whereas the bond angle between the C (12)-C (13)-C (14) compounds in the opposite phenyl ring is also found to be 119.93 (13).The fact that this is the case demonstrates that the bond angle between a sp2 carbon and a C (5)-C (8)-C (9) is almost identical. The distance between the carbonyl group in the molecule shown in the title is 1.279 (15) ú, which is the C=O bond distance between C (8) and O (2).Specifically, the C–O bond distance between C (9) and O (3) is 1.4096 (18), which indicates the length of the C–OH bond. Specifically, the length of the C (2)-O (1) bond is 1.3492 (16), which indicates that the C–OCH3 bond exhibits a slight amount of sp2 character. This suggests that there is an overlap of n-π. On the other hand, the length of the C (9)-O (3) bond that corresponds to C-OH is 1.4096 (18), which suggests that it is a single bond character. The length of the link between C (5) and C (8) is 1.5184 (16), but the bond strength between C (9) and C (10) is 1.4683

(17). The bond length C (5)-C (8) corresponds to a overlap of orbital of adjacent bonds. This is because there is no possibility of any form of π-π overlap that occurs between the C=O and C=C of the benzene ring. [Fig. 4] shows that the bond angle C (10)-C (9)-C (8) is 110.00 (10), which is single bond since there is no chance of any type of overlap. In the first scenario, the decrease in bond length can be attributed to the almost identical to the tetrahedral angle of 109o28′.

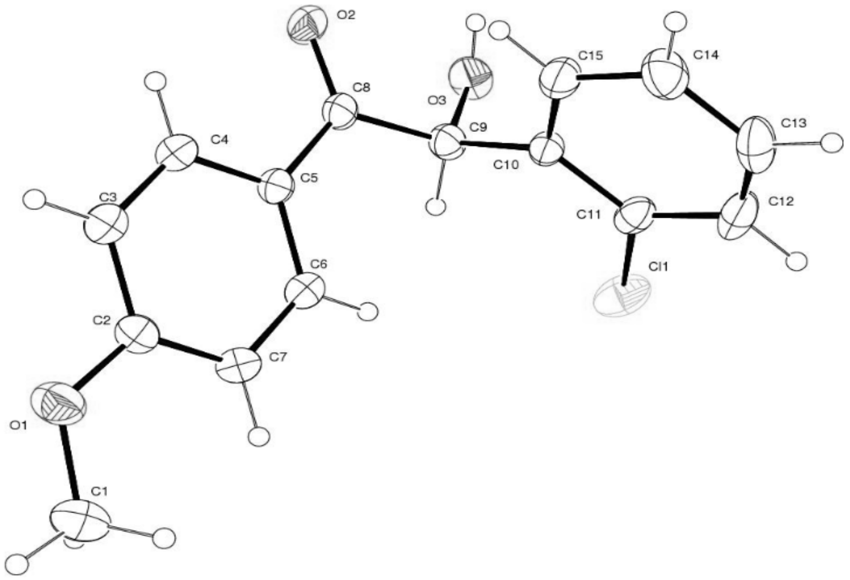


Figure 4. ORTEP diagram of 2C4MB

3.5. Dielectric studies

The dielectric study of 2C4MB, within the low frequency range, there is a significant shift in the dielectric loss, accompanied by a slight hump at the dielectric loss 2. At slightly higher frequencies, there is essentially no dielectric loss between the logF values of 15 and 40, with a minor hump between 18 and 41.There seems to be a change in the intermolecular bonding at the log F value 5[Fig 5]. The reduced dielectric loss at higher frequency ranges demonstrates that the 2C4MB crystal has acceptable quality with fewer defects, which is significant for NLO applications. [16].

