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p-N,N-DIMETHYLAMINOBENZALDEHYDE (DAB) GROWN BY SOLUTION TECHNIQUE USING CCl_4 AS GROWTH MEDIUM
Thermal studies and spectral characterization

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As an asymmetric organic molecular crystal, *p-N,N*-dimethylaminobenzaldehyde (DAB) exhibits peculiar optical property. It was first grown by solution technique adopting slow evaporation method at room temperature using CCl_4 as growth medium. The solubility of DAB increases with temperature. Good quality transparent crystals of *p-N,N*-dimethylaminobenzaldehyde were carefully collected and subjected various characterization studies such as UV, FTIR, ^{1}H and ^{13}C NMR spectral studies and thermal (TG-DTG) studies to determine the purity and application oriented properties of the grown crystals.

Keywords: *p-N,N-dimethylaminobenzaldehyde, solution technique, spectral analysis, thermal studies*

Introduction

Organic crystals are increasingly being recognized as materials of the future because of their molecular nature combined with the versatility of synthetic chemistry can be used to alter and optimize their molecular structure in order to maximize nonlinear properties. Organic crystals were intensively investigated due to their high nonlinearities, rapid response in electro-optic effect and tailor made flexibility [1–5]. Organic molecular materials have emerged as a new class of promising nonlinear materials because of their superior qualities over inorganic materials [6] some of the advantages of the crystalline organic materials are large damage thresholds in laser beam and large birefringence.

Organic materials are in increasing demand, as they are better candidates for nonlinear optical (NLO) and electro-optic device applications than those of inorganic materials. Although organic materials have been known for their applications in semi-conductors [7], superconductors [8] and NLO devices [9, 10] very little attention has been focused on the dielectric and polar properties of pure and binary organic materials. Future photonics technology is dependent on the design, synthesis and characterization of materials exhibiting, in particular, second-order NLO properties [11]. Madhurambal and Anbusrinivasan [12] reported the growth of high quality anthracene crystals by simple solution technique. The crystals of 2-bromo-4-chloroacetophenone crystals were grown by solution technique and the harvested crystals were subjected to various characterization studies to determine its application oriented properties [13]. Synthesis and characterization of a novel NLO material endoanthracene maleicanhydride was also studied for its optical and electronic properties [14]. Solution growth and characterization of benzophenone and 2,4-dinitrophenyl hydrazone of benzophenone was studied [15]. Thermal properties, induction period, interfacial energy and nucleation parameters of solution grown benzophenone were also studied [16]. Spectral, thermal and X-ray analyses are key methods for materials characterization. Therefore, it is not surprising that many authors have used these methods for various materials characterization [17–50]. In this work, we have made a detailed investigation on asymmetric organic molecular crystal of p-*N,N*-dimethylaminobenzaldehyde (DAB) and characterize it using various spectral, thermal and X-ray analyses. The structure of *p-N,N*-dimethylaminobenzaldehyde (DAB) is given in Fig. 1.

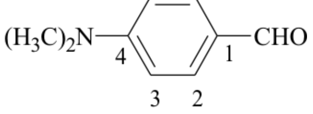

Fig. 1 Structure of *p-N,N*-dimethylaminobenzaldehyde (DAB)

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Experimental

Crystal growth of p-N,N-dimethylamino-benzaldehyde

The analar grade *p-N,N*-dimethylaminobenzaldehyde (DAB) was purified by repeated crystallization from CCl_4 as solvent. The pure crystals of DAB were taken for crystal growth. A known mass of DAB was carefully dissolved in CCl_4 at 40°C. This saturated solution of DAB in CCl_4 is filtered and the solution was allowed for slow evaporation at room temperature, by covering the beaker with a thick sheet of paper for controlled evaporation. Good transparent crystals of DAB were obtained in 2 days. These crystals were carefully harvested and subjected to various characterization studies. The solubility studies show that the solubility increases with temperature which is shown in Fig. 2.

