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Synthesis, Growth, Characterization and Comparative Thermal Studies of Novel Non-linear Optical Chalcone Derivative: (E)-1-(2-hydroxyphenyl)-3-(4-Methoxyphenyl) prop-2-en-1-one

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Abstract: The novel organic non-linear optical material, (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one has been synthesized by standard method. 2-Hydroxy acetophenone was made to undergo Claisen-Schmidt condensation with anisaldehyde to form corresponding chalcone. The newly synthesized compound was characterized by spectral analysis. Its thermal properties like thermal stability and phase transitions have been studied in oxygen and nitrogen atmosphere in the temperature range 30 to 850 °C by Thermogravimetric analysis (TGA), Differential thermal analysis (DTA), and Differential scanning calorimetric (DSC) techniques. Single crystal of title compound was grown by slow solvent evaporation technique at room temperature. The grown crystal was characterized by Powder-XRD study.

Key words: Thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetric (DSC), powder-XRD.

1. Introduction

There is currently much interest in organic NLO materials. Aromatic compounds with delocalized π-electrons systems and large dipole moments have been synthesized to improve nonlinear susceptibilities and their large second or third order hyperpolarizabilities compared to inorganic NLO materials [1, 2]. Owing to the high polar nature they often tend to crystallize as long needles or thin platelets [3]. Among several organic compounds reported for the simple harmonic generation (SHG) applications, chalcone derivatives are among the notable materials for their excellent blue light transmittance, good crystal stability, large NLO coefficient and relatively short cutoff wavelengths of transmissions [4-6]. It is observed that substitution on either of the phenyl rings greatly influence non-centrosymmetric crystal packing. It is speculated that in order to improve the activity more bulky substituents should be introduced to increase the spontaneous polarization of acentric crystal [7]. The molecular hyperpolarizability β, is strongly influenced not only by the electronic effect but also by the steric effect of the substituents [8]. Prompted by this and in continuation of our quest to synthesis the newer materials [9, 10] which can find use in photonics industries, many biologicals and medicinal applications, we have synthesized present chalcone.

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Chalcones are 1,3-diphenyl-2-propene-1-one, in which two aromatic rings are linked by a three carbon α, β-unsaturated carbonyl system [11]. These are abundant in edible plants and are considered to be precursors of flavonoids and isoflavonoids. Chalcones possess conjugated double bonds and a completely delocalized π-electron system on both benzene rings. Molecules possessing such a system have relatively low redox potentials and have a greater probability of undergoing electron transfer reactions [12]. Chalcones, either natural or synthetic, are known to exhibit various biological activities [13], such as antioxidant [14], anti-inflammatory [15], antimalarial [16], antileishmanial [17], anticancer [18] and antitumor [19] etc. In addition, chalcones are very important compounds as a Michael acceptor in organic syntheses.

In this paper, we report the synthesis, growth, characterization and comparative thermal studies of NLO chalcone derivative (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one.

2. Experiment

The (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one (chalcone) was synthesized by the commercially available AR-grade Anisaldehyde, 2-Hydroxy acetophenone and ethanol (99%) by Claisen-Schmidt condensation method [9]. This is the reaction of substituted acetophenone with benzaldehyde in presence of an alkali. The mixture of substituted acetophenone (0.01 mol) and Anisaldehyde (0.01 mol) was stirred in ethanol (20 mL) and then an aqueous solution of NaOH (40%) was added to it with constant stirring till red mass was obtained. The mixture was kept overnight at room temperature and then it was acidified with cold conc. HCl. The chalcone derivative precipitates out as solid. It was then filtered and washed with 10% $NaHCO_3$ and dried. The product was recrystallized two times with ethanol [10].

The reaction scheme for preparation of chalcone is shown in Fig. 1. The characterization data such as melting point, percentage yield and elemental analysis are given in Table 1. The melting point was determined by open capillary method and it may be uncorrected. The elemental analysis performed on Thermo-Finnigan, Italy (Flash Ea 112 Series) elemental analyzer at sophisticated analytical instrumental facility (SAIF), IIT Powai, Mumbai.

3. Spectral Studies

3.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FT-IR spectrum of the synthesized material was recorded in the wave number range 400-4000 cm^{-1} by KBr pellet technique by Shimadzu FT-IR detector (FT-IR 8101A) and DR 8031 spectrophotometer.

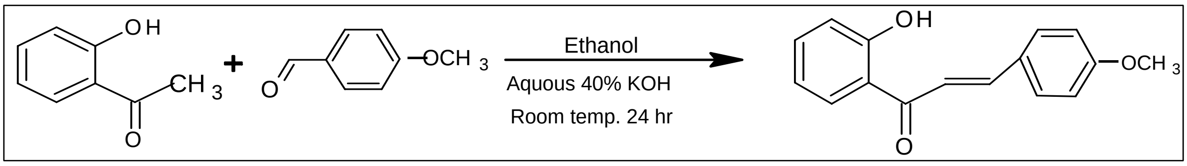


Fig. 1 Synthesis of chalcone.

Table 1 Physical characterization data of chalcone.

