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Growth and Characterization of 1-(2,4-dichlorophenyl)-3-(4-dimethyl amino- phenyl)-2-propenone : A New Nonlinear Optical Chalcone

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Abstract

The single crystals of organic nonlinear optical material 1-(2, 4-dichlorophenyl) -3-(4-dimethyl amino- phenyl)-2-propenone (DDAP) were grown by solvent evaporation technique using ethanol as solvent. The grown crystals were characterized by IR, ^{1}H NMR and single crystal X-ray crystallography. The DDAP crystals crystallise in the monoclinic system with space group $P2_1/C$. The UV – VIS spectrum shows a cut – off wavelength less than 500nm. The second harmonic generation efficiency was found to be 0.07 times that of KDP.

Keywords: A1. Optoelectronics; A2. Evaporation technique; B1. Methyl groups; B2. Bond lengths

Introduction

Optoelectronics has stimulated the search for highly nonlinear organic crystals for efficient signal processing [1-3]. In recent years, organic Non Linear Optical (NLO) materials have been the subjects of intensive study because of their advantages in comparison with currently used inorganic materials [4]. To exhibit NLO properties, organic molecules should contain a polar and highly conjugated Π -electron system terminated with electron donor and acceptor groups. In these categories, chalcone derivatives are one of the organic compounds with excellent NLO properties [5]. In this paper, the results of the studies on DDAP synthesis and its characteristics are described.

Experimental Procedure

Material Synthesis and Crystal growth

A mixture of Dichloroaceto phenone (0.01 mol) and N,N-di methyl benzaldehyde(0.01 mol) is taken in a conical flask. A solution of Potassium hydroxide (0.01 mol) was added slowly. The mixture is stirred well, the precipitated solid was filtered and recrystlised from ethanol.

Good quality crystals of the title compound were grown by slow evaporation technique [6-8] using ethanol as the solvent. Laboratory grown crystals of DDAP is shown in Fig.1

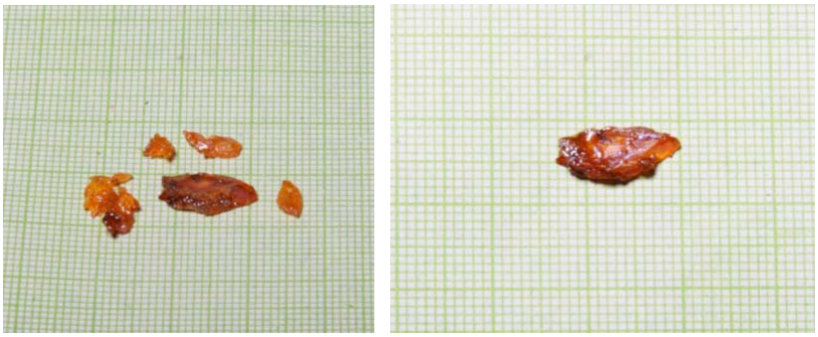

Fig .1 Laboratory grown crystals of 1-2(2,4-dichlorophenyl -3-(4-Dimethyl amino-phenyl) propenone(DDAP)

The chemical structure of DDAP is shown in Fig.2

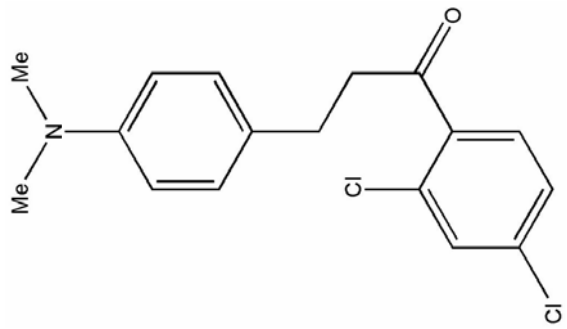

Fig.2. Schematic diagram of 1-2(2,4-dichlorophenyl -3-(4-Dimethyl amino-phenyl)propenone

Crystal characterization

NMR spectrum

The formation of DDAP was confirmed by ^{1}H NMR is shown in Fig. 3. The NMR shows a signal at δ, 3.033 corresponding to two methyl groups attached to N-atom and integrating for six protons. The chalcone protons appeared as two distinct

doublets centered at δ, 7.319 and δ,6.859 with a coupling constant of 15.9 Hz, thus supporting the trans geometry of the chalcone. N, N- dimethylaminophenyl protons appeared as another doublet at δ,6.728 with a coupling constant of J = 8.7Hz. Remaining two protons of this moiety appeared together with 2 protons of dichlorophenyl moiety as a complex multiplet in the region δ, 7.293- 7.490. A singlet observed at δ,7.576 is due to remaining one proton of dichlorophenyl ring.

