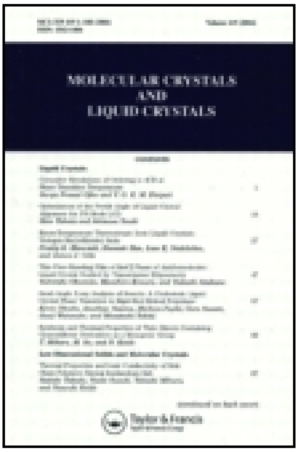

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Crystal Structure and Optical Properties of a New Nonlinear Optical Chalcone Crystal

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Crystal Structure and Optical Properties of a New Nonlinear Optical Chalcone Crystal

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New nonlinear chalcone derivative: 3-(2,3-dichlorophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (DCPP), has been synthesized and crystallized using dimethylformamide as solvent. The lattice parameters for the grown crystals were determined by using single crystal x-ray diffraction analysis; the DCPP crystallizes in the monoclinic system with $P2_1$ space group. The unit cell parameters of the crystal are: $a = 7.4229(2)$ Å, $b = 3.9889(1)$ Å, $c = 21.2685(6)$ Å, $\beta = 98.212(2)$, and $V = 623.29(3)$Å^3. DCPP crystals were characterized by thermal and FTIR and UV-Vis spectral techniques. DCPP crystals are thermally stable up to 146.9°C. The UV absorption cut off wavelength is observed at 350 nm. DCPP crystals generate second harmonics of Nd:YAG laser operating at 1064 nm wavelength. The second harmonic generation (SHG) efficiency of the powdered DCPP sample was measured using Kurtz and Perry technique. The SHG efficiency is found to be equal to that of urea.

Keywords Characterization; crystallization from solutions; nonlinear optic materials

Introduction

Recently, significant research attention has been paid to organic nonlinear optical (NLO) materials due to their large optical nonlinearities and advanced applications in photonics and optoelectronics [1]. Chalcones are interesting organic NLO materials with good crystallizability, high second harmonic generation (SHG) efficiency compared to urea, and optical transparency extending down to the blue region [2–8]. It has been generally understood that the second-order molecular nonlinearity in chalcones can be enhanced by large delocalized π-electron systems with strong donor and acceptor groups [9,10]. The basic strategy of using electron-donor and electron-acceptor substituents to polarize the π-electron system of organic materials has been illustrious for developing the NLO chromophores possessing large molecular nonlinearity, good thermal stability, improved solubility, and processability [11,12]. The SHG efficiency can also be improved by the substitution of a donor group on the para position of the benzoyl group instead of an electron acceptor group [13]. Wu et al. [14] suggested from their theoretical hyper-polarizability studies on these molecules that

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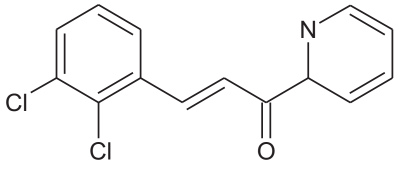
the carbonyl group present at the middle in these molecules splits the conjugated system into relatively two independent parts. Therefore, chalcones can be regarded as cross-conjugated molecules that possess two independent hyperpolarizable parts to have a two-dimensional β character. It was also suggested by Zhao et al. [15] and Wu et al. [16] that electron donors, such as -OCH_3, -CH_3, -Cl and –Br, are the best donor groups for enhancing SHG in chalcones. Several chalcone molecules have been synthesized by many researchers and reported their results on SHG properties [17–19].

In this paper, we present our experimental results on the crystallization, characterization crystal structure, and SHG of chlorine substituted chalcone 3-(2,3-dichlorophenyl)-1-(pyridin-2-yl)prop-2-en-1-one.

Material Synthesis and Crystallization

DCPP was synthesized by a Claisen–Schimidt condensation reaction [20,21]. This is the reaction of substituted acetyl pyridine with substituted benzaldehyde in the presence of an alkali. To synthesize DCPP commercially available AR grade 2-Acetyl pyridine (0.01 mol) and 2,3 dichlorobenzaldehyde (0.01 mol) were dissolved in methanol (60 ml). Sodium hydroxide (5 ml, 20%) was then added dropwise to the solution, and stirred for 2 h. The content of the flask was poured into ice-cold water, and the resulting crude solid was collected by filtration. The compound was dried and re-crystallized twice with dimethylformamide (DMF) solvent. The purity of the compound was checked by thin-layer chromatography. To avoid the formation of microbes charcoal has been added to the solution.