Compound name	(E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one (2-hydroxy-4-methoxy phenyl prop-2-en-1-one)	
Molecular formula	$C_{16}H_{14}O_3$	
Molecular weight	254	
Percentage yield	80%	
Melting point	88-100 °C	
Elemental analysis(calculated)	C = 74.238%	H = 5.111%
Elemental analysis(observed)	C = 75.57%	H = 5.55%

The FT-IR spectrum is shown in Fig. 2. The various functional groups present in the title compound were identified and chemical structure was confirmed on the basis of IR spectrum. The characteristic IR absorption bands observed are consistent with the functional groups present in the compound and the assigned values are as shown in Table 2.

3.2 H^1-NMR Analysis

Nuclear magnetic resonance (NMR) spectrum was recorded to evaluate the presence of various type of proton in titled compound. The NMR spectrum of the title compound in DMSO solvent was recorded using Mercury plus 300 MHz NMR Spectrometer (Varian, USA) at sophisticated analytical instrumental facility (SAIF), IIT Powai, Mumbai. The recorded NMR spectrum is shown in Fig. 3.

The H^1-NMR Spectrum shows, multiplet for aromatic protons at δ = 6.9-7.11 ppm, a singlet resonated at δ = 7.98 ppm was attributed for H-α. A doublet signal at lower field δ = 7.44 was attributed to H-β which was coupled with H-α in a trans relationship. A doublet of doublets signal appeared at δ = 7-6 ppm was ascribed for H-2 and H-6.

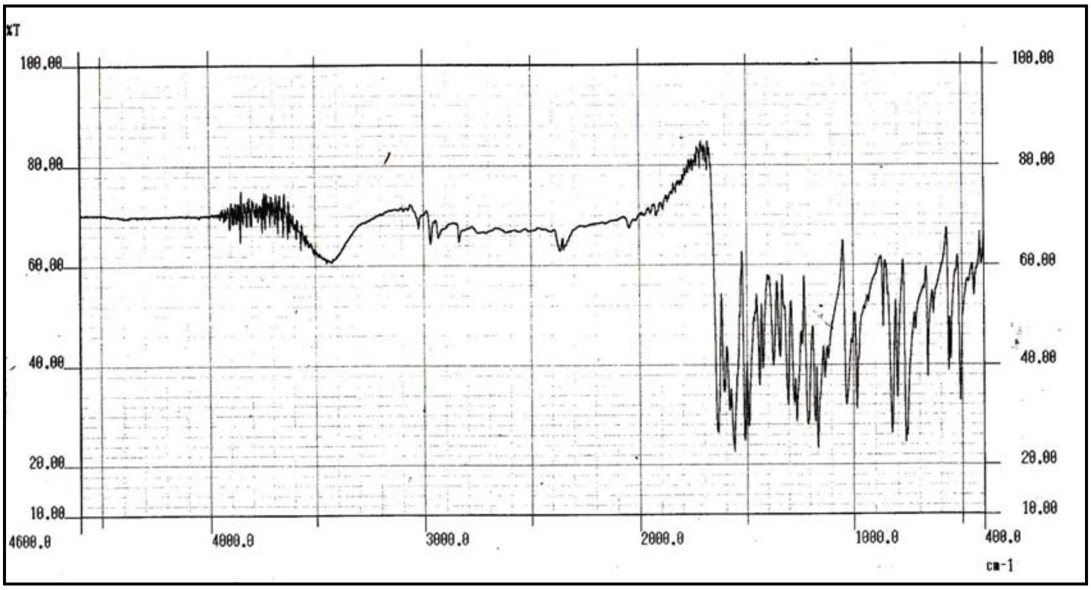


Fig. 2 FT-IR spectrum of (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one.

Table 2 Functional groups assignment of (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one from FT-IR spectrum.

Assignment	Frequency (cm^{-1})
Phenolic-H	
bonded-OH(broad)	3,410 (Strong, broad)
C-H(str)	3,100 (m)
=C-H(str)	2,970 (w)
-C-H(str)	2,934 (m)
C=O(str)	1,686.8, 1,718.0 (s)
C=C(str) chalcone	1,637 (s)
C-O(str)	1,032.0 (s)
Ar. C=C(str)	1,608, 1,583.7(s)
=C-O(str)	1,174.8(s)
-C-H(bending)	1,423.6(s)
C-H(def)	1,441.0(m),1,375.4(s), 1,342.6 (s)
Ar. =C-H (def)	802.5 (m)
=C-H (def)	985.7 (m)