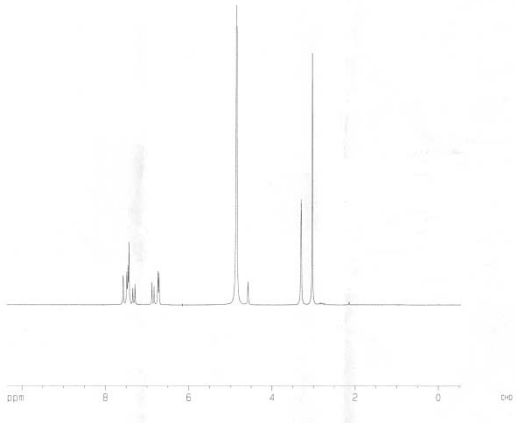

Fig.3

FTIR spectral analysis

In order to qualitatively analyze the presence of functional groups in DDAP, Fourier Transformation Infrared (FTIR) spectrum was recorded (Fig.5) in the region 500 to 4000cm^{-1} using the Thermo Nicolet, Avatar 370 spectrometer. The sample used was in pellet form in KBr. The characteristic absorption peaks were observed in the range from 500 to 4000 cm^{-1} is shown in fig.5. The peak due to aromatic H is at 3080cm^{-1}. The peak at 2856 is due to C-H stretch of CH_3 groups. The chalcone C-H C=O stretching is observed at 1638 cm^{-1}. The aromatic C=C stretching is observed at 1523 cm^{-1}.

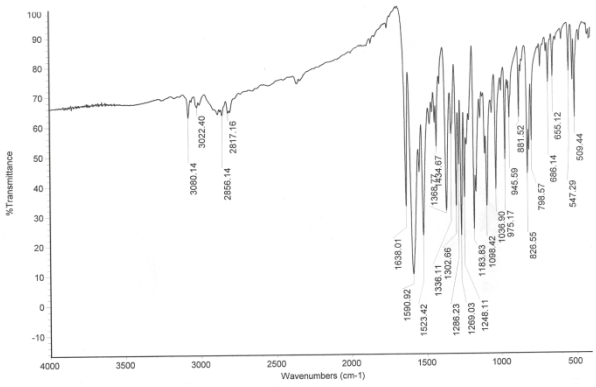

Fig .5

Single crystal XRD

The intensity data were collected using a Bruker SMART CCD diffractometer [9, 10]. The structure was solved using SHELXS-97 and refined using SHELXL-97 [11-13] and the cell parameters obtained in this study is shown in Table1. The molecular structure of DDAP is shown in fig.5

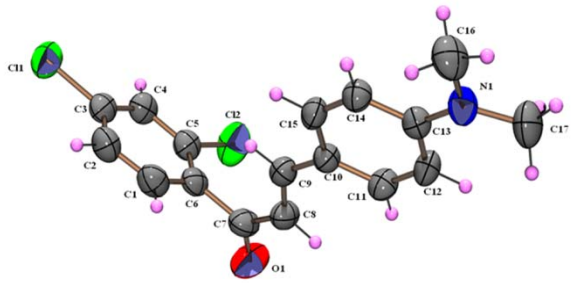

Fig.5

Table.1 : Single crystal XRD data of DDAP

Formula	C17H15Cl2NO
Formula weight	320.20
Crystal system	Monoclinic
Space group	$P2_l/C$
a	8.5741 (19)A˚
b	12.706 (3)A˚
c	14.671(3)A˚
V	1559.5(6)A˚^{3}
Z	4
D (calc)	1.364Mgm^{-3}

The packing diagram of DDAP generated using ORTEP-3 is shown in fig.6 and the corresponding hydrogen bond parameters are given in Table2.

Table 2 : Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12···O1^1	0.93	2.55	3.252 (3)	132

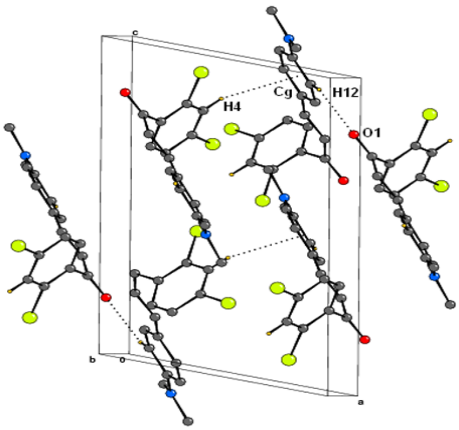

Fig.6

Symmetry codes: (i) −*x*, *y*+1/2, −*z*+1/2.

