Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2017, 9(23):59-63
(http://www.derpharmachemica.com/archive.html)

Synthesis, Characterization and Optical Properties of Novel Zinc Doped Chalcone Organic Crystals-1,3-bis(2-methyl benzal)acetone

Ayyadurai GK[1], Thanuja B[1*], Kayalvizhi[1], Charles Kangam[2]

[1]*Department of Chemistry, Sri Sairam Engineering College, Chennai, Tamil Nadu, India*
[2]*Department of Chemistry, Presidency College, Chennai, Tamil Nadu, India*

ABSTRACT

A new nonlinear chalcone organic crystal 1,3-bis(2-methylbenzal)acetone (TAZn) doped with zinc chloride has been synthesized and single crystal has been grown by slow evaporation method. TAZn single crystal of has been subjected to X-ray Diffraction (XRD) analysis to estimate the lattice parameters and the space group. TAZn was found to be crystallizes in the orthorhombic system, with space group Pbca having lattice parameters: a=13.7471(4)Å, b=8.6498(8)Å, c=25.5629(16)Å, α=β=λ=90°. The qualitative analysis of TAZn crystal has been carried out using Fourier Transform Infrared (FTIR) and Raman spectra measurements. The presence of zinc in TAZn crystals was also confirmed by elemental analysis. The Kurtz powder technique was adopted preliminarily to check the optical nonlinearity of the crystal. SHG efficiency of TAZn is found to be 2.5 times that of KDP.

Keywords: Organic crystal, Characterization, XRD, Growth from solutions, NLO

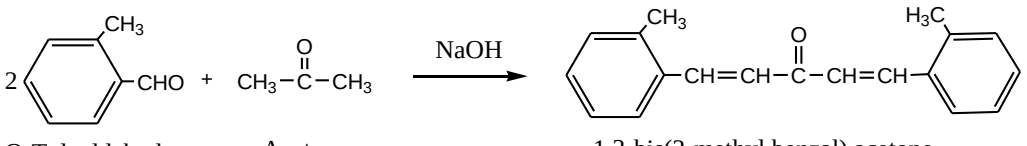
INTRODUCTION

Optical materials with non-linear property play a significant role in the photonics field. Molecular systems with conjugated π-systems are of considerably great interest and they are found to be more potential materials for the applications related to the Nonlinear Optical (NLO) properties [1]. These organic compounds are found to more attracting and considerable attention because of their potential applications in the optoelectronics, photonics, memory devices [2,3]. The substituent attached to the conjugated π-system plays a vital role in terms of NLO activity. The nonlinearity a property of the organic compound was enhanced by the donor-acceptor substituent's attached to the π-conjugated system. Many of the chalcones and its derivatives are reported to show interesting NLO properties [4,5]. The molecular design of TAZn has one electron donor (methyl) and one electron acceptor (carbonyl) moiety which provides with a push-pull configuration, which is a well-known way of enhancing the optical non-linearity's [6,7]. Moreover, the semi organic crystals have good mechanical, chemical, thermal properties compared to organic counterpart. Hence the grown materials are thermally stable and so, attempt has been made to grow semi organic NLO crystal [8]. TAZn crystallizes in the orthorhombic system, with space group Pbca having lattice parameters: a=13.7471(4)Å, b=8.6498(8)Å, c=25.5629(16)Å, α=β=λ=90°.

MATERIALS AND METHODS

Synthesis

0.01 mol of the o-toluvaldehyde and 0.01 mol of the acetone were dissolved in 10 ml of 95% ethanol in a 25 ml Erlenmeyer flask and using magnetic stirrer, the clear solution was stirred. 3.5 ml of 6 M NaOH solution was then added to the reaction flask using a Pasteur pipette. The reaction mixture was stirred for 10 min. The reaction progress and purity of the synthesized compounds was monitored by TLC. The mixture was allowed to cool in an ice-water bath until crystal formation is complete. 2 ml of ice-cold water was added to the flask and filtered [9]. The crystals were washed with 5 ml of water followed by 3-5 ml of ice-cold ethanol (Scheme 1).



O-Tolualdehyde Acetone 1,3-bis(2-methyl benzal) acetone

Scheme 1: Schematic representation of 1,3-bis(2-methyl benzal) acetone

The 1:1 ratio of TAZn and anhydrous zinc chloride was taken in a 100 ml beaker and the mixture was dissolved in 10 ml ethanol and the mixture was allowed for slow evaporation. Needle shape colorless crystal was obtained.