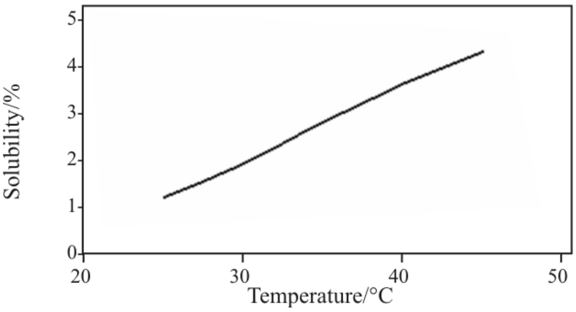

Fig. 2 Solubility of DAB in CCl_4

Measurements

The UV-VIS spectrum of DAB was scanned between 200–900 nm using Shimadzu UV 240 spectrometer.

FTIR spectral analysis of the solution grown DAB was performed on a Perkin-Elmer 1600 series FTIR spectrometer using Nujol mules between KBr plates in the 400–4000 cm^{-1} spectral range.

The ^{1}H NMR and ^{13}C NMR spectra of DAB grown by solution technique, was recorded on a Varian XL-200 Spectrometer operating at 200 MHz using $CDCl_3$ as solvent.

Powder X-ray diffraction studies of solution grown DAB was carried out using a RICH-SEIFERT X-ray diffractometer with CuK_α radiation of wave length 1.5418 Å.

The thermal stability of solution grown DAB was determined using a simultaneous SDT Q600 TA Instrument in inert nitrogen atmosphere at a heating rate 10°C min^{-1}.

Results and discussion

UV-VIS-spectral analysis

The UV-VIS spectrum is due to the electronic transitions of the molecule. This is characteristic of a particular compound. Qualitative and quantitative estimations of compounds are possible by this non-destructive technique.

The solution grown DAB was subjected to UV-VIS spectral analysis to determine its transparency. The recorded spectrum is shown in Fig. 3.

This spectrum shows the characteristic absorption around 220–280 nm which is due to aromatic C=O. This spectrum also confirms the aromatic nature of the grown crystal. This recorded spectrum is in accordance with the theoretical values [51–53]. The recorded UV-spectrum of solution grown DAB gives an idea about the highly transparent nature for a wide range of the grown crystal, which is the important requirement for the optical materials.

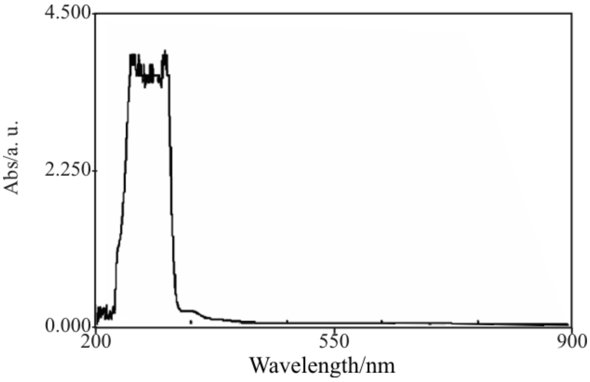

Fig. 3 UV-VIS spectrum of solution grown DAB

FTIR spectral analysis

The absorption of IR radiation causes the various bands in a molecule to stretch and bend with respect to one another. The range 4000–400 cm^{-1} is of prime importance for the study of an organic compound by spectral analysis. In this technique almost all functional groups in a molecule absorb characteristically with in a definite range of frequency.

The FTIR spectrum of DAB grown by solution technique adopting slow evaporation method using CCl_4 as growth medium is shown in Fig. 4.

In the FTIR spectrum the peak at 3066.67 cm^{-1} is observed which is assigned to C–H stretching in aromatic compounds. The peaks at 1681.62 and 1629.03 cm^{-1} are characteristic of C=O in aldehyde. The peaks at 1954.60 and 1887.52 cm^{-1} show the grown crystal having the substituted benzene ring. The peaks at 1494.69, 1449.09 and 1420.26 cm^{-1} are

