

A novel class of new organic NLO hexamine: *m* – cresol material

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The new organic NLO material of hexamine: *m* – cresol material (1:2) has been synthesized by slow – evaporation technique. The good crystalline nature of the material is identified through Powder XRD analysis. FT – IR tool is used to confirm the formation of O – H --- N hydrogen bonding and non proton transfer of the material. The charge transfer (CT) through hydrogen bonding is also established. The possible vibration modes are predicted through factor group analysis theoretically. The charge transfer interaction is confirmed by UV -Vis analysis in addition to the bathochromic shift behavior. That the candidate has greater second harmonic generation (SHG) efficiency than the KDP is identified through Powder Kurtz – Perry technique.

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Keywords: Organic material, Charge transfer (CT), Second harmonic generation (SHG)

1. Introduction

The design and search for non – linear optical (NLO) materials has been a matter of interest in recent years because of their potential applications to laser devices, telecommunications and optical data storage [1]. Second harmonic generation (SHG), the second – order effect of NLO properties of crystalline materials depend both on the magnitude of the molecular hyperpolarizability (β) (microscopic non – linearity) and on the orientation of the molecules in the crystal lattice [2]. Organic molecules, in general are potentially more attractive and versatile than inorganic compounds for NLO materials because of their large β – values, fast response time, high resistance to optical damage threshold and the almost unlimited possibilities of designing molecules suitable for SHG [3]. Nevertheless, the transfer of these materials into actual devices is not simple because of some of the demanding requirements such as non – centro symmetric packing of NLO chromophores, low optical losses either absorption or scattering and environmental and photochemical stabilities. The NLO chromophores need to be packed with an ideal orientation in the crystals for even to achieve non – centro symmetry with phase matching conditions [4 – 7]. In organic NLO materials, the structure is decided mostly by the π – π bond system extended over a large length scale of the molecules. This can be very easily manipulated by substitution of electron donating and electron withdrawing groups around the aromatic moieties, which in turn can increase the optical non – linearity [8, 9].

In our present work an attempt has been made to grow single crystals of D – π – A conjugated system of

hexamine: *m* – cresol adducts which is a new organic NLO material. Here hexamine molecule acts as a donor and *m* – cresol molecule acts as acceptor. The material has been characterized by FT – IR and UV – Vis techniques and the powder SHG measurements by Kurtz – Perry Powder technique.

2. Results and discussion

2.1. Material synthesis

The saturated solution of 1:2 mole ratio of hexamine: *m* – cresol was prepared in ethanol. The solution was stirred well and then filtered to remove the impurities. The filtered solution was collected in a 100ml beaker and kept unperturbed at room temperature for slow evaporation. Colorless crystals were harvested after two days. The material crystallizes under orthorhombic system of non – centro symmetric space group Ccc2 whose unit cell parameters are $a = 10.63 \text{ \AA}$, $b = 26.33 \text{ \AA}$ and $c = 7.199 \text{ \AA}$ with $Z = 4$. The hexamine molecule occupies the site of symmetry 2 and is linked to two *m* – cresol molecules via N --- H – O hydrogen bonds [10]. The Powder XRD diffraction pattern for the powder sample was recorded using the instrument Shimadzu XRD 600 diffractometer. The recorded Powder X – ray diffraction pattern is shown in Fig. 1. The sharp and well defined peaks at specific 2θ angles indicate the good crystallinity of the material.

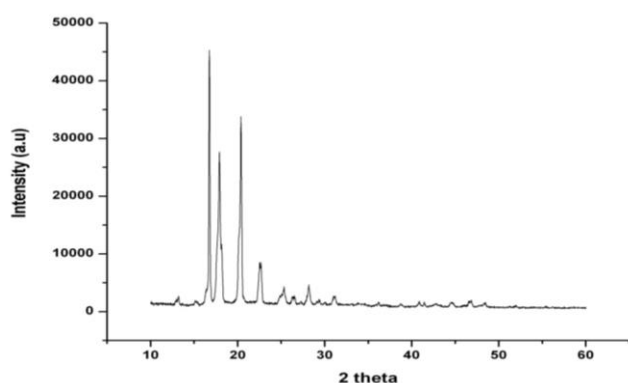


Fig. 1. Powder XRD pattern of hexamine:
m-cresol material.

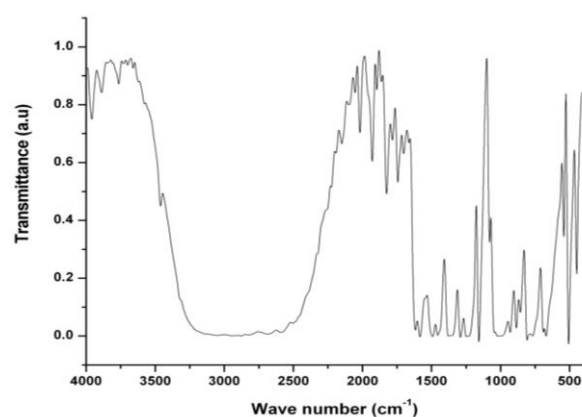


Fig. 2. FT-IR spectrum of hexamine:
m-cresol material.

