Studies on thermal and biological properties of 2,3,4-trihydroxybenzophenone single crystal

M.L. Lima Rose[1,2], T. Suthan[3,*], C. Gnanasambandam[4]

[1]*Research Scholar (Reg.No:18133152132034) Department of Physics & Research Centre, S.T. Hindu College, Nagercoil – 629002, Affiliated to Manonmaniam Sundaranar University, Tirunelveli – 627012, India*

[2]*Department of Physics, Malankara Catholic College, Mariagiri-629153, India*

[3]*Department of Physics, Lekshmipuram College of Arts and Science, Neyyoor – 629802, India*

[4]*Department of Physics, S.T. Hindu College, Nagercoil – 629002, India*

Abstract

The organic compound 2,3,4-trihydroxybenzophenone single crystal was grown by slow evaporation technique. The grown crystal structure was confirmed using powder XRD studies. The melting and decomposition points of the grown crystal were identified using TG/DTA analyses. The kinetic and thermodynamic parameters of the grown crystal were calculated using the Coats-Redfern method. The antibacterial activity of the grown crystals was analyzed for two gram-positive bacterial strains (Bacillus subtilis and Staphylococcus aureus) and two gram-negative bacterial strains (klebsiella pneumoniae and Escherichia coli) by the Agar Well diffusion method. The grown 2,3,4-trihydroxybenzophenone crystal exhibited powerful antibacterial activities against all the tested bacterial strains in higher concentrations.

1. Introduction

The organic single crystals are used for various technological and optical applications, especially for optoelectronic switching, electro-optic modulation, and laser frequency conversion [1-3]. The benzophenone derivatives have been observed as having good optical characteristics and biological activity. So, many researchers have grown various benzophenone derivative crystals using different methods and their structural and optical properties were analyzed [4]. Plants in the Clusiaceae and Hypericaceae families are the most important sources of biologically active benzophenones, which have proven to be extremely beneficial to human health. The benzophenone derivative 2,3,4-trihydroxybenzophenone-4-methylol has been widely used in the field of optoelectronics as a photo-resists in microelectronic circuits [5,6]. The benzophenone derivative 2,3,4-trihydroxybenzophenone were successfully grown by slow evaporation technique. The grown crystal was characterized by powder XRD, TG/DTA and antibacterial studies.

2. Experimental

The organic 2,3,4-trihydroxybenzophenone were commercially purchased from the sigma Aldrich with 99% purity. The solvent ethanol was used for growing 2,3,4-trihydroxybenzophenone single crystal. The solution was filtered and covered with perforated polythene sheets. It was kept in an undisturbed place for crystallization at room temperature. The good quality 2,3,4-trihydroxybenzophenone crystals were collected. The grown 2,3,4-trihydroxybenzophenone crystal was used for characterization studies.

3. Result and Discussions

3.1 Powder XRD Analysis

The powder XRD pattern of the grown 2,3,4-trihydroxybenzophenone single crystal was observed using the BRUKER D8 ADVANCE X-Ray Diffractometer. The powder sample was recorded over the range of 10 to 80°. Figure 1 depicts the powder XRD pattern of grown 2,3,4-trihydroxybenzophenone. The sharp and strong peaks detected in the powder XRD pattern revealed that the grown 2,3,4-trihydroxybenzophenone crystal possesses good crystalline nature. The hkl parameters are indexed using 2θ software [7].

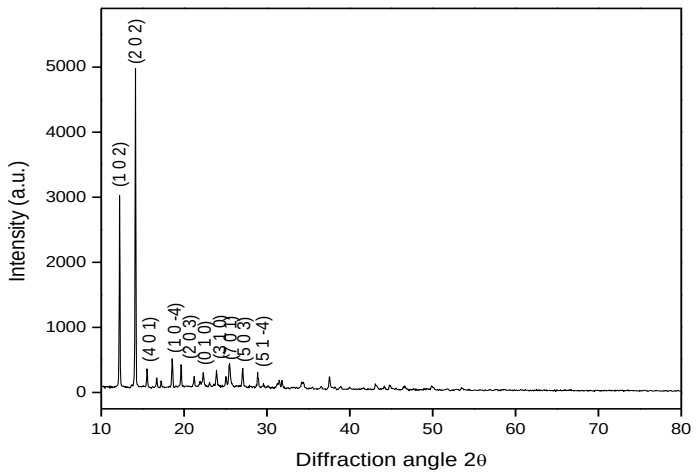

Fig.1 Powder XRD pattern of 2,3,4-trihydroxybenzophenone

3.2 Thermal Analysis

The thermogravimetric (TG) and differential thermal analyses (DTA) are extremely important in technology because they provide the thermal stability of the material for fabrication, where a significant amount of heat is generated during the cutting process. Thermal

analyses were carried out on the grown crystals to determine their thermal stability and melting point. The thermal properties of the grown 2,3,4-trihydroxybenzophenne single crystal were determined by TG/DTA studies using a Perkin Elmer Diamond TG/DTA analyzer with a heating rate of 10°C/min in a nitrogen atmosphere. The TG/DTA curve of the grown single crystal is shown in Fig.2.