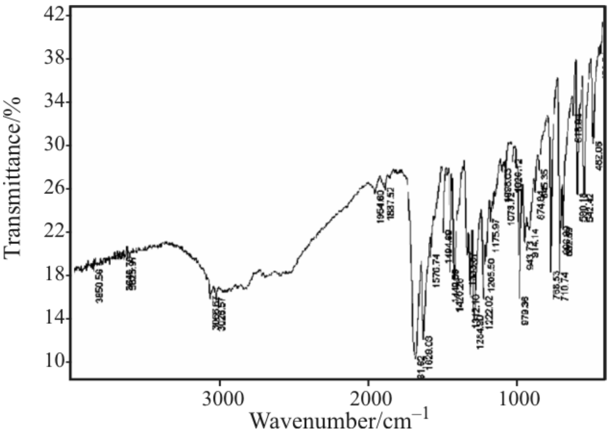

Fig. 4 FTIR spectrum of solution grown DAB

the characteristic of C–N stretching. The C–N stretching in aromatic amine is assigned to the peaks at 1284.90, 1222.02, 1205.50 cm^{-1}. The peak at 976.36 cm^{-1} is due to =CH out of plane deformation and the peak at 482.06 cm^{-1} is characteristic of C–N–C in amines.

From the above discussion it is evident that the FTIR spectrum of solution grown of DAB is well in accordance with the theoretical values and shows the purity of the grown crystal [52–54].

^{1}*H NMR spectral analysis*

NMR spectral analysis is used to determine the molecular structure based on the chemical environment of the magnetic nuclei ^{1}H, ^{13}C, ^{31}P, etc. even at low concentrations. The recorded ^{1}H NMR spectrum of solution grown DAB is shown in Fig. 5.

In this spectrum the signal around 9.393–9.708 ppm is assigned to CH=O proton [54, 55]. The doublet at 7.6 is assigned to the ortho-protons which are present in *o*-position to $N(CH_3)_2$.

This is due to the electronegative character of $N(CH_3)_2$. The doublet at 6.6 ppm is assigned to *m*-protons (which are present in adjacent positions to CHO group) due to the deshielding effect of nitrogen, the methyl protons show a high intensity singlet.

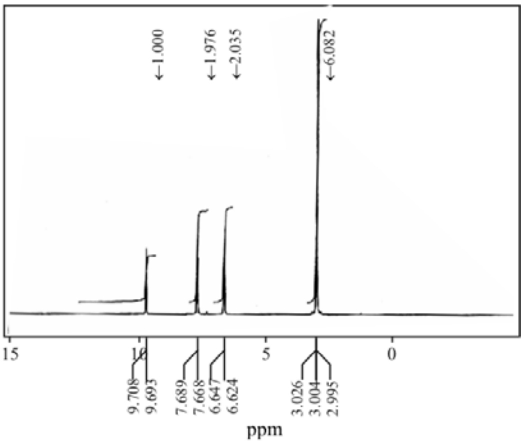

Fig. 5 ^{1}H NMR spectrum of solution grown DAB

^{13}*C NMR spectral analysis*

The observed peaks in the ^{13}C NMR spectrum of solution grown DAB are assigned to the respective carbons with reference to the theoretical values. The recorded spectrum is shown in Fig. 6.

The signal at 189.76 ppm is assigned to an aldehyde carbon. The ipso carbons (attached to nitrogen atom) of phenyl group are observed at 153.89 and 124.64 ppm. The phenyl carbon which is adjacent to $N(CH_3)_2$ group is observed at 131.523 ppm. This is due to de-shielding effect. The phenyl carbon which is adjacent to CHO group is observed at 110.622 ppm. The peak at 124.647 ppm is assigned to ipso carbons attached to aldehyde group. The signal at 39.614 ppm is assigned to methyl carbons attached to nitrogen atom.

X-ray diffraction studies

The internal structure of crystals can be investigated with the help of X-ray diffraction studies. The crystal was scanned over the range of 10–70° at the scan rate