The solubility of the compound was determined by adding the solvent to a known amount of DCPP compound till it completely dissolved. The synthesized DCPP compound is insoluble in water, sparingly soluble in benzene and acetone. It is also moderately soluble in DMF. Crystallization of DCPP was performed by the slow evaporation technique at room temperature by using DMF as a solvent. Solution of DCPP was prepared in a vessel covered with perforated sheet, and kept in a dust-free atmosphere. At the period of super saturation, tiny crystals were nucleated. They were allowed to grow to a maximum possible dimension and then harvested. The schematic diagram of the title compound is shown.



Characterization

CHN Analysis. To confirm the chemical composition of DCPP, carbon (C), hydrogen (H) and nitrogen (N) analysis was carried out on the recrystallized sample using the Elementar Vario EL III CHNS analyzer. The result of the analysis is presented in Table 1. Theoretical values of CHN were found by the molecular formula $C_{14}H_9Cl_2NO$. The experimental and calculated values of C, H, and N agree with each other, confirming the formation of DCPP with composition: $C_{14}H_9Cl_2NO$.

Table 1. CHN Analysis of DCPP

Element	Experimental (%)	Computed (%)
Carbon	60.43	60.46
Hydrogen	3.23	3.26
Nitrogen	5.00	5.04

Density and Melting Point Measurement

The density of the DCPP compound was measured using Archimedes's principle, and it was found to be 1.35 gmcm^{-3}. The melting point, determined by the capillary tube method, was found to be 146.9°C.

Thermal Analysis

Thermal characteristics such as differential thermal (DT) and thermo gravimetric (TG) for DCPP crystal were obtained in the temperature range of 30°C to 800°C under nitrogen atmosphere at a heating rate of 10°C using Perkin Elmer simultaneous TG/DT analyzer. The DT and TG characteristics with different stages of mass losses for DCPP are shown in Fig. 1. In DT curve, only one sharp endothermic peak was observed at 146.9°C, which corresponds to the melting point of the material. The sharpness shows the good crystalline nature and purity of the grown crystal. DCPP sample is thermally stable upto 146.9°C. Beyond that it undergoes a broad endothermic transition, which corresponds to the melting point of the material. Thermo-gravimetric analysis shows the softening of the DCPP around 146.9°C accompanied by a loss of material due to decomposition. There is no phase transition occurred before the melting point.

FT-IR Spectral Analysis

The FT-IR analysis of DCPP was carried out to investigate the presence of functional groups and their vibrational modes. The sample was prepared by mixing DCPP with KBr pellet.

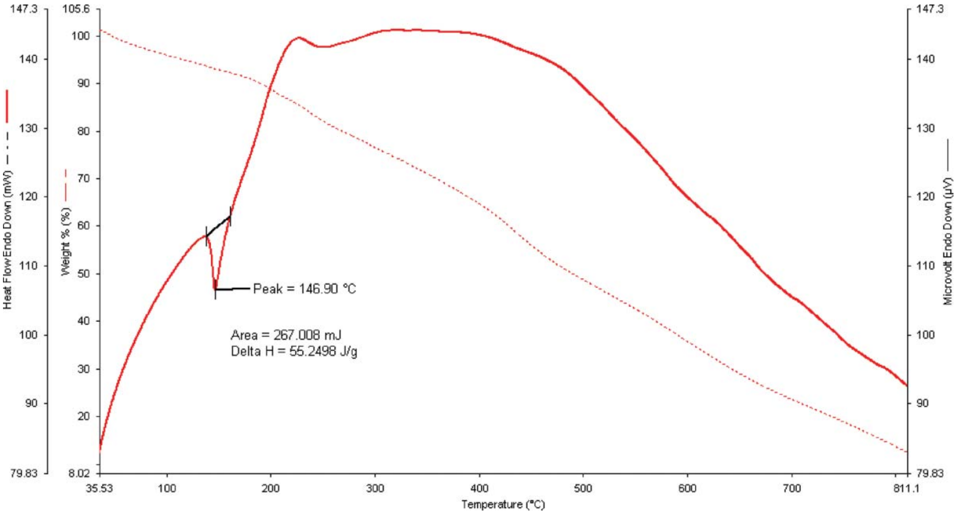


Figure 1. TGA/DTA curve of DCPP crystal.