Characterization studies

Single crystal XRD was carried out for grown crystal using Bruker AXS Kappa Apex (II) CCD X-ray diffractometer with MoKα radiation (λ=0.71073 Å). Crystal structure was solved by direct method using SHELXS-97 program [10]. The positions of all the non-hydrogen atoms were included in the full matrix least square efinement using ShelXle-97 program [11]. From the XRD analysis it was found that the TAZn crystal crystallizes in orthorhombic structure with space group Pbca. The elemental analysis (Perkin Elmer optima 5300 DV ICP-OES) of the synthesized crystal revealed the presence of zinc. FTIR spectrum was recorded on a Bruker 66V FTIR spectrometer by the KBr pellet technique in the range 400-4000 cm^{-1} for the identification of the functional groups. Raman spectra were recorded using Bruker RFS 27. The NLO property of the title compound was confirmed using Kurtz and Perry powder technique [12]. A Q-switched Nd: YAG laser beam of wavelength 1064 nm and 10 ns pulse width with an input rate of 10 Hz was used to test the NLO property of the sample.

RESULTS AND DISCUSSION

FTIR spectral analysis of TAZn

The IR spectrum of TAZn taken in KBr pellet. The presence of C=O (Stretching) group shows the peak at 1642 cm^{-1} (Figure 1). The absorption at 3024 cm^{-1} indicates the presence of C-H stretching. The absorption at 2914 cm^{-1} is due to the presence of -CH_3 stretching. The peak at 819 cm^{-1} is corresponds to the aromatic bending. The peak assignments were shown in the Table 1.

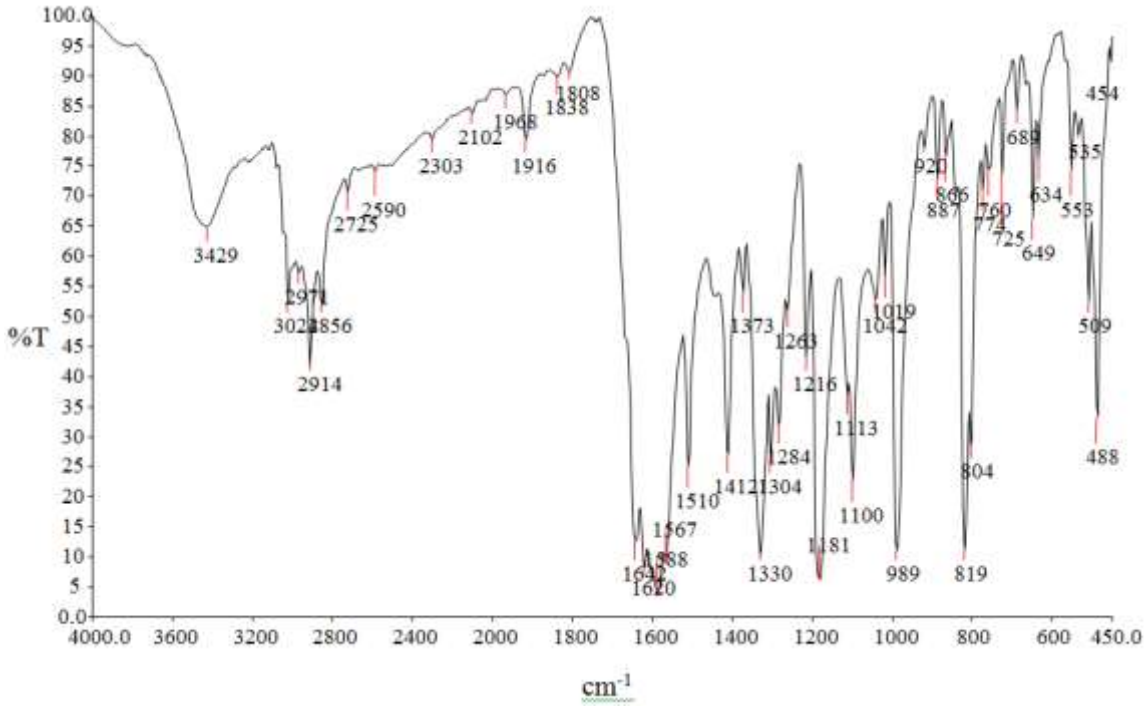


Figure 1: IR spectra of TA and TAZn in KBr pellet

Table 1: IR spectra of TA and TAZn in KBr

Peak assignments	TAZN (cm^{-1})
C-H aromatic stretching	3435
C=O stretching	1662
-C-H stretching	3060
C-H in-plane methyl	2945
di-substituted benzene ring	763

FT-Raman spectral analysis for TAZn

FT-Raman spectrum was recorded using Bruker: RFS 27 (Figure 2). The band assignments were discussed in the Table 2.