2.2. FT-IR analysis

The FT-IR spectrum was recorded using a Perkin-Elmer FT-IR spectrum RX1 spectrometer by KBr pellet technique. Fig. 2 shows the FT-IR spectrum recorded in the range 4000 – 400 cm^{-1} at room temperature. The assignments of FT-IR data are given in Table 1. It can be taken as evidence to show the presence of different functional groups of the reactants. The adduct formation that exists between the amino (NH_2) group of hexamine and the OH group of *m*-cresol is due to very high intermolecular hydrogen bonding forces. In pure *m*-cresol the broad OH stretching frequency occurs at 3350 cm^{-1} . This is blue shifted in our synthesized material to 3461 cm^{-1} . This shift comes from the hydrogen bonding of type O-H...N which confirms the hydrogen bonding of type O-H...N. Generally we can expect a proton transfer to occur from phenol to the amino group NH_2 of hexamine when the PKa difference is equal or greater than 2.95 [11]. In our case the PKa difference between hexamine and *m*-cresol is 1.1; hence we infer that an O-H...N hydrogen bonded type has taken place in the material without any proton transfer. FT-IR also supports the non proton transfer nature of the material. The intense multiplet bands in the 3400 – 2150 cm^{-1} region indicate the proton vibration in all hydrogen bonds (Fig. 3). A less intense absorption band below 690 cm^{-1} and another low intensity band above 1824 cm^{-1} are typical features of Fermi resonance. This resonance effect is attributed to medium-strong O-H...N hydrogen bonds with an asymmetric double minimum potential [12 - 14]. In addition the blue shift indicates a charge transfer (CT) from proton acceptor N atom to remote electronegative O atom which gives rise to O-H...N hydrogen bonding [15 - 17]. Thus the material crystallizes as a non proton transferred charge transfer complex.

Table 1. Vibrational assignments of hexamine:
m-cresol material.

Wave number (cm^{-1})	Assignments
3461	Inter molecular hydrogen bonding of OH
1663	Stretch. (C = C) in <i>m</i> -cresol
1661	Stretch. (C = C) in <i>m</i> -cresol
1583	Stretch. (C = C) in <i>m</i> -cresol
1491	Stretch. (C - C) in hexamine
1454	CH_2 scissors in hexamine
1377	CH_2 wagging in hexamine
1247	CH_2 rock in hexamine
1156	Stretch. of C - O in <i>m</i> -cresol
1080	C - H in plane bending
1021	C - H in plane bending
930	CH_3 rock in <i>m</i> -cresol
886 - 690	C - H in plane bend in Phenyl ring
670	N - C - N bend in hexamine.
542	Ring deformation
448	C - C - C out of plane bend in <i>m</i> -cresol

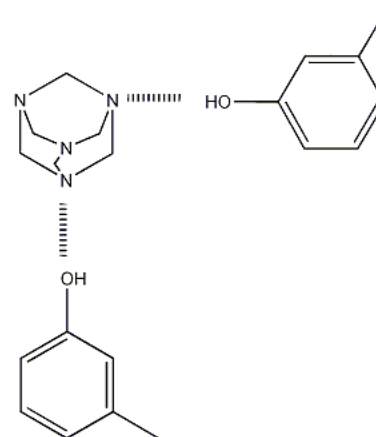


Fig. 3. Molecular structure of hexamine:
m-cresol.

2.3. Factor group analysis

The complex of 1:2 mole ratios of hexamine: *m*-cresol belongs to the non-centro symmetric C_{cc2} space group, with $Z = 4$, which indicates the number of molecules per unit cell. The 54 atoms of hexamine: *m*-cresol in the unit cell give rise to a total 648 modes, which can be characterized according to the C_{2v} factor group of the crystal using standard group theoretical methods [18] based on the literature [19]. The representation corresponding to the total degrees of freedom, Γ_{total} , is given by $162 A_1 + 162 A_2 + 162 B_1 + 162 B_2$ among which the three acoustic modes are $1 A_1 + 1 B_1 + 1 B_2$. The

remaining 645 optical modes are further divided into 576 internal and 69 external modes. Among the 576 internal modes, the irreducible representations for *m*-cresol molecule $4[C_7H_8O]$ is given by $84 A_1 + 84 A_2 + 84 B_1 + 84 B_2$ and the remaining 240 [$60 A_1 + 60 A_2 + 60 B_1 + 60 B_2$] for hexamine $4[C_6H_{12}N_4]$ molecule. All the fundamental lattice vibrations of the hexamine and *m*-cresol molecules, as predicted by the group theoretical method have been listed in Table 2 along with the lattice vibrations of the individual atoms of the present crystal to cross check the correctness of the predictions.

