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SINGLE CRYSTAL GROWTH OF COUMARIN DYES AND STUDY OF THEIR ELECTRICAL CONDUCTIVITY

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ABSTRACT

Three coumarin derivatives i.e., 7-hydroxy-2H-1-benzopyran-2-one (umbelliferone) 3a, 4-methyl umbelliferone (C-4), 3b and 7-amino-4-methyl-benzopyran-2-one (C-120), ***3c*** *were synthesised by both conventional and microwave assisted synthetic methods and characterized. The pure compounds were initially grown into seeds (minute crystals having potential to grow into large crystals) and developed into single crystals using solution growth technique in a cryostat under careful monitoring. The desired single crystals were isolated and studied for their electrical conductivity properties by two terminal method. The results are promising and these pure organic compounds (coumarins) can act as promising semi-conductors.*

Keywords: Coumarin, Single crystal, Electrical conductivity, Semi-conductor.

1. INTRODUCTION

Coumarins are important group of oxygen containing fused heterocyclic compounds that are used as additives in food and cosmetics, optical brightening agents and dispersed fluorescent and laser dyes [1]. They belong to the family of lactones having benzopyran-2-one system. Naturally coumarins occur as secondary metabolites present in seeds, roots and leaves of many plant species and regulate the growth of plants [2].

Owing to the importance of these compounds in various fields, it was proposed to synthesise some known coumarins and study their photo-physical and conductivity properties. Generally Coumarins can be synthesised by either Claisen rearrangement or Perkin reaction or Pechmann reaction [3, 4] or Knoevenagel condensation [5, 6] with various catalysts [7, 8] by conventional heating or by microwave irradiation [9]. Semiconducting organic materials have received increased attention in the last several years because they promise bulk processing of flexible, large-area devices at low cost [10-12]. However, the molecular nature of organic systems also presents a different set of challenges when compared to inorganic systems.

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In particular, the energetic spectral bands of the molecular unit are extremely narrow, in addition to vibrational modes that have the potential to strongly scatter and even localise charge carriers [13]. This feature suggests a strong dependence of the electronic band structure, optical, and transport properties on the molecule type. In view of the above said properties of coumarin molecules, it was proposed to synthesise three coumarin derivatives by both conventional and microwave assisted methods and study their electrical conducting properties adopting two-terminal method.

2. EXPERIMENTAL METHODS

2.1. Synthesis

2.1.1. General Procedure for Synthesis of Coumarins in Conventional Method

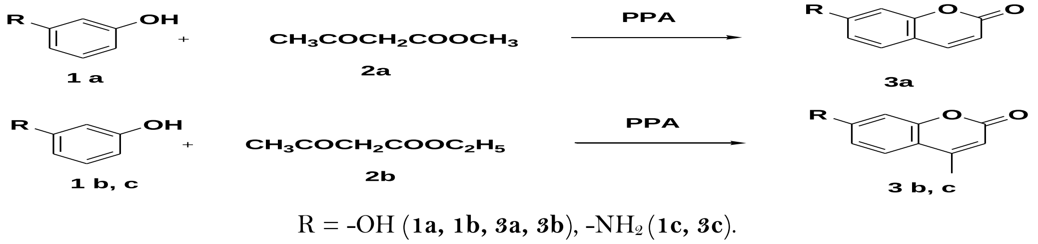
The corresponding phenol (1a, 1b, 1c, 20 mmol), and acetic anhydride (2a)/ ethyl acetoacetate (2b, 30 mmol) were mixed thoroughly with the help of a stirrer, to which polyphosphoric acid (PPA)(10 mmol) was added slowly with continuous stirring at room temperature. The reaction mixture was poured onto crushed ice and the resulting crude product was filtered off and recrystallised from hot ethanol/water (9/1) to give the pure products 3a, 3b, 3c.

2.1.2. General Procedure for Synthesis of Coumarins in Microwave Method

All the three coumarin derivatives (3a, 3b, 3) which were synthesised by conventional method were also synthesised by adopting microwave assisted technique using a domestic micro-oven at 150W for five minutes. At the end of exposure of microwave irradiation of the reaction mixture, it was cooled to room temperature, and the crude product was recrystallised from an appropriate solvent i.e., either methylated spirit or rectified spirit to afford the corresponding coumarin 3a, 3b or 3c. In this method, the products were formed within five minutes and gave improvement yields over conventional method in shorter times. The obtained products were characterised and compared with the reference.

2.2. Electrical Conductivity Studies

In the present study, it was aimed to synthesise three coumarin dyes (**3a, 3b, 3c**) and study their electrical conductivity. These were 7-hydroxy-coumarin (Umbelliferone) (**3a**), 7-hydroxy-4-methyl coumarin (Coumarin 4) (**3b**) and 7-amino-4-methyl coumarin (Coumarin 120) (**3c**) respectively.