Table 2: Raman spectra of TA and TAZn

Peak assignments	Wave number (cm^{-1})
CH_3 symmetrical stretching	1513.00
-C=O stretching	1654.88
C=C stretching	1629.15
Aromatic benzene ring	1170

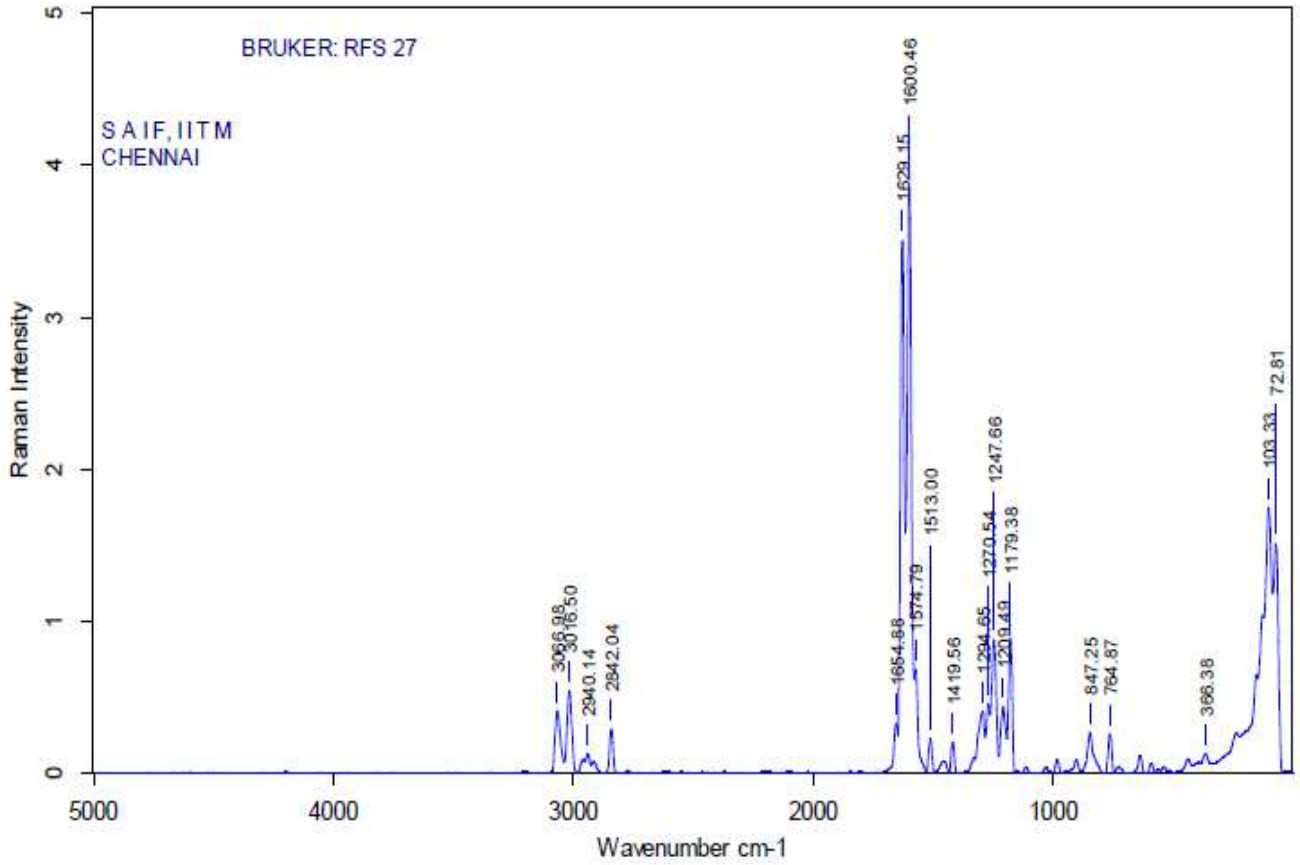


Figure 2: Raman spectra of TA and TAZn

Elemental analysis

The concentration of TAZn was determined by Perkin Elmer optima 5300 DV ICP-OES, the concentration of zinc in the crystal are found to be 0.254 mg/l and 0.005 mg/l respectively and at 206 nm of wavelength. This confirms the presence of Zinc doped in the compound (Table 3).