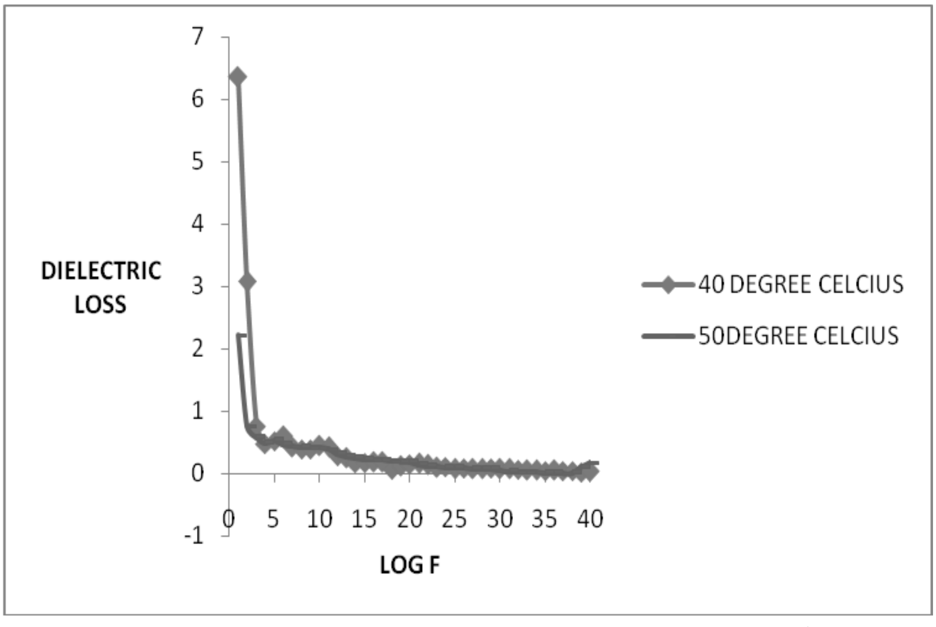


Figure 5. Log F versus dielectric constant of 2C4MB at 40 and 50^0C

3.6. Thermal studies

TGA-DSC of 2C4MB was recorded using NETZSCHSTA 409 C/CD instrument. The first endothermic peak on the DTA diagram of the chemical (2C4MB) shows a transition due to melting of the molecule. At 89.4 degrees Celsius, the melting is complete [Fig. 6]. Further heating causes an endothermic reaction. This is followed by an exothermic shift beginning at 312°C.The weight loss is observed starting from the temperature of 312°Cupto 365°C .At this temperature a weight loss of 97 % is noticed.

