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RESEARCH ARTICLE

Crystal Growth and Characterization of 1-(2,4-Dichlorophenyl-2yl)-3-(4-hydroxyphenyl)prop-2-en-1-one

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Abstract: A potential crystal for nonlinear optical application and monomer namely 1-(2,4-dichloro-phenyl-2yl)-3-(4-hydroxyphenyl)prop-2-en-1-one (DHPP) was synthesized and grown by slow evaporation technique. The functional groups present in the compound were identified by FTIR spectrum. The optical cut-off wavelength and structural characteristics were analyzed using UV-Vis-NIR spectra and single crystal x-ray diffractometer. The crystal belongs to non centrosymmetric orthorhombic system with space group Pna21 with cell parameters a= 18.015(3) Å, b= 18.218(3)Å, c= 4.1029(6) Å, Z=4 and V= 1346.56Å^3. Thermal studies show that the crystal is stable up to 250 ^{0}C implying good processability.

Keywords: Hydroxychalcone, Crystal growth, Single crystal studies, X-ray diffraction

Introduction

Chalcones are a group of compounds reported to exhibit a wide spectrum of biological activities[1-5]. They are also well explored for their optical applications, because of their distinctive blue light transmittance, excellent crystallizability, relatively good thermal and environmental stability in comparison to other classes of compounds[6-10]. Chalcone derivatives are also reported to act as charge transfer compounds in matrix polymers. Chalcone derivatives are explored for their potential applications in the field of telecommunications, optical switching and optical information storage devices[11]. Phenolic compounds find major utility as a monomer in the syntheses of resole and novolac type resin which could be cured under varied reaction conditions[12]. In this context, we explored novel hydroxy chalcones for their potential use in preparation of resole type resins. Moreover, these monomers offer a direct access to functional polymers which are otherwise difficult

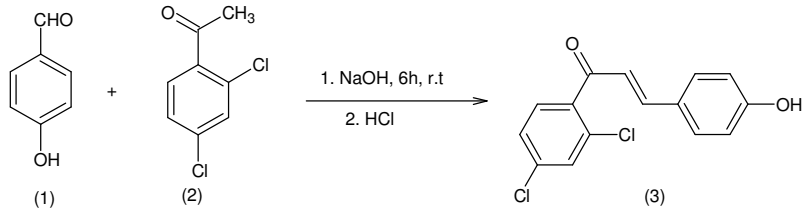
to synthesize. The objective of the present work is to synthesize the chalcone derivative having a hydroxyl function (Scheme 1), growth of single crystals using slow evaporation technique and its characterization by IR, UV-Vis spectroscopy, TGA and single crystal studies.

Experimental

The chemicals and solvents required for the synthesis were obtained from commercial sources and were used without further purification. Melting point of the compound was determined using open capillary method and is uncorrected. Thin layer chromatography was carried out using silica gel plates and ethyl acetate: hexane (2:3) solvent system. Infrared spectra were recorded using SHIMADZU- 8400S FT-IR spectrometer in the wave number range 400-4000 cm^{-1} by KBr pellet technique.

Synthesis of DHPP crystals

The required chalcone (**3**) were synthesized by aldol condensation of equimolar quantities of 2,4-dichloroacetophenone (**2**) with 4-hydroxybenzaldehyde (**1**) using ethanol as solvent[8]. The reaction was carried at room temperature with gradual addition of NaOH solution (Scheme 1). The progress of the reaction was monitored using thin layer chromatography. After continuous stirring for 6 h, the reaction was complete. The solution was then acidified by adding HCl (4 N) till a pH of 3 is obtained. The solid product so obtained was collected by vacuum filtration and is further purified by crystallization from methanol. A dirty yellow slimy product is obtained which upon refrigerating overnight yielded a yellow, powdery product with a melting point of 134-137 °C in 60% yield.



Scheme 1. Synthesis of hydroxychalcone (**3**)

Results and Discussion

Characterization

Fourier transform infrared (FT-IR) analysis

The spectrum shows strong absorption at wave number 1649 cm^{-1} due to the presence of C=O stretch of α,β-unsaturated ketone, confirming the formation of chalcone derivative. A broad band observed at 3300 cm^{-1} corresponds to the presence of phenolic group.

UV-Visible absorption spectrum

UV–Vis–NIR absorption spectrum of the crystal was recorded using a SECOMOM ANTHELIE 70M UV–VIS spectrophotometer in the wavelength range of 200-800 nm. A solution of DHPP in DMF was placed in a 1 cm cuvette for measurement. The recorded spectrum is shown in Figure 1. The crystal has a wider transparency range extending into the entire visible and IR region with UV cut off wavelength of 375 nm. Wider transparency is needed for most of the practical applications. As the visible region does not bear any absorption band, the DHPP crystal can be explored for NLO applications. At 375 nm a sharp

rise of absorption to maximum was observed indicating a single transition in the near visible region of the spectrum. The absorption at 375 nm is attributable to extensive conjugation present in the molecule due to –OH, -CO-CH=CH- and phenyl groups. The absorption at 250 nm may be due to the substitution of chlorine atoms in the benzene ring.