Table 3: Elemental analysis

Wavelength (nm)	Concentration (mg/l)
206.200	0.254 mg/l
206.200	0.005 mg/l

Single crystal X-ray Diffraction (XRD) analysis

From the single crystal analysis, it was observed that the crystal belongs to orthorhombic crystal system having non-centrosymmetry with Pbca space group. Lattice parameters have been determined as: a=7.4652 Å, b=17.7859Å, c=5.3299Å, α=β=λ=90° and the volume of the unit cell is found to be 707.68 Å3. These values are in good agreement with the reported values: a=13.7471(4)Å, b=8.6498(8)Å, c=25.5629(16)Å, α=β=λ=90° and the volume of the unit cells is found to be 1192.64(14)Å^3. There is an intermolecular hydrogen bonding between the carbonyl oxygen (O_2) of one molecule and the hydrogen of the group of another molecule (Figure 3). The crystal contains –CH_3 group at C14 position act as an electron donor and –CO group (C10-O1) act as electron acceptor, which contributes to large second order optical nonlinearity arising from the intramolecular charge transfer between the two groups opposite nature. The details of crystal data, parameters used for data collection are summarized in Table 4.

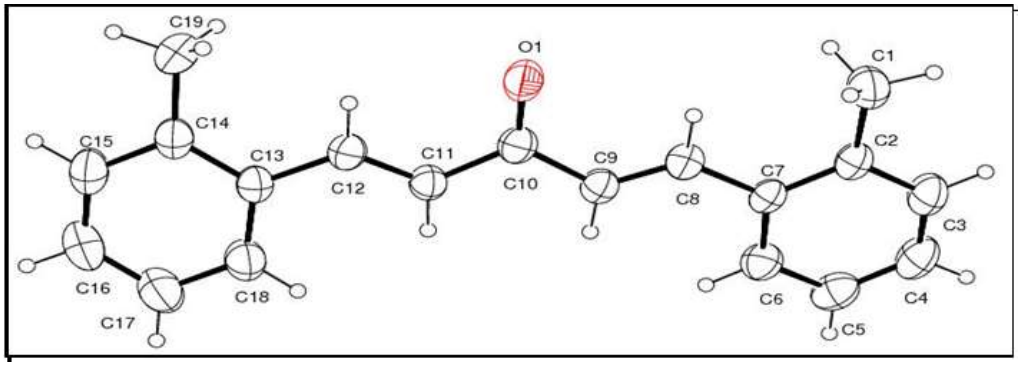


Figure 3: ORTEP view of TAZn

Table 4: Crystal data and structure refinement of TAZN

Identification code	ShelXle
Empirical formula	$C_{19}H_{18}O$
Formula weight	262.33
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a=13.7471(4)Å, α=90°
	b=8.6498(8)Å, β=90°
	c=25.5629(16)Å, λ=90°
Volume	3039.7(4) A^3
Z, Calculated density	8, 1.146 Mg/m^3
Absorption coefficient	0.069 mm^-1
F(000)	1120
Crystal size	0.30 × 0.15 × 0.10 mm
Theta range for data collection	2.18-21.05°
Limiting indices	-9 < = h < = 13, -7 < = k < = 8, -25 < = l < = 25
Reflections collected/Unique	9572/1643 [R(int)=0.0384]
Completeness to theta=21.05	99.80%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9989 and 0.9658
Refinement method	Full-matrix least-squares on F^2
Data/Restraints/Parameters	1643/0/182
Goodness-of-fit on F^2	1.066
Final R indices [I > 2 sigma (I)]	R1=0.0405, wR2=0.0972
R indices (all data)	R1=0.0701, wR2=0.1175
Largest diff. peak and hole	0.089 and -0.117 e.A^-3

Optical absorption

In order to identify the suitability of the TAZn crystal for optical applications. UV-Visible spectrum was recorded. From the spectrum, it is evident that the grown crystal has a very low cutoff wavelength of 240 nm. There is no absorption in the visible region (Figure 4). This lower cutoff is well suited for SHG and other applications in green wavelength region. The characterized absorption peak observed at 270 nm is due to the electron n → π^* transition. Between 400-1000 nm there is no strong absorption which confirms that the TAZn crystals are useful for the SHG application