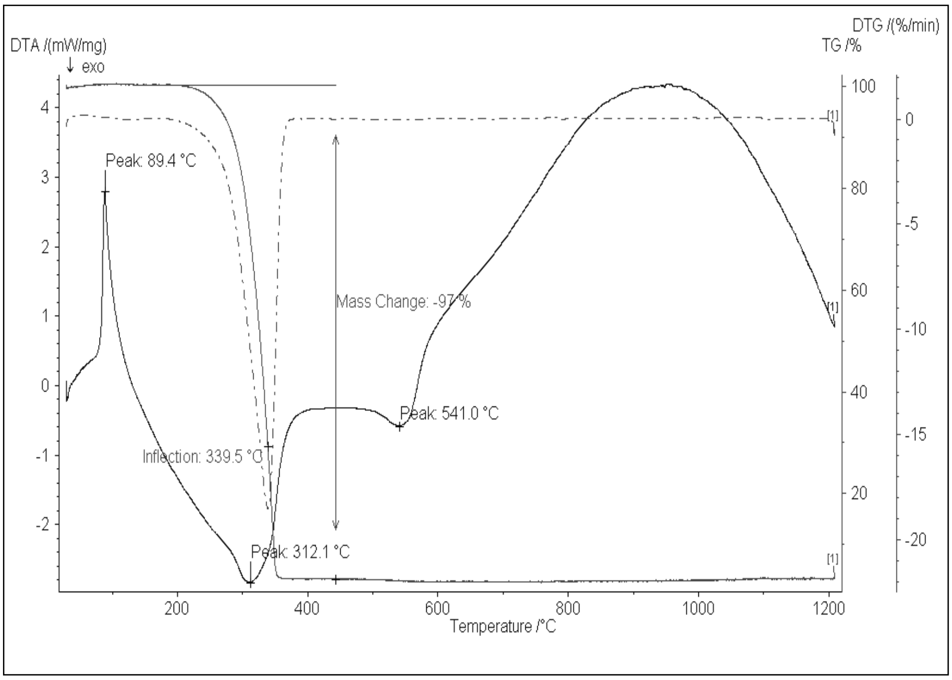


Figure 6. TGA-DTA curve of 2C4MB

3.7. Z-Scan studies

The Z-scan approach has been used to assess the non-linear optical characteristics of third order in semiconductors [17], dielectrics [18], organic or carbon-based molecules [19], and liquid crystals [20]. The open aperture Z-scan technique was used to evaluate the nonlinear optical absorption (NOA) of 2C4MB compounds at the nanosecond scale. The normalized Z-scan transmittance of 2X10^{-4}mol/L solutions of 2C4MB compound in DMF is shown in Figure 7. A Q-switch locked Nd:YAG (1064 nm) laser source with a second harmonic generation of 532 nm, pulse width of 12 ns, repeat frequency of 10 Hz, average pulse energy of 0.114 mJ, and peak irradiance of 0.670 GW/cm2 was used. The transmittances of 24MB were practically a flat line as the sample was moved away from the focus point, demonstrating linear absorption under weak light irradiation. The transmittances dropped when the sample was pushed closer to the focus point and the laser irradiance rose. The normalized transmittance declined to negative at the focus point (Z¼0), where the laser irradiation was at its greatest. These findings suggested that the 2C4MB molecule exhibited obvious reverse saturation absorption (RSA).

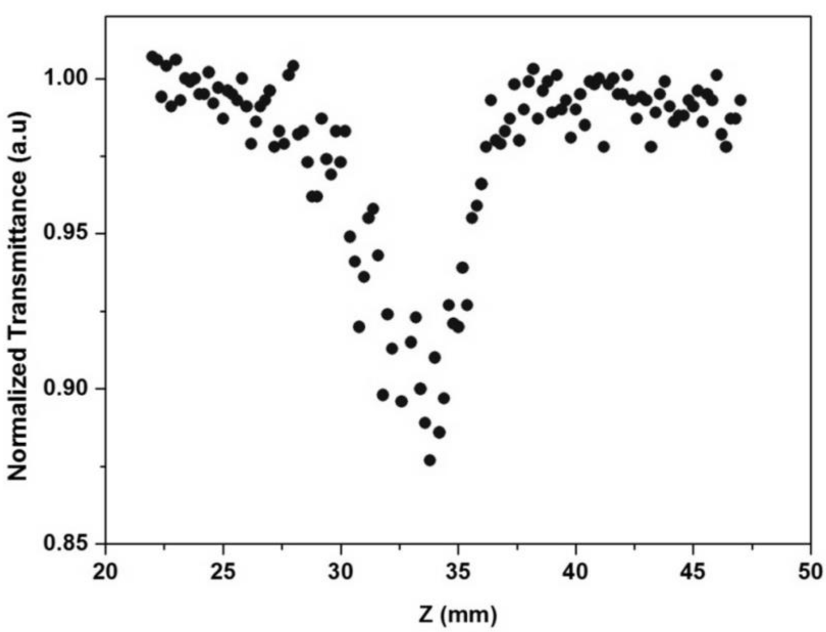


Figure 7. Non linear absorption coefficient of compound 2C4MB

4. Conclusions

The slow evaporation solution growth approach was used to successfully generate single crystals. Single crystal X-ray diffraction measurements validated the crystal structure of the generated crystal and computed the lattice parameters. The cut-off wavelength for the UV-visible spectrum is discovered to be 400nm.The molecular structure is determined using FTIR and FT-Raman spectrum methods. The Z-Scan technique used to measure the closed and open apertures demonstrates that 2C4MB has saturable absorption. The third-order nonlinear features obtained indicate its usefulness for optical limiting and switching applications. Thus, the comprehensive investigation of various features showed that the investigated chemical could be a suitable candidate for applications in the nonlinear optical sector.

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