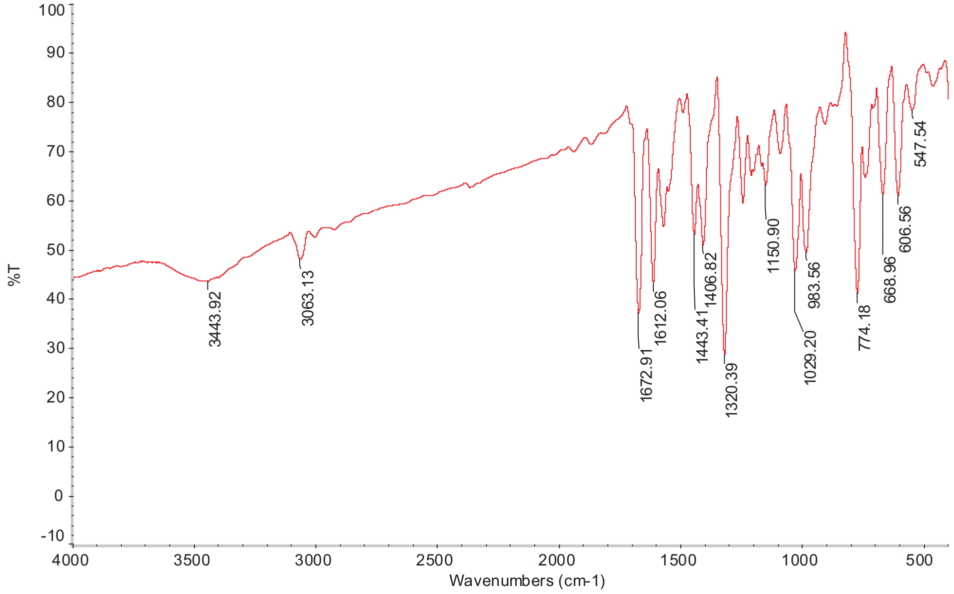


Figure 2. FTIR spectrum of DCPP.

The spectrum was recorded between 400 cm^{-1} and 4000 cm^{-1} using a BRUKER 66V FT-IR spectrometer and the spectrum is shown in Fig. 2. The FT-IR spectrum confirms the formation of DCPP and its characteristic frequencies and the corresponding assignments are recorded in Table 2. In the FTIR spectrum the peak due to aromatic C-H stretching appears as a week absorption band at 3063 cm^{-1} and, hence, the hydrogen bonding interactions should be strong. The sharp absorption band at 1673 cm^{-1} is assigned to C=O stretching vibration. The medium absorption band at 1443, 1407, and strong absorption band at 1320 cm^{-1} attributed to alkyl C-H bending vibrations. The strong absorption band at 1612 cm^{-1} is assigned to aromatic C=C stretching vibrations.

Table 2. Assignment of vibrational frequencies

Wave number (cm^{-1})	Assignment
3443.92	N-H stretching
3063.13	C-H Stretching
1672.91	C=O stretching vibration
1612.02	Aromatic C=C vibration
1443.41, 1406.82 & 1320.39	Alkyl C-H bending vibrations
1150.9	C-H wagging
1029.2	C-Cl stretching vibrations
983.56, 774.18	Characteristic C-H out-of-plane aromatic bending
668.96, 606.56	C-H bending

UV VIS NIR Spectrum

UV–vis–NIR absorption spectrum of the crystal was recorded using a SECOMOM ANTHELIE 70M UV–VIS spectrophotometer in the wavelength range of 200–1000 nm. A solution of DCPP in DMF was placed in a 1 cm cuvette for measurement. The recorded spectrum is shown in Fig. 3. The crystal has a wider transparency range extending into the entire visible and IR region with UV cut off wavelength of 330 nm. Optical transparency is one important parameter that an NLO material possesses. Wider transparency is needed for most of the practical applications. As the visible and near infrared region does not bear any absorption band, the DCPP crystal can be used for NLO applications. At 330 nm, a sharp rise of absorption to maximum was observed indicating a single transition in the near visible region of the spectrum. The sharp rise in absorption at 330 nm suggests similar distribution of photon energies among all molecules of the crystal. The absorption at 330 nm is found to be due to extensive conjugation shifts in electronic spectra of the DCPP crystal, because of this crystal appears with pale yellow color. The absorption at 210 nm may be due to the substitution of chlorine in the benzene ring. The absorption coefficient at 210 nm and 330 nm are calculated using the relation $\alpha = 2.303\left(\frac{\mathrm{A}}{\mathrm{x}}\right)$, where x is the thickness of the sample in cm and A is the absorbance. A is found to be 35 cm^{-1} and 96 cm^{-1} 210 and 330 nm, respectively.

