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Growth and Characterization of Benzophenone and Mixed Crystal of Benzophenone and 2,4-Dinitrophenyl hydrazone of Benzophenone

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Good quality benzophenone crystals were grown by solution technique using $CHCl_3$ as solvent by adopting slow evaporation method at room temperature. The grown crystals were subjected to various characterization studies to analyze of its purity and applications. The condensation product 2,4-dinitrophenyl hydrazone of benzophenone (DNPBP) was prepared by adopting standard procedure. Then mixed crystal of benzophenone and DNPBP was grown by solution growth. Both the condensation product and mixed crystals were characterized by UV, FTIR, ^1H NMR thermal studies reveals the purity of the product. SHG efficiency of the grown crystals was determined.

Key Words: Benzophenone, Solution growth, Mixed crystal, Characterization studies, SHG efficiency.

INTRODUCTION

Organic non-linear optic materials have greater importance due to their high non-linear optical properties, rapid response in electro optic effect and large second or third order hyper polarizabilities compared to inorganic NLO materials. In recent years considerable interest has developed in the study of organic compound exhibiting NLO properties[1]. Benzophenone is one such materials having NLO property and its derivative have been studied using powder SHG method. The results show several compounds generate SHG signals stronger than that of urea[2,3]. In the literature the benzophenone single crystal was first grown by the Czochralski technique[4] followed by reports from the solution method[5] and Bridgmann technique[6]. The study of band gap measurement of solution grown benzophenone was recently reported[7]. Vijayan *et al.*[8] reported the growth of semi carbazone of benzophenone by slow evaporation solution growth technique. Semicarbazone of acetophenone was grown by slow evaporation technique and the grown crystals were characterized by X-ray, FTIR, UV-Visible spectral analysis[9]. In this paper, the growth of benzophenone and mixed crystals of benzophenone and 2,4-dinitrophenyl hydrazone of benzophenone is reported for the first time.

EXPERIMENTAL

Crystal growth of benzophenone: The analaR grade benzophenone was purified by repeated recrystallization from $CHCl_3$ as solvent. The pure crystals of benzophenone were taken for crystal growth. The saturated solution of benzophenone was prepared in $CHCl_3$. It was allowed for slow evaporation at room temperature. Good transparent crystals were obtained in 3-4 d. These crystals were harvested and subjected to various characterization studies.

Solubility: The solubility of benzophenone was measured in various temperature ranges. The temperature of the solution was maintained above the chosen constant temperature and continuously stirred to ensure homogenous temperature and concentration throughout the entire region of the solution. A volume of 50 mL of $CHCl_3$ was taken in a container and recrystallized benzophenone was added once the saturation was reached, the equilibrium concentration of the solute was analyzed gravimetrically. The experiment was repeated for various temperatures from room temperature to 40 ºC in steps of 2 ºC. Solubility determination shows that the solubility increases with temperature. This is evidenced by the solubility curve shown in Fig. 1.

Metastable zone width: In order to determine metastable zone width of the solutions, conventional method was employed. The solution of benzophenone in $CHCl_3$ saturated at 30 ºC was cooled from slightly overheated temperature at a constant cooling rate till the first visible crystal was observed. Uniform concentration gradient was achieved by stirring the solution. The temperature difference between the saturation and nucleation temperature of the experimental solution was determined as its metastable zone width. The same procedure was adopted to measure the metastable zone width of benzophenone for different temperatures *viz*., 32, 37 and 40 ºC. From the values of solubility, saturation temperature and nucleation temperature, the metastable zone width is determined and shown in Fig. 1.