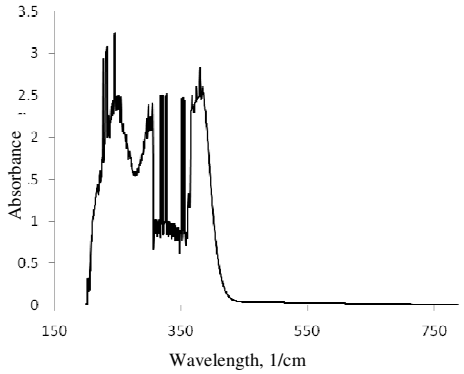


Figure 1. UV-Visible absorption spectrum of DHPP crystal

Thermogravimetric analysis

The thermal property of 1-(2,4-dichlorophenyl-2yl)-3-(4-hydroxyphenyl)prop-2-en-1-one was studied in the powder form by recording the TGA response curve in the temperature range 30 ^{o}C to 580 ^{o}C, at a rate of 10 ^{o}C/min, in air using SHIMADZU Thermal Analyzer (DTG-60). The TGA plot shown in Figure 2 shows good thermal stability for the compound up to 250 ^{0}C.

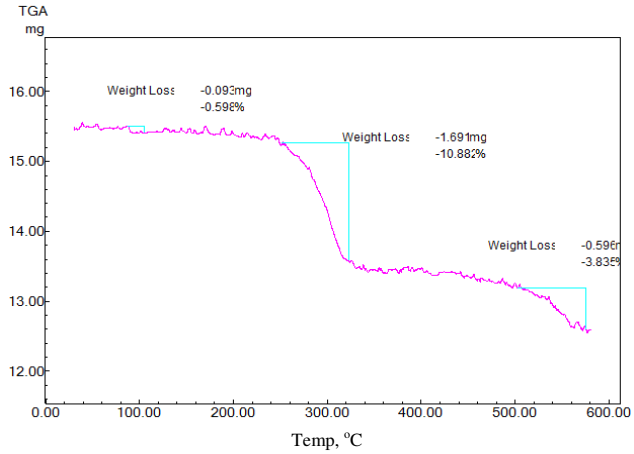


Figure 2. TGA curve of 1-(2,4-dichlorophenyl-2yl)-3-(4-hydroxyphenyl)prop-2-en-1-one.

Single crystal growth and characterization

The solubility studies in different solvents showed that the compound is insoluble in water and easily soluble in *N,N*-dimethylformamide (DMF) with methanol being the optimum solvent as it is moderately soluble. Methanol was used as solvent system to grow single crystals of title compound. A known volume of solvent was taken in a conical flask, which was immersed in a constant temperature bath. The finely powdered sample was added until the dissolution ceased. Then the solution was kept for slow evaporation at room temperature for 72 h.

A good quality single crystal of dimension 0.35x0.25x0.2 mm was used for data collection using Bruker kappa Apex II diffractometer. The data was collected at room temperature using Mo K alpha radiation at a generator setting of 50 KV and 30 mA. Cell refinement was done using APEX2/SAINT. Data reduction was done using SAINT/ XPREP. Multi-scan absorption correction method was followed with reference to SADABS. The structure was solved using SIR92 in Wingx suite and refinements were done with SHELXL-97[13] in the WinGx package suite (Version 1.80.05[14]). The crystallographic details are provided in Table 1.

Table 1. Crystal data and structure refinement for the compound [CCDC deposition No. 905181]

Identification code	Shelxl
Empirical formula	C_{15} H_{10} Cl_2 O_2
Formula weight	293.13
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pna21
Unit cell dimensions	a = 18.015(3) A alpha = 90 deg. b = 18.218(3) A beta = 90 deg. c = 4.1029(6) A gamma = 90 deg.
Volume	1346.6(3) A^3
Z, Calculated density	4, 1.446 Mg/m^3
Absorption coefficient	0.475 mm^-1
F(000)	600
Crystal size	0.40 x 0.35 x 0.30 mm
Theta range for data collection	1.59 to 28.21 deg.
Limiting indices	-23<=h<=23, -23<=k<=24, -5<=l<=2
Reflections collected / unique	6355 / 2332 [R(int) = 0.0407]
Completeness to theta = 28.21	94.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8706 and 0.8327
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2332 / 1 / 177
Goodness-of-fit on F^2	1.135
Final R indices [I>2sigma(I)]	R1 = 0.0504, wR2 = 0.1252
R indices (all data)	R1 = 0.0736, wR2 = 0.1764
Absolute structure parameter	0.06(16)
Extinction coefficient	0.012(3)
Largest diff. peak and hole	0.408 and -0.619 e.A^-3