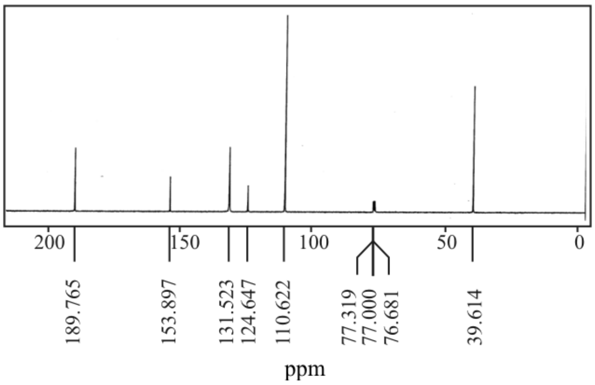

Fig. 6 ^{13}C NMR spectrum of solution grown DAB

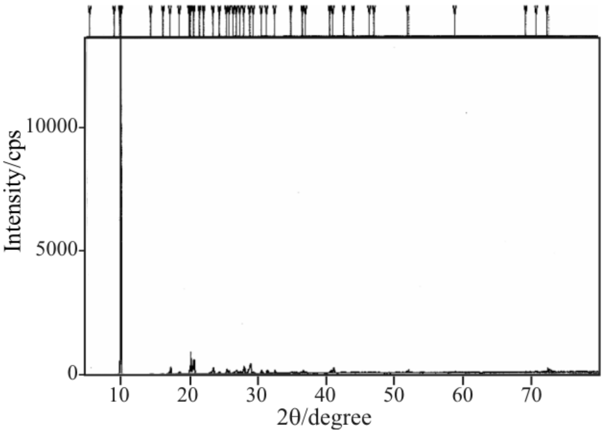

Fig. 7 X-ray diffraction pattern of solution grown DAB

of 2° min^{-1}. The diffraction pattern of solution grown DAB confirms the crystalline nature of the harvested crystal, which is shown in Fig. 7.

Thermal studies

Thermal analysis is a very useful technique for materials characterization. It provide with various information about the studied materials such as thermal stability, crystallization, purity and structure. The thermal properties of solution grown *p-N,N*-dimethylaminobenzaldehyde (DAB) are studied by TG-DTG studies on a SDT Q600 thermal analyzer in inert nitrogen atmosphere. The TG-DTG curves of solution grown DAB is shown in Fig. 8. The TG curve indicates that it is thermally stable up to 176.18°C where the decomposition process commences and follows by three mass loss steps. Thermal analysis confirms the purity and single crystalline nature of solution grown DAB. The main DAB decomposition step took place between 176.18 and 215°C accompanied with 80.33% mass loss on TG curve corresponding to the exothermic DTG peak at 221.61°C.

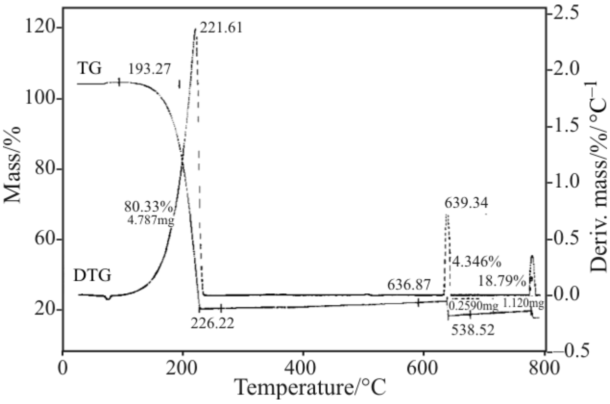

Fig. 8 TG-DTG curves of solution growth DAB

Conclusions

The solubility of *p-N,N*-dimethylaminobenzaldehyde in various solvents was determined and finally CCl_4 was selected as the growth medium. The solubility of *p-N,N*-dimethylaminobenzaldehyde in CCl_4 was determined at different temperatures. Solubility determination shows that the solubility increases with temperature.

After solubility determination, *p-N,N*-dimethylaminobenzaldehyde was grown by solution technique by adopting slow evaporation method at room temperature in CCl_4 as the growth medium. The harvested crystals were subjected to various characterization studies. It is subjected to UV-Visible spectral study to determine its transparency. It is found that the grown crystal is transparent for a wide range which is a characteristic property for a NLO material. The presence of disubstituted benzene ring and functional groups is supported by FTIR spectral analysis. To confirm its structure as well as purity, the grown crystals was subjected to ^{1}H and ^{13}C NMR spectral studies. The ^{1}H and ^{13}C NMR spectral studies confirm the presence of the functional groups and purity of the grown crystals. This also gives an idea about the non-centre of symmetric structure of *p-N,N*-dimethylaminobenzaldehyde which is important requirement for a material to be NLO active. Powder X-ray diffraction studies were also carried out which confirms the crystalline nature of grown crystal. Thermal studies confirm the purity and single crystalline nature of solution grown *p-N,N*-dimethylaminobenzaldehyde. This further supports the thermal stability of solution grown *p-N,N*-dimethylaminobenzaldehyde.

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