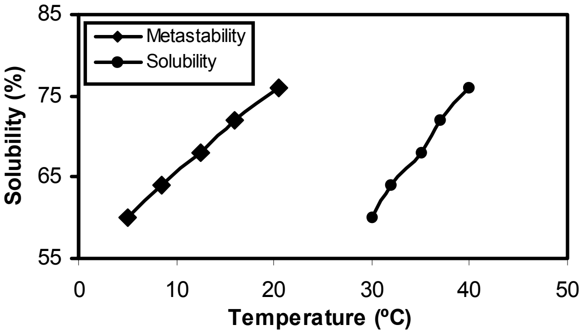

Fig. 1. Solubility and metastability of benzophenone in chloroform

Preparation of 2,4 dinitro phenylhydrazone of benzophenone: 5 g of 2,4-dinitrophenyl hydrazine was suspended in 10 mL of methanol. To this 0.5 mL of concentrated sulphuric acid was added cautiously. The warm solution was filtered and a solution of 0.5 g of benzophenone was added in small volume of methanol. Solid separates within 5 min. The solid derivative was separated and washed with aqueous methanol. The melting point of the derivative was found[10] to be 237 ºC.

Crystal growth of mixed crystal: Saturated solutions of benzophenone and 2,4-dinitrophenyl hydrazone of benzophenone were prepared in $CHCl_3$. These two saturated solutions were mixed thoroughly and allowed for slow evaporation at room temperature. Good transparent mixed crystal of benzophenone and DNPBP obtained in 1-2 d. These crystals were harvested and subjected to various characterization studies.

RESULTS AND DISCUSSION

UV-Visible spectrophotometer (Version 02.00) was used to record the UV visible spectrum of the grown crystals. Since BP crystal is colourless the absorption is not observed between 400 to 800 nm. The maximum absorption is at 347 and 480 nm due to C=O group. The DNPBP is a coloured compound. The absorption is observed between 400 to 799 nm. The maximum 280 nm absorption is assigned to C=N. Mixed benzophenone is coloured compound. Hence the absorption is observed at 400 to 800 nm. The presence of C=N and N-H group absorption were at 244 and 337 nm. Generally C=N groups are coloured. The resonance interactions between C=N and aromatic rings could provide more resonance energy.

The FTIR spectrum of benzophenone and 2,4-dinitrophenyl hydrazone of benzophenone were scanned in the range of 4000 to 400 cm^{-1} and analyzed[11,12]. The C=O group is found at 1650 cm^{-1}. The aromatic skeletal vibration is at 1447 cm^{-1}. The C-H deformation is found at 935 cm^{-1}. The NO_2 group stretching is assigned to 1444 cm^{-1}. The N-H deformation is found at 1558 cm^{-1}. The C=N stretching is observed at 1689 cm^{-1} and the NO_2 asymmetric stretching is at 1540 cm^{-1}. The NO_2 in aromatic compound symmetric stretching is found at 1361 cm^{-1}. The NO_2 deformation is found at 596 cm^{-1}. Phenyl ring deformation is observed at 717 cm^{-1}. The FTIR spectrum of mixed crystal. The higher wave number region gives interesting information with regard to bonding of the groups in the crystal. The doublet at 800 cm^{-1} in the spectrum is the characteristic of the aromatic 1,4-substitution. A strong singlet peak is observed at 1080 cm^{-1} also represents the same. Weak and variable peaks observed at 1160 and 1440 cm^{-1}, respectively further support the presence of aromatic 1,4-substitution. The variable strong doublet peak in the frequency range 1275-1300 cm^{-1} gives the presence of conjugated NO_2 group. The variable doublet peak at 1560 and 1580 cm^{-1}

shows the stretching of aromatic C=N. The two peak observed at 2805 and 2950 cm^{-1} support the aromatic C-H stretching. The C=O carbonyl stretching is at 1650 cm^{-1}. The aromatic ring skeletal vibration is at 1447 cm^{-1}. The C=N group in due 1593 cm^{-1}. The peaks below 1500 cm^{-1} would be due to C=N and N-H bending. The peaks lying between 3200 to 3000 cm^{-1} is due to N-H and C-H stretching.

^{1}H NMR spectrum recorded for the benzophenone in $CDCl_3$ at 400 MHZ in Jeol instrument showed multiplet of 14 peaks in the aromatic region. All the 10 protons of two phenyl rings are existing in the deshielding region of both the carbonyl group and the benzene ring.