The title compound exists as the most stable (*E*)-configuration, crystallizes orthorhombic system, Pna21 space group with Z=4. The molecular structure of DHPP with thermal ellipsoid drawn at 50% probability level is shown in Figure 3. The non-centrosymmetric crystal packing of DHPP is consolidated by two weak C-H···O intermolecular hydrogen bond interactions and the corresponding geometric parameters are tabulated in Table 2. Packing of the molecules when viewed along the crystallographic 'c' direction is shown in Figure 4. Anisotropic displacement parameters, hydrogen coordinates, isotropic displacement parameters, list of bond lengths, bond and torsion angles can be

obtained free of cost by referring to CCDC deposition No. 905181. It is interesting to note that the dihedral angle between benzene ring and hydroxyphenyl ring is 49.98°, which indicates the non-planar geometry of the crystal structure. The hydroxyphenyl ring is connected to the phenyl group through the C10-C9=C8-C7-C6 chain with the C=C bond length being 1.329 (8) Å. The analysis of intermolecular interactions reveals that the crystalline lattice is held together by weak intermolecular C–H···O hydrogen bond. The mean plane of phenyl ring (C1-C6) is deviated from a plane (C6-C7-C8-C9) by an angle of 50.56°. In the same way the there is no deviation in the mean plane of hydroxy phenyl ring (C10-C15) and a plane (C6-C7-C8-C9).

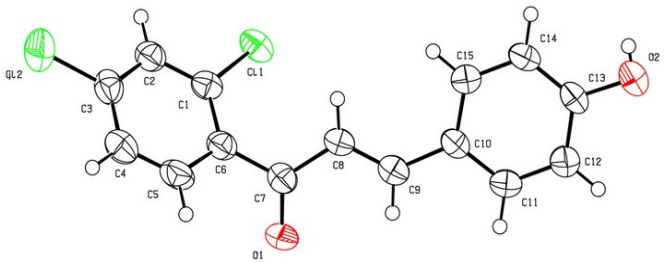


Figure 3. ORTEP of hydroxychalcone drawn with 50% probability

Table 2. Geometries of intermolecular interactions obtained from structural analysis of DHPP crystal

Interactions	X–H (Å)	H···D (Å)	X···D (Å)	X–H··· D (°)	Symmetry
C5-H5…O2	0.930(5)	2.488	3.281(8)	143.3(4)	½-x, ½+y, ½+z
C13- O2…O1	1.365(7)	2.789	3.610(7)	116.5(4)	1/2+x, ½-y, z
O2- H1O2…O1	0.69(6)	2.160	2.789(5)	152(7)	1/2+x, ½-y, z

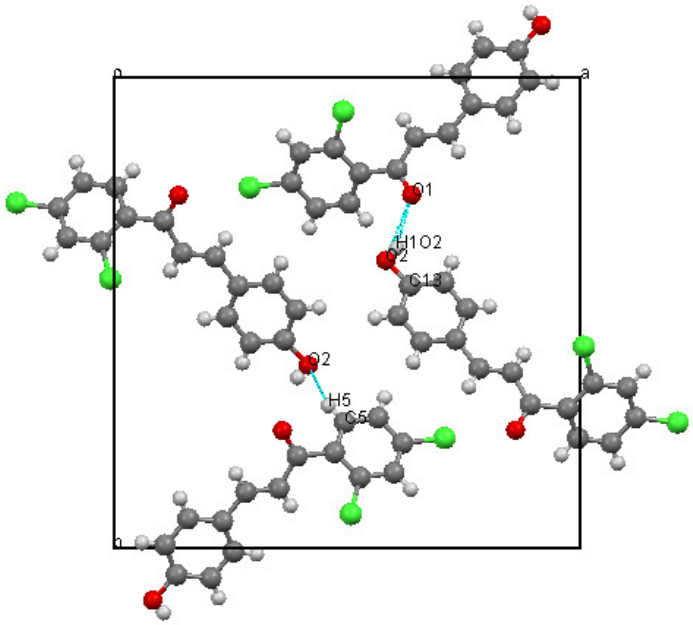


Figure 4. Packing of the molecules when viewed down along crystallographic ‘c’ direction

Conclusion

A novel DHPP compound is synthesized and crystals of this compound were successfully grown by the solution growth technique at room temperature. The various functional groups present in the compound were identified using FTIR spectrum. Single crystal XRD studies indicated the orthorhombic structure of the crystal. The crystal is thermally stable up to 250 ^{0}C. There is ample scope for further study on optical properties and has the potential for the molecule to be explored as a monomer in the synthesis functionalized resole type resins.

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