R = -OH (**1a, 1b, 3a, 3b**), $-NH_2$ (**1c, 3c**).

Scheme-1. Synthetic scheme of coumarin dyes (**3a-3c**)

2.3. Recrystallisation and Solubility

The synthesised crude coumarin compounds (3a, 3b and 3c) were thoroughly recrystallised from spectroscopic grade ethanol to obtain in high state of purity which were further assessed adopting high pressure liquid chromatography (HPLC), with acetonitrile as mobile phase. The purity of these target molecules were found to be greater than 99% by HPLC. Further the solubility of these synthesised coumarins were recorded at various temperatures in ethanol(which showed better solubility of these compounds) in order to grow the crystals at suitable temperatures, and thereby study their electrical conductivities. It was observed that optimum solubility of the compounds 3a, 3b and 3c was found to be between 30°C to 35°C in ethanol. Hence, the crystal growth studies of these compounds were conducted at 35°C.

2.4. Preparation of Seed Crystals and Single Crystal Growth Using Cryostat

In the present study, seeded growth technique was widely used to grow large size single crystals which are adopted in the present study. To obtain good single organic crystals, seeds were grown using cooling method and solvent evaporation method. Saturated solutions of the compound (3a,3b, 3c) were prepared at room temperature and filtered into conical flask with cork stoppers, in which small holes were bored to allow slow evaporation. The flasks were kept in constant temperature bath at 30°C until small transparent well-formed crystals were obtained. The process took nearly 3-4 days. In slow cooling method, more of the compound (3a or 3b or 3c) in saturated solution at higher temperature was prepared and then cooled the solution up to 15-16°C in a cryostat. Seed crystals, thus obtained were isolated and fine seeds of these compounds were suspended for single crystal growth in a cryostat maintaining the temperature at 31°C. Spectroscopic grade ethanol was used as solvent for the purpose. After 35 to 40 days, seeds of compounds (3a, 3b and 3c) were grown to single crystals. The single crystals grown by the above process were collected, dried and measured for crystal dimensions.

The dimensions of single crystals of compound 3a, 3b and 3c were, 5.4mm x 4.2mm x 1.85mm, 4.0mm x 4.4mm x 1.43mm and 4.4mm x 4.3mm x 1.88mm respectively.

These crystals were observed under high resolution microscope, which showed good surface texture and no unwanted multinucleation occurred.

2.5. Conductivity Studies of the Single Crystals of Compounds 3a, 3b and 3c

Conductivity measurements of these crystals (3a, 3b and 3c) were done by using a two-terminal method. The crystals were shaped evenly on all the four sides by rubbing them gently on a carborundum paper. Then they were cut, evenly faced on all the four sides and ground into a square piece, where all the surfaces were evenly textured. The areas of the crystals were now calculated. To these evenly surfaced crystals, silver paste was uniformly applied for better ohmic contact. The crystals of compounds 3a, 3b and 3c which were smeared with silver paste, were connected to positive and negative terminals of the Keithley 614 electrometer and were kept in between the two electrodes of a measurement cell. The conductivity of these crystals was measured separately as follows.

Voltage given to crystal 3a: 5 volts

Conductivity of the crystal 3a: 3×10^{-8} mho.cm^{-1}

Voltage given to crystal 3b: 1.85 volts

Conductivity of the crystal 3b: 1.19×10^{-10} mho.cm^{-1}

Voltage given to crystal 3c: 2.2 volts

Conductivity of the crystal 3c: 2.8×10^{-9} mho.cm^{-1}

Formula for calculating the conductivity of the crystals

$\sigma = 1/\rho$

$\rho = RA/I$

$R = V/I$

$V = IR$

$I_R = E\text{-}V/Rs$

σ : Conductivity of the crystal, ρ : Resistivity, Rs : resistance of the standard., I :current,

A : area of the crystal, E : voltage supplied, V : voltage across resistance.

3. RESULTS AND DISCUSSION

The synthesised coumarins (3a, 3b and 3c) which were purified and subjected for single crystal growth were found to conduct in the range of 10^{-8} to 10^{-10} mhos.cm^{-1}, indicating the semi-conductor property of the material. Further these materials were studied for their electric conductivity in pure organic molecular form i.e., without any complex formation or dopents added. A plausible explanation for the conductivity exhibited by these compounds could be the excessive Pi-electrons present in these molecules having extended conjugation throughout their structures. The results were just preliminary and promising. Based on the results obtained from the above studies, further investigation on the modification of structure and conductivity are in progress.

4. CONCLUSION

In conclusion, three coumarins were synthesised adopting both traditional and microwave assisted synthetic methods. The yields in microwave assisted synthesis of these coumarins were good with high purity and less reaction times. Moreover the recovery of the product was high and easy. The electrical conductivity studies of these coumarin molecules was very interesting and showed promising results for these to act as potent semi-conductor material.

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