Second Harmonic Generation

A Q-switched Nd:YAG laser with a pulse energy of 4.95 mJ/pulse was used as a source. Microcrystalline 125–250 μm powdered sample of DCPP was tightly packed in a glass capillary and exposed to a fundamental wave with a pulse width of 10 ns, repetition frequency10 Hz, and a wavelength of 1064 nm. A urea crystal, powdered to the identical size of DCPP particle was used as a reference material in the SHG measurement. The generated second harmonic wave of 532 nm was detected by a photomultiplier tube and

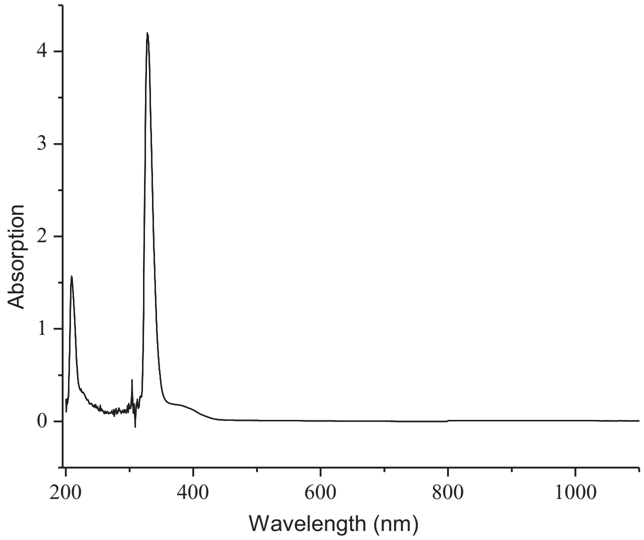


Figure 3. Optical absorption spectrum of DCPP crystal.

Table 3. Crystal structure details of DCPP, (CCDC No: 890494)

Molecular formula	$C_{14}H_9Cl_2NO$
Formula weight	278.12
Crystal shape and colour	Block, Pale Blue
Crystal System	Monoclinic
Space group	$P2_1$
a (Å)	7.4229(2)
b (Å)	3.9889(1)
c (Å)	21.2685(6)
β (°)	98.212(2)
Volume (Å^3), Z	623.29(3), 2
λ (Å)	0.71073 (Mo-K$_\alpha$)
T (K)	296(2)
Reflections measured	11,330
Unique reflections	2613
$R_1(F^2)$, $wR_2(F^2)$ $[I > 2\sigma(I)]$	0.0420, 0.0966
Goodness-of-fit	1.036
Flack parameter	0.10(8)
$\nabla\rho_{\text{min, max}}$ (eÅ^{-3})	−0.195, 0.187

converted into electrical signal. The electrical signal was displayed on the oscilloscope. The signal amplitudes in volts indicate the SHG efficiency of the sample. The SHG conversion efficiency of DCPP crystal was found to be equal to that of urea.

Crystal Structure Determination

Single crystal of DCPP was selected under a polarizing microscope and subjected to single crystal diffraction data collection using an Oxford Xcalibur, Eos(Nova) CCD diffractometer [22]. The X-ray generator was operated at 50 kV and 1 mA using enhanced Mo Kα radiation. The complete datasets were measured with a scan width of 1°. The data reduction, an empirical absorption correction, and space group determination were carried out using CrysAlisPro RED [22]. The crystal structure was solved by direct methods and refined by full matrix least-squares method using SHELXL97 [23], in the WinGx package suite (Version 1.80.05 [24]. The positions of all hydrogen atoms were fixed geometrically and refined isotropically using the riding atom model. Geometrical and intermolecular interactions analyses were done using PARST95 [25] and PLATON [26]. The crystallographic details are provided in Table 3. Tables 5–7 give the list of bond lengths, bond angles, and torsion angles, respectively.