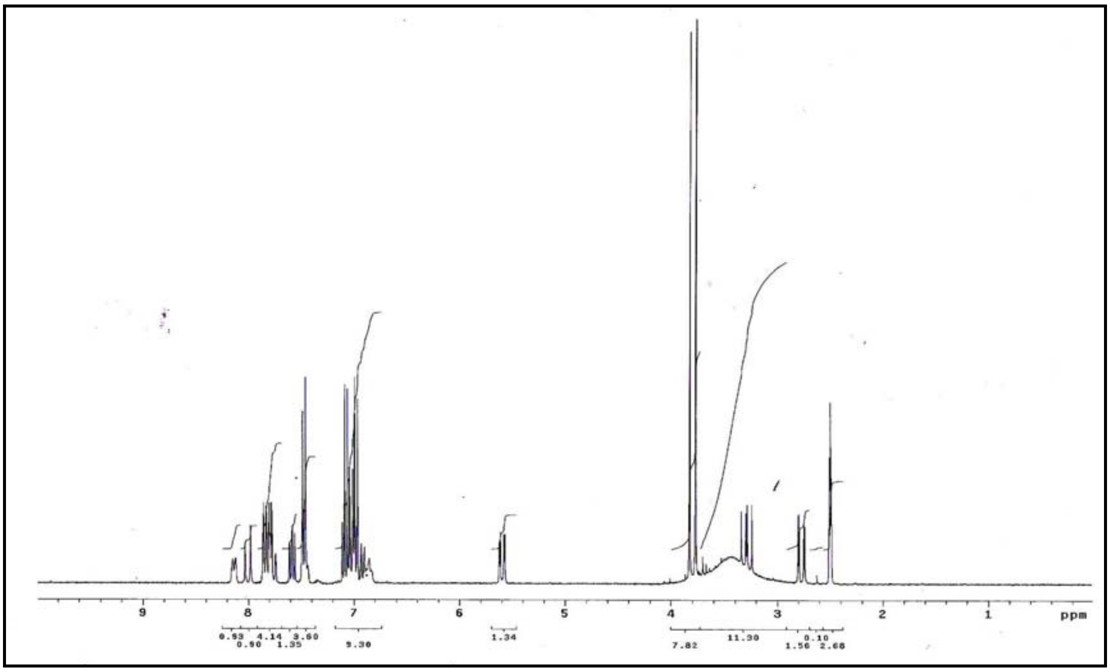


Fig. 3 NMR spectra of (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one.

3.3 UV-Visible Analysis

The UV-visible absorption spectrum of the synthesized compound was recorded using double beam UV-visible spectrophotometer (Spectrascan-2600) Chemito, India in the range 190-550 nm, Using methanol as a solvent and corresponding cut off wavelengths are listed. Generally it is observed that the Chalcones absorb light in the UV region and transmitted into the visible region. The recorded spectrum is shown in Fig. 4, it is clear that the crystal is transparent in the entire visible region and the absorption takes place in the UV range between 210.5 nm to 364 nm. The maximum absorption takes place at a wavelength of 364 nm, this absorbance maximum at 210.5 nm was assigned to n-π* transition and the absorption band at 240.5 nm and 364 nm are assigned to π-π* and n-σ* transitions respectively, these bands may be attributed to the excitation in the aromatic ring and C=C of chalcone and C=O groups respectively. The absence of absorption in the visible region is the necessity for this compound as it is to be exploited for NLO applications in the room temperature.

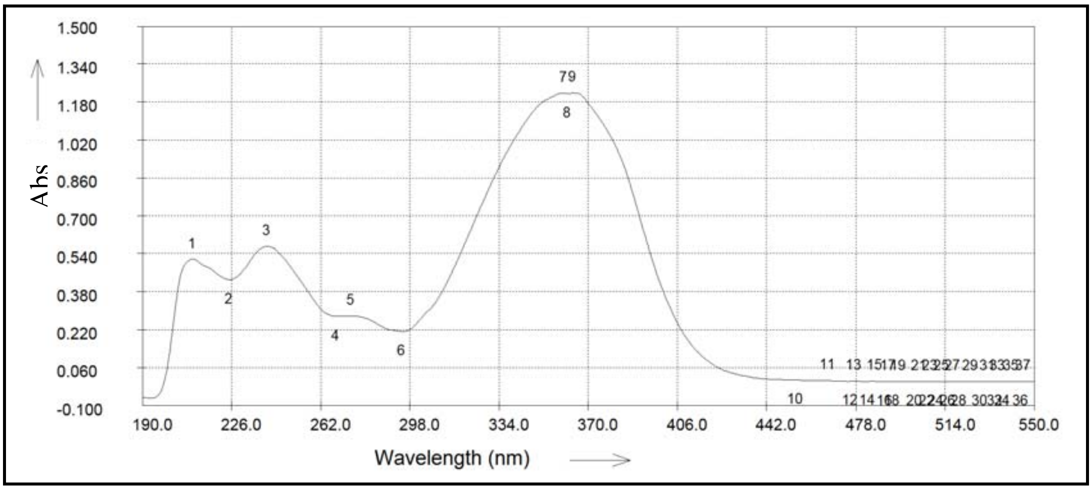
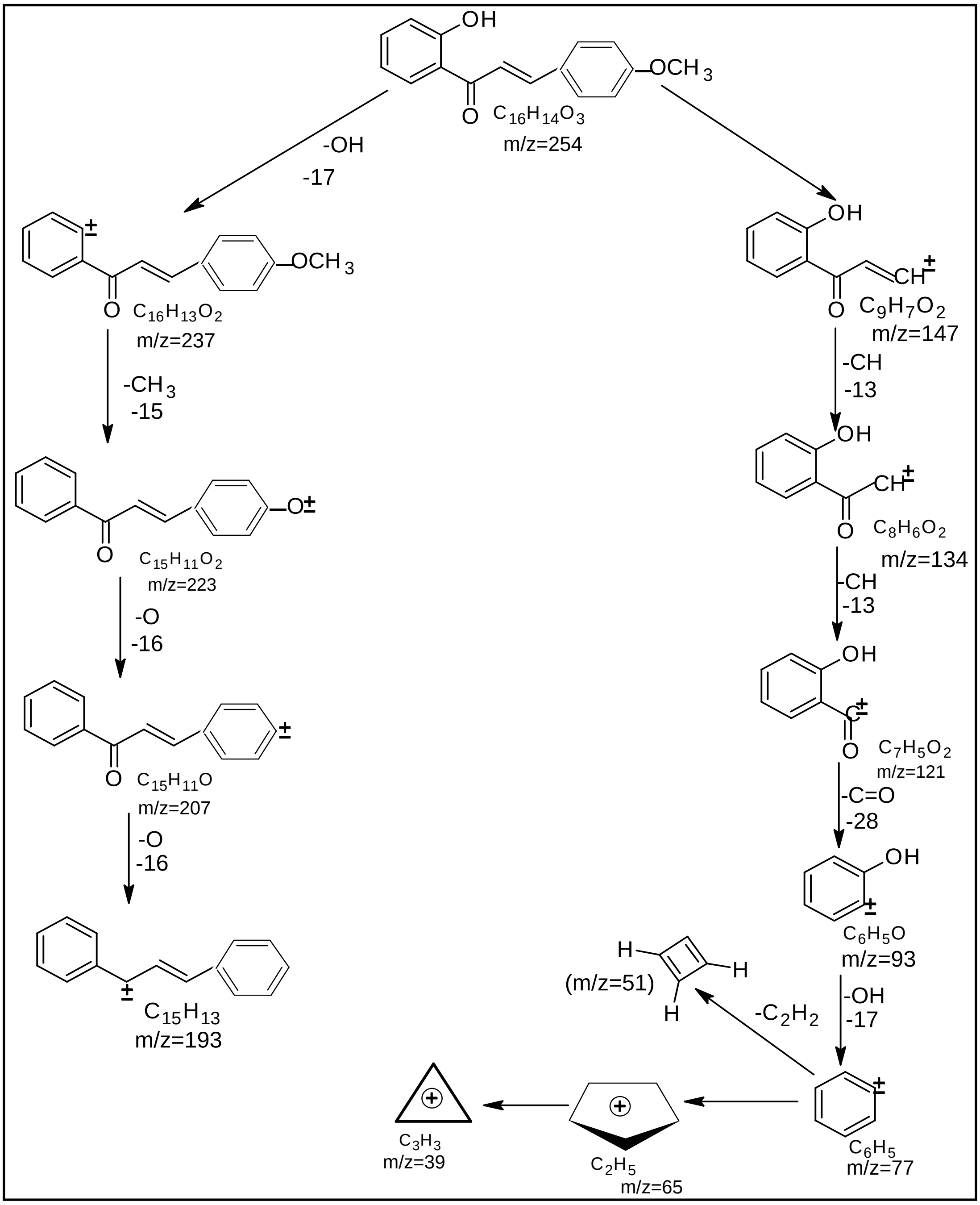