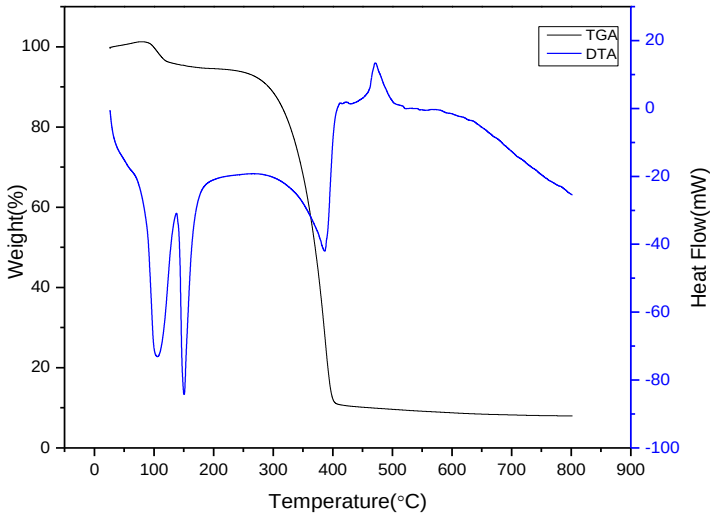

Fig.2 TG/DTA curve of a 2,3,4-trihydroxybenzophenone

The sharp endothermic peak observed around 149°C indicates the melting point of the grown crystal. The peak observed around 384°C assigned as the decomposition point. The sharpness of the peak observed in DTA indicates the good crystallinity of the sample [8, 9]. The kinetic parameters, such as activation energy, frequency factor, and order of reaction, are calculated using TGA data. The data is evaluated using various mathematical methods. In the present study, using the Coats-Redfern method, the kinetic parameters are evaluated. For thermal reaction, the rate of conversion at a constant heating rate is expressed as [10, 11].

$$\frac{d\alpha}{dT} = k(T)f(\alpha)$$

Where α is the conversion degree, f(α) is the function of degree, t is the time, k(T) is the rate constant, T is the Kelvin temperature. Based on Arrhenius equation,

$$k(T) = Aexp\left(\frac{-E_a}{RT}\right)$$

A is the frequency factor, R is the gas constant (R = 8.317 $Jmol^{-1}$ K^{-1}), and E_a is the activation energy. The rate of conversion can be written as,

$$\frac{d\alpha}{dt} = Aexp\left(\frac{-E_a}{RT}\right) f(\alpha)$$

The function of the conversion,

$$f(\alpha) = (1-\alpha)^n$$

where n is the empirical order of the reaction. The rate of conversion can be written as

$$\frac{d\alpha}{dt} = Aexp\left(\frac{-E_a}{RT}\right)(1-\alpha)^n$$

If the heating rate is β=dT/dt then the above equation is written as

$$\frac{d\alpha}{dT} = \frac{1}{\beta}\frac{d\alpha}{dT} = \frac{A}{\beta}\ exp\left(\frac{-E_a}{RT}\right)(1-\alpha)^n$$

By separation of variable we obtain,

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} exp\left(\frac{-E_a}{RT}\right) dT$$

The foundations for the equation of the kinetic parameters of the crystal thermal degradation process The Coats-Redfern used the equation for calculating the activation energy from the TG data [12,13].

$$ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = ln\left[\left(\frac{AR}{\beta E_a}\right)\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \quad for\ n \neq 1$$

The Fractional weight lossα can be calculated using the formula.

$$\alpha = \frac{W_0 - W}{W_0 - W_f}$$

where W_0 is the starting weight and W is the instantaneous weight, Wf is the final weight at the end of the thermal deterioration process, n is the order of the reaction, T is the absolute temperature, A is the frequency factor, R is the gas constant (R = 8.317 $Jmol^{-1}$ K^{-1}), β is the rate of heating per second and E_a is the activation energy. The Coats-Redfern formula for first-order reaction (n=1) is

$$ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = ln\left[\left(\frac{AR}{\beta E_a}\right)\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \quad for\ n=1$$

By plotting the graph in-between $ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ and 1000/T we obtain a straight line and it is shown in Fig.3.