Table 4. Geometries of intermolecular interactions obtained from structural analysis

Interactions	X–H (Å)	H···A (Å)	X···A (Å)	X–H···A (°)	Symmetry
C3−H3···O1	0.930	2.687	3.444(4)	139.0	−X+2, Y+1/2, −Z+1

Table 5. Bond lengths (Å)

Atoms	Length
Cl2-C14	1.734(3)
Cl1-C13	1.729(4)
O1-C6	1.212(3)
N1-C1	1.323(4)
N1-C5	1.340(3)
C1-H1	0.930(3)
C1-C2	1.374(5)
C2-H2	0.930(3)
C2-C3	1.365(4)
C3-H3	0.930(3)
C3-C4	1.380(5)
C4-H4	0.930(3)
C4-C5	1.378(4)
C5-C6	1.496(4)
C6-C7	1.473(4)
C7-H7	0.930(3)
C7-C8	1.312(4)
C8-H8	0.930(3)
C8-C9	1.473(4)
C9-C10	1.395(4)
C9-C14	1.405(4)
C10-H10	0.930(3)
C10-C11	1.383(5)
C11-H11	0.930(4)
C11-C12	1.366(6)
C12-H12	0.930(4)
C12-C13	1.380(5)
C13-C14	1.364(4)

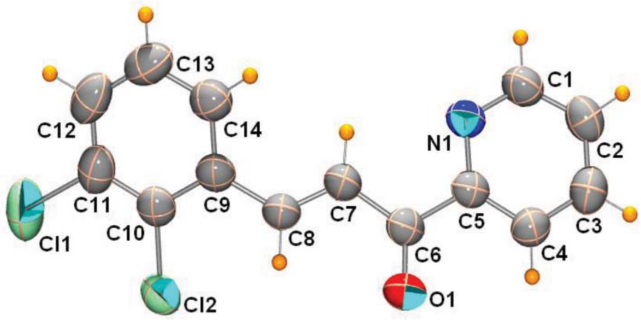


Figure 4. ORTEP of the molecule with 50% ellipsoidal probability and H atoms are shown as small spheres of arbitrary radii.

Table 6. Bond angles (°)

C1-N1 C5	116.3(3)
N1-C1-H1	117.4(3)
N1-C1-C2	125.1(3)
H1-C1-C2	117.5(3)
C1-C2-H2	121.2(3)
C1-C2-C3	117.7(3)
H2-C2-C3	121.1(3)
C2-C3-H3	120.4(3)
C2-C3-C4	119.3(3)
H3-C3-C4	120.4(3)
C3-C4-H4	120.7(3)
C3-C4-C5	118.7(3)
H4-C4-C5	120.6(3)
N1-C5-C4	123.0(3)
N1-C5-C6	116.3(2)
C4-C5-C6	120.7(3)
O1-C6-C5	120.5(3)
O1-C6-C7	121.7(3)
C5-C6-C7	117.8(3)
C6-C7-H7	118.8(3)
C6-C7-C8	122.3(3)
H7-C7-C8	118.9(3)
C7-C8-H8	116.5(3)
C7-C8-C9	126.8(3)
H8-C8-C9	116.6(3)
C8-C9-C10	120.4(3)
C8-C9-C14	121.6(3)
C10-C9-C14	118.0(3)
C9-C10-H10	120.0(3)
C9-C10-C11	120.0(3)
H10-C10-C11	120.0(3)
C10-C11-H11	119.4(4)
C10-C11-C12	121.3(4)
H11-C11-C12	119.3(4)
C11-C12-H12	120.5(4)
C11-C12-C13	119.1(4)
H12-C12-C13	120.4(4)
Cl1-C13-C12	118.1(3)
Cl1-C13-C14	121.0(3)
C12-C13-C14	120.9(3)
Cl2-C14-C9	119.1(2)
Cl2-C14-C13	120.2(2)
C9-C14-C13	120.7(3)