Fig. 4 UV-visible spectrum of (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one.

3.4 GC-MS Analysis

Mass spectrum of the synthesized compound was recorded using EI Source Quadrupole Analyzer (mass range: 10-425 amu. Model-GCD-1800A; Make-Hewlett Packard) by using Acetone as a solvent. The GC-MS analysis was studied to determine the molecular weight and possible fragmentation of (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one. The molecular ion peak was observed at m/z = 254 conforming its formula weight (Fw) = 254. The schematic fragmentation of chalcone is depicted in Scheme 1 and its spectrum is recorded in Fig. 5.



Scheme 1 The schematic fragmentation of (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1- one where the values each of fragment denoted as calculated.

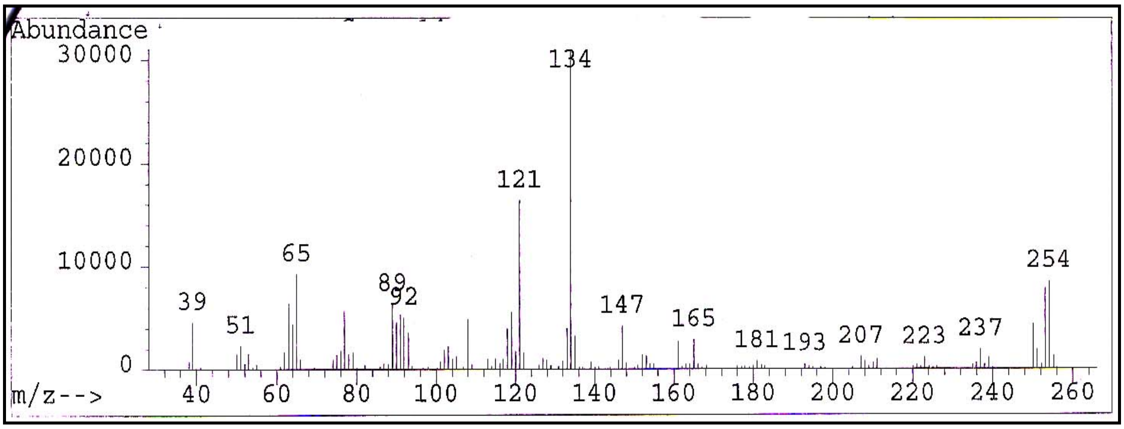


Fig. 5 **Mass spectra of (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one.**