Table 2. Factor group analysis of hexamine: *m* – cresol material.

Factor group species C_{2v}	$4[C_6H_{12}N_4]$		$4[C_7H_8O]$		C	H	O	N	Optical modes	Acoustic modes	Total
	I	E	I	E	C1	C1	C1	C1			
					site	site	site	site			
A1 (IR)	60	3T,3R	84	6T,6R	60	84	6	12	161	1	162
A2 (R,IR)	60	3T,3R	84	6T,6R	60	84	6	12	162	0	162
B1(R,IR)	60	3T,3R	84	6T,6R	60	84	6	12	161	1	162
B2(R,IR)	60	3T,3R	84	6T,6R	60	84	6	12	161	1	162
					240	336	24	48	645	3	648

2.4. UV – Vis analysis

The UV – Vis spectra were recorded in the solvent ethanol for better stabilization of excited states using UV – 1700 series. Since this material is a charge transfer material to identify the solvatochromic behavior we have recorded the spectrum in the liquid state rather than in the solid state. Fig. 4 displays the UV – Vis absorption spectrum of the title material. From the spectrum we identify the peak at 340 nm with less intensity which is attributed to the $\pi \rightarrow \pi^*$ transition. The less intensity of absorption is due to the steric hindrance effect of hexamine. In pure *m*-cresol the maximum absorption peak is found at 282 nm. The contribution towards the bathochromic shift (red shift) indicates that the CT excited state has higher polarization than the ground state. This red shift leads to the higher value of first hyperpolarizability (β) [20]. Further the material shows good optical transmittance in the entire visible region. Therefore this new organic material is most suited for electro – optic modulation [21].

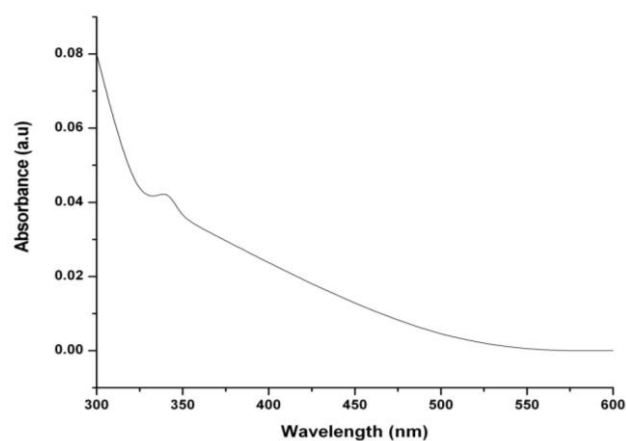


Fig. 4. UV – Vis absorption spectrum of hexamine: *m* – cresol material.

2.5. SHG measurements

The higher NLO response of the material was confirmed by Kurtz – Perry Powder method [22], with KDP as reference material whose output is of the order of 22.4 mV. In this method the crystal was ground into powder of known grain size of 100 – 150 microns and it was packed densely between two transparent glass plates. An input beam of 1064 nm Q – switched laser beam was made to fall normally on the sample cell. The generated

second harmonic signal was passed through a 532 nm narrow pass filter and fed to another channel of power meter. The ratio of fundamental to harmonic intensities determines the efficiency of the sample. The input power of the laser beam was measured to be 1.9 mJ/Pulse. Throughout the experiment the laser power was kept constant. The SHG output of the material has been identified as 42 mV and it has nearly 2 times greater efficiency than KDP.

3. Conclusion

The novel organic NLO material of hexamine: *m* – cresol was synthesized. From the sharp and well defined peaks from the Powder XRD pattern, we confirm the good crystalline nature. FT – IR confirms the linkage of hexamine and *m* – cresol through hydrogen bonding of the type O – H ... N by the shifting of the stretching frequency OH. The blue shift also indicates the charge transfer from N atom to O atom in O – H ... N bonding. Further, the non proton transfer of the material is identified through the broad band in the region 3400 – 2150 cm⁻¹ and the Fermi resonance effects. Factor group analysis is used to predict the 648 possible vibrational modes in the material theoretically. The charge transfer interaction is confirmed through the maximum absorption peak at 340 nm in UV – Vis analysis which is attributed for $\pi \rightarrow \pi^*$ transition. In addition the red shift of this CT band indicates higher value of first hyperpolarizability (β). The absence of absorption peak in the entire visible region indicates the better optical quality of the material. The two times greater SHG efficiency of this material with KDP is confirmed by Kurtz – Perry Powder technique.

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