Table 7. Torsion angles

C5-N1-C1-H1	−178.4(3)
C5-N1-C1-C2	1.7(5)
C1-N1-C5-C4	−1.3(4)
C1-N1-C5-C6	178.7(3)
N1-C1-C2-H2	178.6(3)
N1-C1-C2-C3	−1.4(5)
H1-C1-C2-H2	−1.3(5)
H1-C1-C2-C3	178.6(3)
C1-C2-C3-H3	−179.2(3)
C1-C2-C3-C4	0.8(5)
H2-C2-C3-H3	0.8(6)
H2-C2-C3-C4	−179.3(3)
C2-C3-C4-H4	179.5(3)
C2-C3-C4-C5	−0.5(5)
H3-C3-C4-H4	−0.5(5)
H3-C3-C4-C5	179.5(3)
C3-C4-C5-N1	0.8(4)
C3-C4-C5-C6	−179.3(3)
H4-C4-C5-N1	−179.2(3)
H4-C4-C5-C6	0.8(5)
N1-C5-C6-O1	178.6(3)
N1-C5-C6-C7	−1.5(4)
C4-C5-C6-O1	−1.4(4)
C4-C5-C6-C7	178.5(3)
O1-C6-C7-H7	166.4(3)
O1-C6-C7-C8	−13.6(5)
C5-C6-C7-H7	−13.6(4)
C5-C6-C7-C8	166.4(3)
C6-C7-C8-H8	1.9(5)
C6-C7-C8-C9	−178.1(3)
H7-C7-C8-H8	−178.0(3)
H7-C7-C8-C9	2.0(5)
C7-C8-C9-C10	−22.4(5)
C7-C8-C9-C14	157.7(3)
H8-C8-C9-C10	157.5(3)
H8-C8-C9-C14	−22.3(5)
C8-C9-C10-H10	−0.1(5)
C8-C9-C10-C11	179.9(3)
C14-C9-C10-H10	179.7(3)
C14-C9-C10-C11	−0.2(5)
C8-C9-C14-Cl2	−0.3(4)
C8-C9-C14-C13	−179.2(3)
C10-C9-C14-Cl2	179.8(2)
C10-C9-C14-C13	1.0(5)
C9-C10-C11-H11	−179.9(4)
C9-C10-C11-C12	0.1(6)
H10-C10-C11-H11	0.1(6)

(Continued on next page)

Table 7. Torsion angles (*Continued*)

H10-C10-C11-C12	−179.9(4)
C10-C11-C12-H12	179.4(4)
C10-C11-C12-C13	−0.6(6)
H11-C11-C12-H12	−0.6(7)
H11-C11-C12-C13	179.4(4)
C11-C12-C13-Cl1	−178.6(3)
C11-C12-C13-C14	1.4(6)
H12-C12-C13-Cl1	1.4(6)
H12-C12-C13-C14	−178.6(4)
Cl1-C13-C14-Cl2	−0.4(4)
Cl1-C13-C14-C9	178.4(3)
C12-C13-C14-Cl2	179.6(3)
C12-C13-C14-C9	−1.6(5)

The compound (Fig. 4) crystallizes in space group $P2_1$ with $Z = 2$. The second harmonic generation observed in this compound may be attributed to the arrangement of molecules in the $P2_1$ space group. It is interesting to note that the dihedral angle between pyridinyl ring and dichlorophenyl ring is 33.13(1)°, which indicates the nonplanar geometry of the crystal structure. The analysis of weak intermolecular interactions reveals that the crystal structure in the crystalline lattice is held together by weak intermolecular C—H···O hydrogen bond (involving carbonyl oxygen O1 and hydrogen atom H3) along a 2_1 screw axis in crystallographic b axis (Fig. 5 and Table 4). In addition, the crystal structure is further stabilized by very weak aromatic stacking interactions (Fig. 5). Figures 6–8 represent the packing of the molecules when viewed along the a, b, and c axes, respectively.