4. Results and Discussion

4.1 (TGA/DTA /DSC) Analysis

The TGA/DTA, DSC of the synthesized chalcone where recorded using Perkins Elmer Diamond TG/DTA, USA at 10 to 850 °C in oxygen and nitrogen atmosphere. The TGA/DTA, of the synthesized chalcone was carried out by using Perkins Elmer Diamond TG/DTA, USA at the rate of 10 °C/min from ambient temperature to 850 °C in oxygen and nitrogen atmosphere. The thermogram of (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one is shown in Fig. 6 in oxygen and Fig. 7 in nitrogen. Thermogram of the compound indicates the two steps decomposition in oxygen and one step in nitrogen atmosphere. The first step indicates nearly 63.38% weight loss against the calculated 64.527% in the temperature range 35-330 °C. This weight loss may be attributed because of loss of $C_{10}H_9O_2$ mass. The second step shows decomposition of chalcone in the temperature 330 °C to 570 °C may be assigned to loss the mass of C_2H_2 which corresponds to nearly 30% weight loss against the calculated 31.959% and above 570 °C there was complete wt loss occur in oxygen atmosphere. And in nitrogen atmosphere decomposition of the chalcone occur in the temperature range 35-570 °C may be assigned to loss –$C_9H_9O_2$ mass of chalcone corresponds to nearly 57.48% against calculated 57.867% and above the temperature range 570 °C there was nearly complete decomposition of