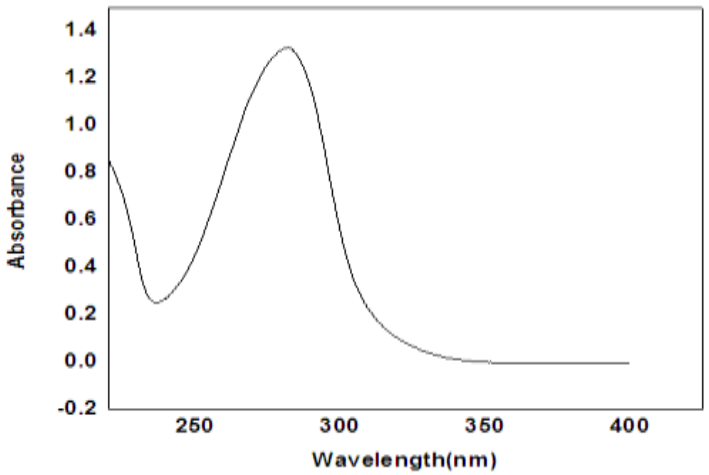


Figure 4: UV spectra of TA and TAZn

Nonlinear optical studies

The NLO behaviour of the title compound was subjected to the Kurtz and Perry powder technique. The SHG test on the TAZN crystal was performed by Kurtz powder SHG method. The powdered sample of TAZN crystal was illuminated using the fundamental beam of 1064 nm from Q-switched Nd: YAG laser. KDP sample was used as reference material. The SHG signal generated in the crystalline sample was confirmed from the emission of green radiation, which was finally detected by the photomultiplier tube and displayed in the oscilloscope (CRO). The measured SHG efficiency of TAZN crystal was 2.5 times that of KDP which indicates the suitability of TAZn crystals for used in the field of photonic and NLO applications.

CONCLUSION

TAZn single crystal was synthesized and single crystal was obtained by a slow evaporation method and confirmed by single crystal XRD analysis. The concentration of zinc in the crystal was experimentally determined by Perkin Elmer optima 5300 DV ICP-OES. This confirms the presence of zinc doped in the compound. The SHG efficiency of the grown crystals is about 2.5 times higher than that of KDP sample which also confirmed by the absence of absorption in the visible region between 400-1000 nm. This property was found to useful for SHG applications.

ACKNOWLEDGEMENT

The authors are grateful to acknowledge SAIF, IIT-Madras for Supporting in all the spectroscopic studies. The authors also acknowledge Sri Sairam Engineering College for continuous support to carry our work.

REFERENCES

[1] P. Santhana Raghavan, P. Ramasamy, Recent Trends in Crystal Growth, Pinsa 68, New Delhi, **2002**, 235.
[2] S. Boomadevi, H.P. Mittal, R. Dhanasekaran, *J. Cryst. Growth*., **2004**, 261, 55.
[3] G. Anandha Babu, S. Sreedhar, S. Venugopal Rao, P. Ramaswamy, *J. Cyrst. Growth.*, **2010**, 312, 1957.
[4] R. Gandhimathi, G. Vinitha, R. Dhanasekaran, *J. Cystallisation Process and Technology.*, **2013**, 3, 148.
[5] A.B. Sawant, R.S. Nirwan, *J. Pure Appl. Phys.*, **2012**, 50, 308.
[6] D.R. Kanis, M.A. Ratner, T.S. Marks, *Chem. Rev*., **1994**, 94, 195.
[7] H.S. Nalwa, S. Miyata, Nonlinear optical Properties of Organic Molecules and Polymers, CRC Press, Boca Raton, Florida, **1996**.
[8] H. Ringertz, *Acta Crystallogr. B.*, **1971**, 27, 285.
[9] D.S. Noyce, W.A. Pryor, *J. Am. Chem. Soc*., **1958**, 81, 618.
[10] G.M. Sheldrick, Program for solution of crystal structure, University of Gottingen, Germany, **1997**.
[11] G.M. Sheldrick, Program for solution and refinement of crystal structure, University of Gottingen, Germany, **1997**.
[12] S.K. Kurtz, T.T. Perry, *J. Appl. Phys*., **1968**, 39(8), 3798.