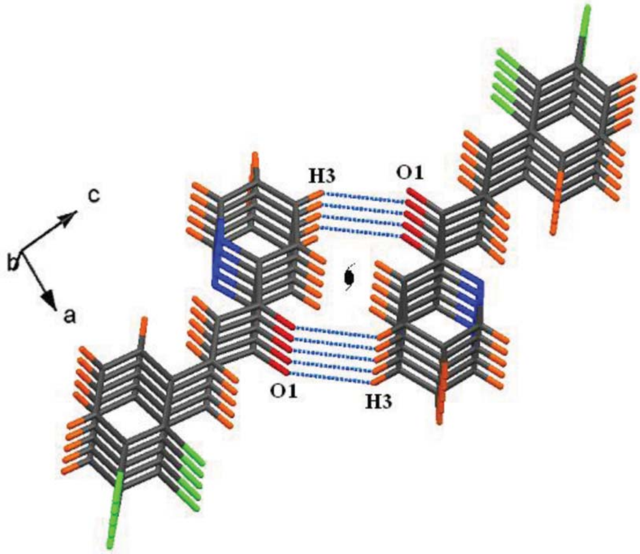


Figure 5. A packing diagram of molecule depicting C—H···O intermolecular hydrogen bond along 2_1 screw axis in crystallographic b axis.

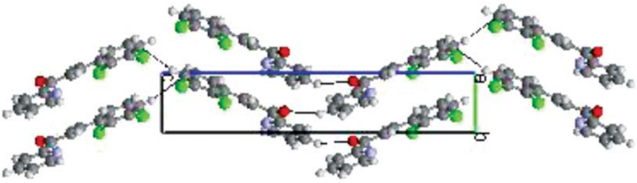


Figure 6. Packing of the molecules when viewed down the a axis.

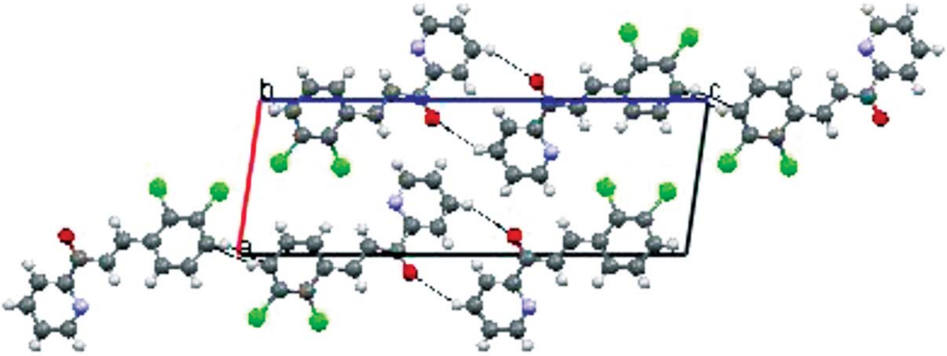


Figure 7. Packing of the molecules when viewed down the b axis.

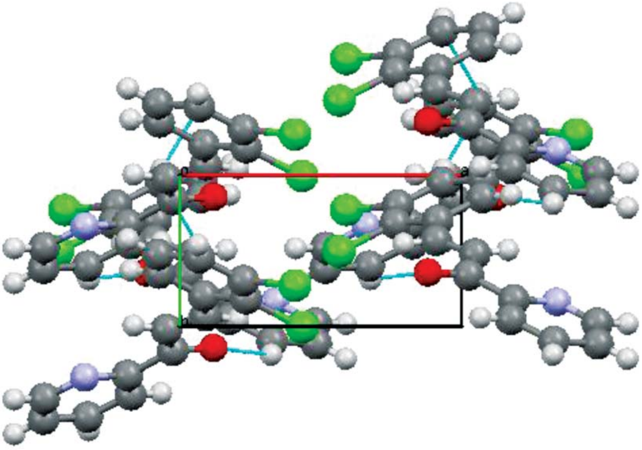


Figure 8. Packing of the molecules when viewed down the c axis.

Conclusions

A new second harmonic generating nonlinear optical chalcone derivative, DCPP was synthesized and crystals of this compound were successfully grown by the solution growth technique at room temperature using DMF as a solvent. The various functional groups present in the newly synthesized crystal were identified using FTIR spectrum and the molecular structure for DCPP was established. Single crystal XRD studies indicated the noncentro symmetric structure of DCPP. The UV VIS NIR spectrum reveals that, in the crystal, the absorption takes place in the UV region and the crystal is transparent in the entire visible and NIR region. DCPP crystal has powder SHG efficiency equal to that of urea. Due to the presence of a wide transparency range and higher second harmonic efficiency, the crystal may be used for nonlinear optical applications. DCPP crystal is thermally stable up to 146.9°C, and can be suggested for NLO applications below this temperature.

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