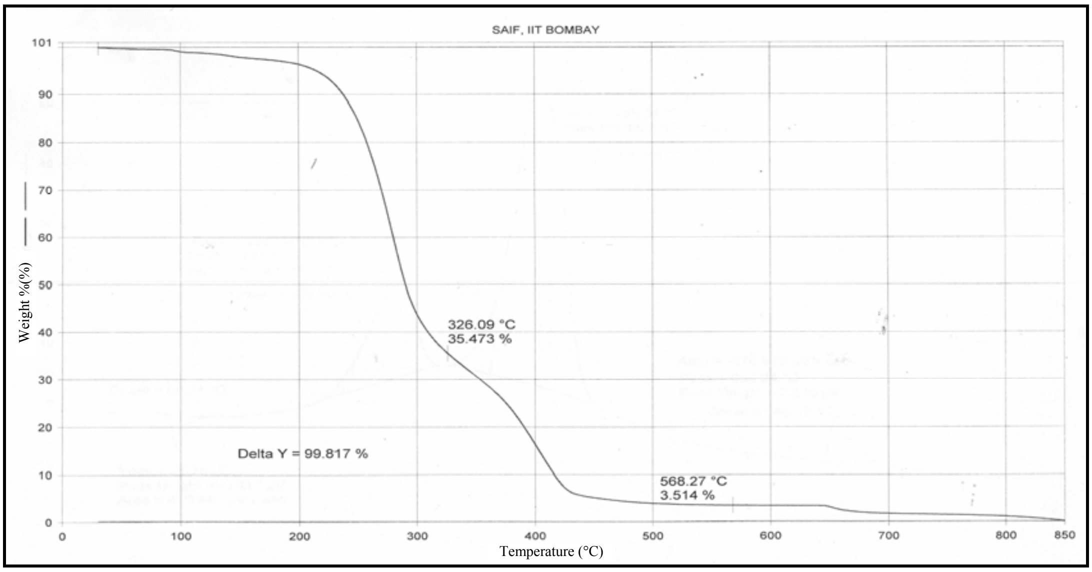


Fig. 6 **TGA spectrum of chalcone in presence of oxygen atmosphere.**

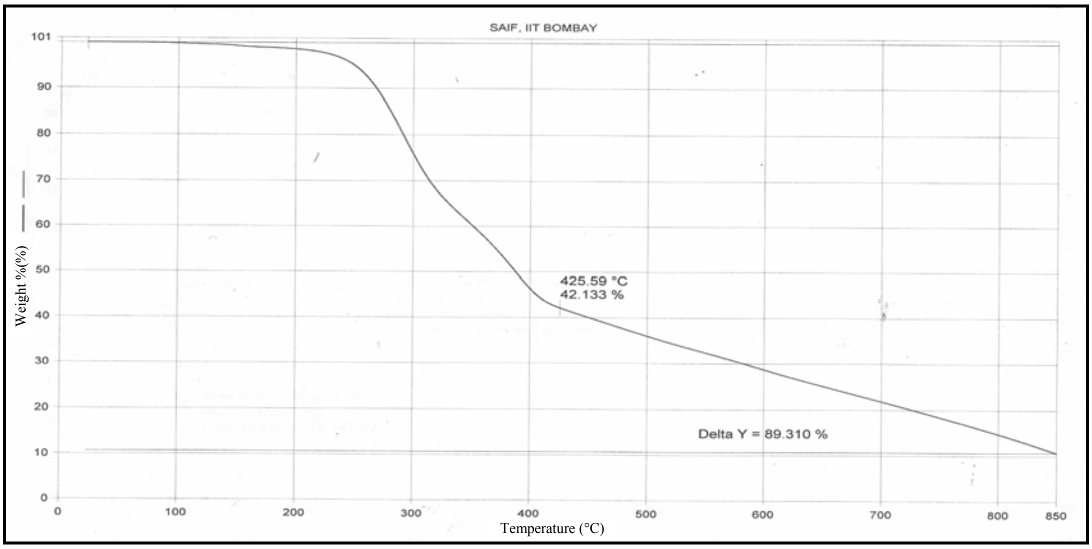


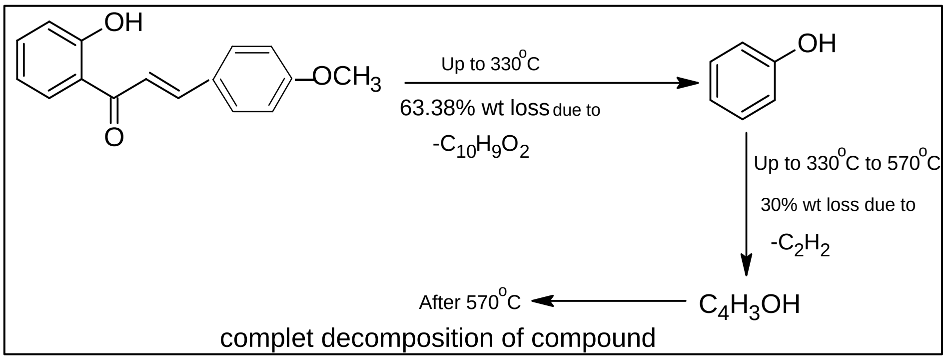
Fig. 7 TGA spectrum of chalcone in presence of nitrogen atmosphere.

compound observed in both oxygen and nitrogen atmosphere the total weight loss in oxygen atmosphere was found to be 99.817% and in nitrogen atmosphere 90%. The experimental weight loss at different steps agrees with calculated weight losses. By considering above decomposition reaction it is observed that the weight losses in different steps were not due to the influence of change in atmosphere but due to change in temperature. Thus TGA study in different atmosphere confirms the formation of compound in the stiochiometric ratio as shown by its formula.

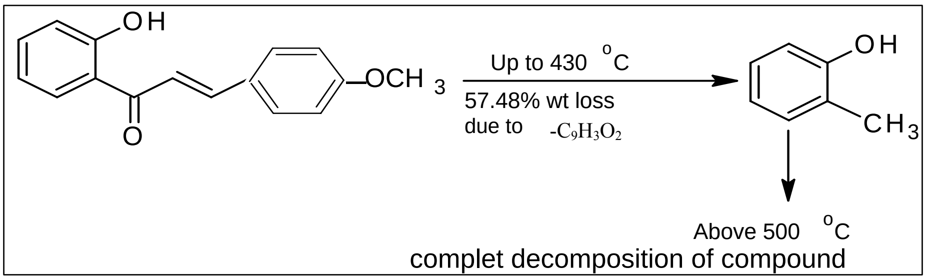
Thermochemical reaction takes place during TGA in oxygen and nitrogen atmosphere as shown in Schemes 2 and 3.

4.1.1 DTA

The derivatogram (DTA) of (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one is shown in Fig. 8 in oxygen and Fig. 9 in nitrogen.



Scheme 2 Formulated decomposition pattern in presence of oxygen atmosphere.



Scheme 3 Formulated decomposition pattern in presence of nitrogen atmosphere.

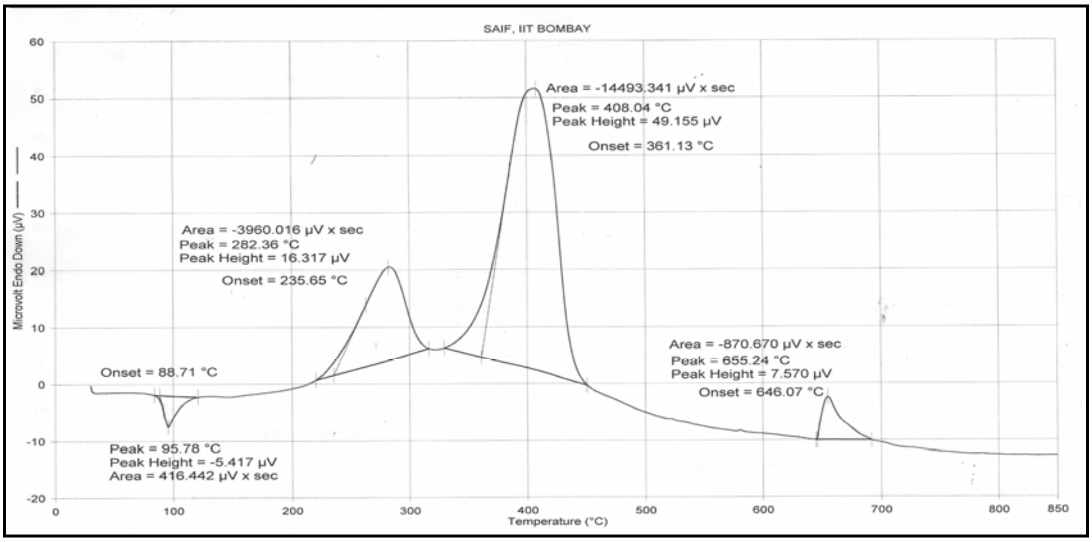


Fig. 8 DTA spectrum of chalcone in presence of oxygen atmosphere.