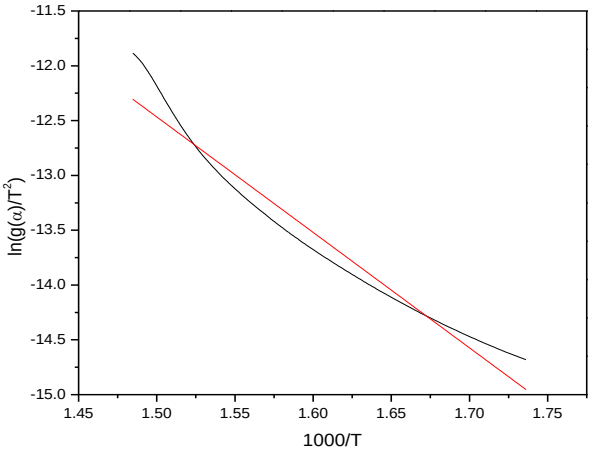

Fig.3. Coats Redfern plot for 2,3,4-trihydroxybenzophenone

The slope of the straight line is used to calculate the activation energy (E_a) and the intercept is used to calculate the frequency factor (A). The kinetic parameters enthalpy of activation(ΔH*), the entropy of activation (ΔS*), and Gibb's free energy(ΔG*) were calculated by using the following equations.

$$\Delta H^* = E - RT$$

$$\Delta S^* = R * \ln\left(\frac{Ah}{kT_m}\right)$$

Where h is Planck's constant ($6{\cdot}626 \times 10^{-34}$ J s), k is Boltzmann constant

$$Z = \frac{kT_m}{h}\exp\left(\frac{\Delta S^*}{R}\right)$$

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

The calculated kinetic and thermodynamic parameter values are shown in Table 1.

Table 1. Kinetic and thermodynamic parameters of the grown 2,3,4-hydroxybenzophenone crystal

Parameters	Calculated Values
Activation energy (E) kJ mol^{-1}	87.57
Frequency factor (Z) S^{-1}	1.39E+6
Entropy, (ΔS^*) J K^{-1} mol^{-1}	-130.235
Enthalpy, (ΔH^*) k J^{-1} mol^{-1}	84.041
Gibb's free energy(ΔG^*) k J mol^{-1}	139.39

The positive value of enthalpy indicates that the dissociation process is endothermic. The negative value of the entropy of activation shows that the activated complex is further ordered than the reactant and the decomposition reaction is slow. It may due to the chemisorption of oxygen and other decomposition products [13]. Gibbs free energy is a value that defines how spontaneous a reaction is, with a negative value meaning the reaction is spontaneous, and a positive value meaning the reaction is nonspontaneous. The positive value of Gibb's free energy indicates that the reaction was nonspontaneous.

3.3 Antibacterial studies

The antibacterial activity of the grown crystal was tested against *Klebsiella pneumoniae, Bacillus subtilis, Staphylococcus aureus and Escherichia coli*to assess their potential against antimicrobial agents. Escherichia coli cause clinical infections (pneumonia and neonatal meningitis), urinary tract infections, bacteraemia, cholecystitis, cholangitis and travelers diarrhea. Hospital implants are easily inhibited by Staphylococcusaureus and thus spread and cause different severe infections. The antibacterial activity of grown crystals has been analyzed by a method called the agar well diffusion method. The glassware that is used in the analysis is initially sterilized at 130°C for 3 h. The tested microbes were prepared using a Muller Hinton medium which supports the growth of bacteria. The solution was placed on the Petri plates which contain the media. Then the Petri plates were maintained under incubation for 24 h and the results were noted. The above-mentioned bacterial species were prepared at 500μg/mm and 750μg/mm concentrations. The standard drug Streptomycin 10 mcg concentration disc was used for positive control and the empty sterile disc was used for negative

control. The plates were kept for incubation at 37°C for 24 hours. At the end of incubation, inhibition zones were examined around the disc (including disc) and measured with a transparent ruler in millimeters (14-16).