D and A are donor and acceptor respectively.

All the H atoms were located and refined isotropically resulting in C—H bond lengths of 0.93 (3)–0.97 (3) Å. [14]

Result and discussion

Conversion efficiency

The Second Harmonic Generation (SHG) intensity of the DDAP crystals was measured using the powder technique developed by Kurtz and Perry [15]. The crystal was powdered and densely packed in a capillary. An Nd: YAG laser beam of wavelength 1064 nm, pulse width 8ns and repetition rate 10 Hz was made to fall normally on the sample in the capillary tube. The second harmonic signal was detected by a photo multiplier tube (Hamamatsu R2059) and displayed on a storage oscilloscope (Tektronix TDS 3052B). The SHG conversion of the newly grown DDAP crystal was weak and was found to be 0.07 times that of KDP. However by using synthetic Chemistry and by adding suitable substitution compound it is possible to engineer the structure of molecules to enhance the conversion efficiency [16-20].

Conclusion

Good quality transparent crystals of DDAP were grown in the laboratory by slow evaporation technique. The formation of the compound was confirmed by the spectral analysis like FTIR and NMR. Though the title compound shows weak SHG conversion efficiency, it is possible by using synthetic chemistry to engineer the structure of molecules to enhance the conversion efficiency. Many chalcone like 4-CH_3 – 2,4-Dichloro Chalcone, 2- Bromo – 1-(4-methylphenyl) - 3-[4-(methylsulfanyl) phenyl]prop-2-en-1-One etc are reported to be of having good SHG property when compared to that of urea . By finding suitable substitution molecule to the DDAP

which is a chalcone, π conjugate D-A-D combination can be strengthened. Chalcone with π conjugate electrons reported to be of exhibiting good SHG conversion efficiency.

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References

[1] Navin N. Bappalige *et al* International J. of Pure and App. Phy. Volume 6, Number 2 (2010), pp. 151–156
[2] N. Bloembergen, Non-linear Optics, Benjamin, New York 1965
[3] J. L. Stevenson and A. C. Skapski 1972.,J. Phy.C: Solid state Phys.SL233-L236. 17(5 sept 1972)
[4] J.Zyss,Molecular Nonlinear optics Materials, Physics and devices, Academic Press/Harcourt Brace and Jovanovich, New York,p.479(1994).
[5] P.S Patil, J.B.J The, H.K.Fun, I.A.Razak and Dharmaprakash,Acta Cryst.E 62.o896,(2006)
[6] H. S. Nagaraja, V. Upadhyaya, P. M. Rao, P. S. Aithal, A. P. Bhat; J. cryst. Growth.193(1998)674.
[7] H. S. Nagaraja; Ph, D. Thesis, Mangalore University, 2001
[8] S . G. Prabhu :Ph. D Thesis, Mangalore University 2001
[9] Bruker (2004). *SMART* (Version 5.628) and *SAINT* (Version 6.45a).
[10] BrukerAXS Inc., Madison, Wisconsin, USA.
[11] Farrugia, L. J. (1999). *J. Appl. Cryst.* 32, 837–838.
[12] Kon, G. A. R. & Nanji, E. R. (1933). *J. Chem. Soc. Trans.* 2, 2434.
[13] Linstead, R. P. (1941). *J. Chem. Soc.* 457.
[14] Bappalige *et al* Acta Cryst.. E65, o1266 (2009).
[15] SK.Kurtz, T.T. Perry,J.Appl.Phys.39(1968)3798.
[16] P.S. Patil,S,M.Dharmaprakash and Hoong – Kun Fun , B.K.Sarojini, B.Narayana and A.Mithun . Proceedings of National Conf. on emerging trends in phys., Electonics and eng.sciences Sept-2006, Mysore,India.
[17] M. Kitazawa, R. Higuchi, M. Takahashi, T. wada and H. Sasabe; Appl.Phys Lett.64(1994)2477
[18] H. Endoh, M. Kawaharada and E. Hasegawa; Appl.Phys.Lett.68(1996)293
[19] P. S. Aithal and P. M. Rao; J. Cryst Growth.153(1995)60
[20] J. Zyss; D. S. Chemla and J. F .Nicoud; J.Chem.Phys. 74(1981)4880.