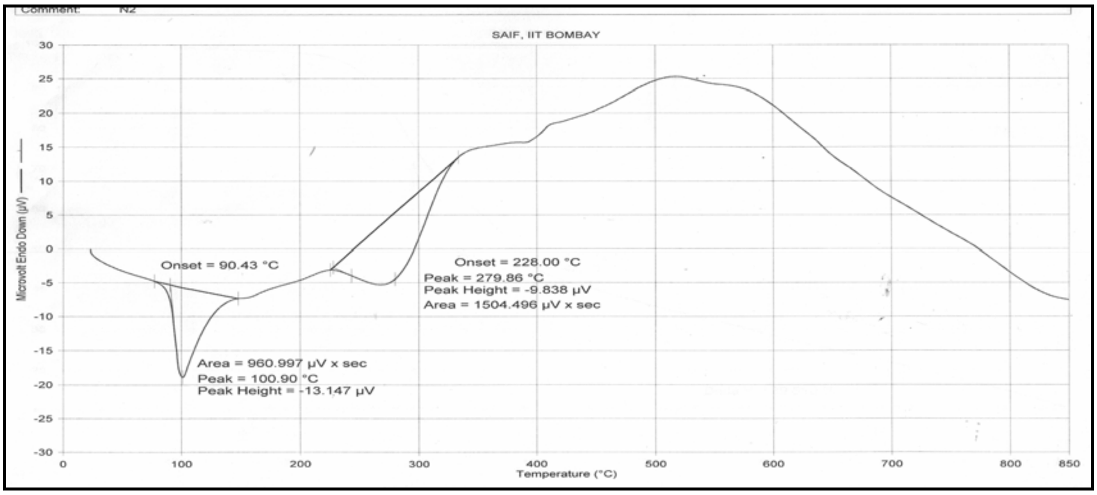


Fig. 9 DTA spectrum of chalcone in presence of nitrogen atmosphere.

Derivatogram (DTA) indicates one endotherm and 3-exotherms. The endotherm at 88.71 °C indicates phase transition from solid state to liquid state. The endotherm at this temperature corresponds to its melting point 88 °C-100 °C. The molten compound decomposes above temperature 100 °C in three different steps corresponding to exotherm at various temperatures as shown in derivatogram. In nitrogen atmosphere the endotherm at 90.43 °C also indicates phase transition from solid state to liquid state and it exact corresponds to its melting point 88 °C-100 °C after which the compound decomposes in to sticky viscous substance. At higher temperature this decomposition process continues up to 850 °C with the removal of entire compound as gaseous products. The sharp endothermic peaks in both atmospheres show the purity and crystalline nature of sample. This TGA/DTA study indicates that in both oxygen and nitrogen atmosphere the chalcone compound is stable up to 88 °C in solid state and further in liquid state it is stable up to 270 °C and after 270 °C thermal decomposition of chalcone occurred.

4.1.2 DSC

The DSC curve was recorded by using Dupont, USA(2000) at 10 °C per minute(E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one was shown in Fig. 10 in oxygen and Fig. 11 in nitrogen atmosphere.

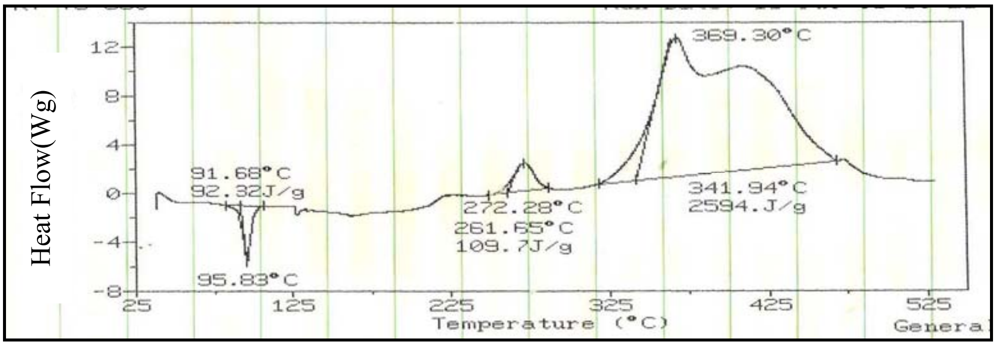


Fig. 10 DSC spectrum of chalcone in presence of oxygen atmosphere.

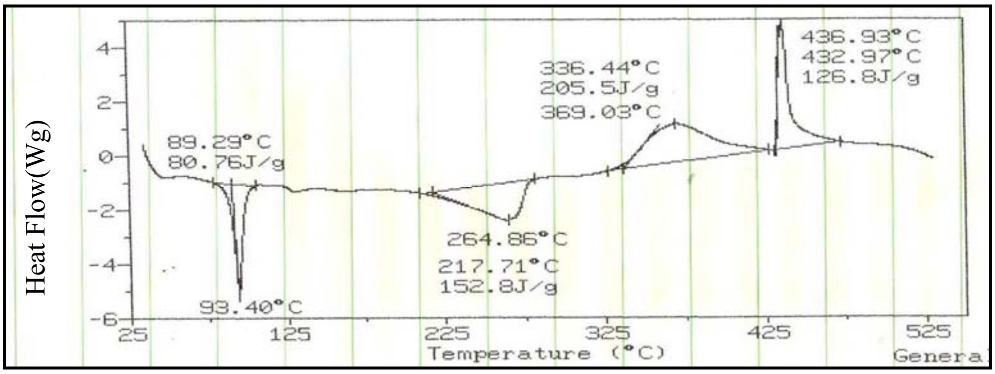


Fig. 11 DSC spectrum of chalcone in presence of nitrogen atmosphere.