This method is a simple, rapid, and inexpensive toxicity test for environmental pollutants based on the growth inhibition of different bacteria and fungi [17]. The results concluded that ethanol dissolved 2,3,4-trihydroxybenzophenone fractions showed significant novel antibacterial potential against all the tested human pathogenic organisms in higher concentrations. It shows the present 2,3,4-trihydroxybenzophenone sample should act as an adequate antibacterial agent against the four treated human pathogenic bacterial organisms.

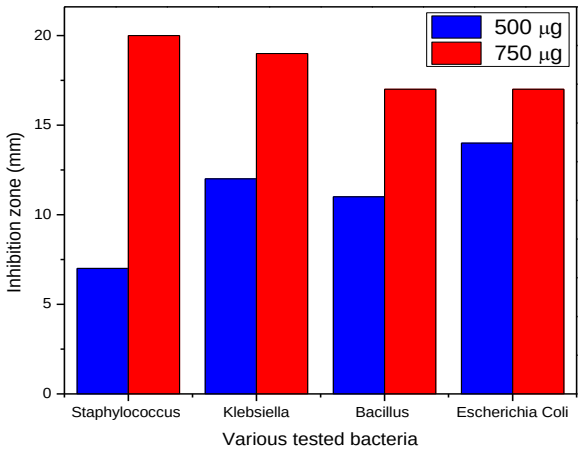

Fig.4.Antibacterial activity of the 2,3,4-trihydroxybenzophenone

4. Conclusion

The organic material 2,3,4-trihydroxybenzophenone single crystal has been grown successfully by slow evaporation solution growth technique using ethanol solvent. The Powder XRD studies confirm the grown crystal. The thermal behaviour of the grown crystal was studied by TG/DTA analyses, the melting and decomposition points are reported. The kinetic and thermodynamic parameters are calculated. The antibacterial activity of the grown crystal shows the inhibitory action against all the tested disease-causing pathogens.

References

1. T. Suthan, N.P. Rajesh, C.K. Mahadevan, G. Bhagavannarayana, Spectrochim. Acta Part A 78 (2011) 771–776.
2. D. Prem Anand, M. Gulam Mohamed, S.A. Rajasekar, S. Selvakumar, A. Joseph Arul Pragasam, P. Sagayaraj, Mater. Chem. Phys. 97 (2006) 501–505.
3. Usharani, V. Natarajan, J. Judes, M. Arivanandhan, P. Anandan, S. Natarajan, Optik 127 (2016)5887–5893.
4. V. Natarajan, M. Arivanandhan, P. Anandan, K. Sankaranarayanan, G. Ravi, Y. Inatomi, Y. Hayakawa, Mater. Chem. Phys.144(2014) 402-408,
5. Martha Isabel Realpe Aranda, Gabriel Andres Tafur Gómez, Mariana de Barros, Marcelo Henrique dos Santos, Leandro Licursi de Oliveira, Junnia Luisa Pena and Maria Aparecida ScatamburloMoreira ,Front. Microbiol. 10 (2019)1-10.
6. Nobuo Okabe and HasuyoKyoyama, Acta Cryst. E58, (2002)0565-0567
7. T. Suthan, N.P. Rajesh, J. Cryst. Growth, 312, (2010)3156–3160
8. T. Suthan, N.P. Rajesh, C.K. Mahadevan, K. Senthil Kumar, G. Bhagavannarayana, Spectrochimica Acta Part A 79 (2011) 1443–1448
9. T. Suthan, P. V. Dhanaraj, N. P. Rajesh,C.K. Mahadevan, G. Bhagavannarayana,Cryst. Eng. Comm., 13 (2011) 4018–4024.
10. M.A. Ashok, B.N. Achar, Bull. Mater. Sci. 31, (2008)29–35.
11. Michael Ikpi Ofem, Musa Muhammed, Muneer Umar, Int J SciTechnol, 4 (2015) 281-288.
12. B. Narasimha, R.N. Choudhary, K.V. Roa, Mater.Sci. 23 (1988) 14-16.
13. K.V.Rao, A. Smakula, J. Appl. Phys. 36, (1965)2031-2038.
14. Kohner PC, Rosenblatt JE, Cockerill FR.1994, J. Clin. Microbial. 32, (1994) 1594 -96.
15. J. Devillers, R. Steiman, and F. Seigle-Murandi, Chemosphere,19 (1989)1693-1700.
16. Mathabe M.C., Nikolova R.V., Lall N., Nyazema N.Z., South Africa, Journal of Ethnopharmacology, 105 (2006) 286-293.
17. Assam A J P, Dzoyem J P, Pieme C A and Penlap V B, BMC Complementary and Alternative Medicine, 10, (2010)