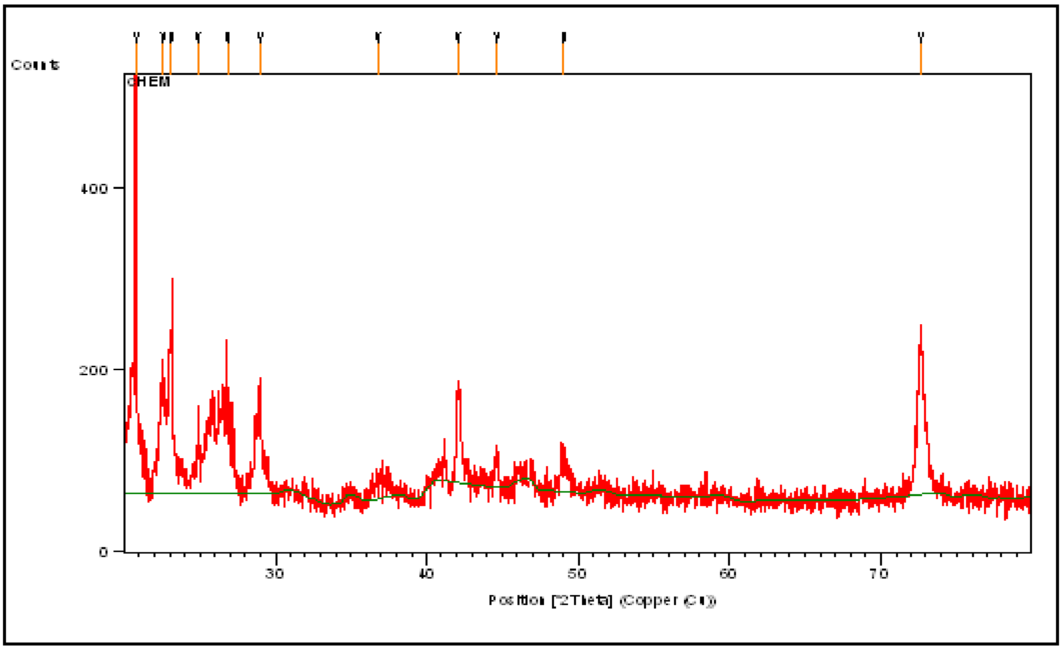


Fig. 12 Powder XRD of synthesized chalcone.

The DSC curve indicates that there is no phase transition before melting. The endothermic peak at 91.68 °C in oxygen and 89.29 °C in nitrogen atmosphere exactly correlates to its melting point (88 °C-100 °C). The sharpness of endothermic peak indicates relative purity and crystalline compound. The heat of fusion (ΔH_{fus}) or enthalpy of fusion of organic compound was found to be 23.449 KJ/mole (92.32 J/gr) and molar heat of fusion as 0.09231 KJ/mole in oxygen atmosphere and 20.513 KJ/mole (80.76 J/gr) and molar heat of fusion as 0.08075 KJ/mole in nitrogen atmosphere, this show exact phase transition from solid state to liquid state. This DSC study of organic compound confirms the TG/DTA curve.

4.2 Powder X-Ray Diffraction Analysis

The title compound was synthesized and crystallized by slow solvent evaporation method at room temperature by using methanol as a solvent. The grown crystal was characterized by powder XRD. The powder XRD study was carried out to confirm the nature of compound using a Bruker D8 Advance X-ray diffractometer operated at 40 kV and 30 mA, using the (θ, θ) geometry, with Cu Kα radiation (λ = 1.54060Å).The sample was scanned at the rate of 25 °C per minute in the range 20 °C-80 °C (Fig. 12). The diffraction pattern has been indexed by minimum second derivative method. The sharpness of the peaks shows good degree of crystallinity. The phases were found that a = 25.4824 Å, b = 17.7506 Å, c = 11.2702 Å. From the above analysis the geometry of crystal was found to be orthorhombic.

5. Conclusions

The different functional group present in the synthesized chalcone was confirmed by FT-IR and H^1-NMR studies, this support the identity of (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one.

UV-visible spectrum of synthesized compound reveals that the compound absorbs in UV region and transparent in visible region which is responsible for its NLO properties. The comparative study of TGA/DTA, DSC analysis in oxygen and nitrogen atmosphere have revealed that the compound is stable up to 60 °C in solid state, further in liquid state it is stable up to 100 °C and after 100 °C thermal decomposition of chalcone occurred and it also indicates that there was no influence of atmosphere on decomposition of chalcone but the decomposition occurred due to the effect of temperature. Mass spectrum of compound shows molecular ion peak at m/z = 254 which corresponds to the molecular weight of synthesized compound shown in Fig.1. All the possible fragments of synthesized compound shown in scheme1 are consistent with different peaks in mass spectrograph of the compound. From powder XRD study it was observed that studied compound was crystalline in nature and orthorhombic shape.

On the above studies it is concluded that this novel material should be better accommodated for optical applications. And it have variety of biological activities so can be used in many pharmacological applications.

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