Here the two-phenyl ring and the carbonyl group are in a same plane and hence all the protons are neighbouring. Radio frequency in the down field region between 7.2476 and 7.8448 ppm. If there is any deviation from the planarity a few protons of one phenyl ring may go to the shielding region of other benzene ring and *vice-versa* and show low delta value.

^{1}H NMR spectrum of 2,4-dinitro phenylhydrazone of benzophenone in $CDCl_3$ at 400 MHz was also recorded using the same instrument showed peaks in the aromatic region. Radio frequency in the down field region between 7.2610 and 7.8168 ppm for benzophenone. The singlet appearing at δ 1.595 ppm is due to the NH proton. The radio frequency in the up field region 8.2064 to 11.2354 ppm due to the presence of dinitrobenzophenone group.

The doublet at 9.1 ppm is assigned to 2,4-dinitro phenyl (3-H). The doublet at 8.3 to 8.4 ppm is assigned to 2,4-dinitro phenyl (5-H) and the doublet at 8.2 ppm is assigned to (6-H).

^{1}H NMR of mixed crystal was also recorded in $CDCl_3$ at 400 MHz using the same instrument showed few more peaks in the aromatic region along with one singlet in the non-aromatic region confirmed that DNPBP was mixed with benzophenone.

The singlet appearing at δ 1.7820 ppm is due to the NH proton. Generally, the NH proton of aromatic compound absorb in between the value of 5 to 3 ppm due to the formation of H-bonding. In this case the proton of nitro substituents on the phenylhydrazone part due to the electron with drawing nature pull the electron cloud from the benzophenone part. Here these electron density around the NH proton increased which accounts for the up field shift of the NH signal due to high shielding of NH-proton.

The high resolution Guinier powder X-ray diffractometer (CSEIFERT, Germany) with CuK_α radiation has been used for X-ray diffraction studies. The predominant X-ray diffration pattern of solution grown benzophenone are in good agreement with the JCPDS values and standard values. The predominant peaks are (0 2 1), (2 1 0), (0 1 2) which are in accordance with the literature values[13]. Further, the narrow and strongest peak along (0 2 1) direction confirms the single crystalline nature of the solution grown benzophenone.

Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) were carried out on the crystal samples for qualitative analysis. These studies were conducted for benzophenone, mixed crystal and DNPBP samples. Both TGA and DTA were carried out on these samples simultaneously. The weight change in the sample with temperature was studied by TGA and the energy change in the sample with temperature was studied by DTA. The analysis was performed in nitrogen atmosphere.

There is an intense single stage weight loss at 272.5 ºC with a total weight loss at 98.85 % is observed in the thermogram of benzophenone. DTA analysis shows a sharp peak at 49 ºC due to the melting point. In the thermogram of DNPBP there is an intense single stage of weight loss between 112 ºC to 478 ºC with a maximum of 272 ºC is observed. The total weight loss corresponds to 98.28 %, clearly illustrates melting point and its subsequent evaporation.

In the thermogram of mixed crystal, there is an intense single stage weight loss at 261 ºC. The total weight loss corresponds to 98.87 %. The DTA analysis showed that the curve produces a sharp peak at 60ºC due to the melting point.

Conclusion

The presence of C=N group in mixed crystal, C=O group in BP, N-H group in DNPBP are confirmed by FTIR spectrum. The NMR spectrum of benzophenone and doped benzophenone crystals shows important absorption peaks which corresponds to functional groups containing different chemical environments. Determination of peak areas in the spectrum reveals the number of protons responsible for each signal. The ratio of peak height in the two triplets due to the protons of two rings are not symmetrical because of the fact that the separation between these two signals is not very large relative to the separation of peaks within a particular triplet. In the recorded NMR spectrum of benzophenone and doped benzophenone, the reason for the appearance of the signal corresponds to N-H proton, aromatic proton in the down field is due to the deshielding effect created by the NO_2 group on these protons. The ^1H NMR spectrum shows the presence of C=O and benzene ring in benzophenone.

When 2,4-dinitrophenyl hydrazone of benzophenone is incorporated in the crystals of benzophenone the C=O is replaced by C=N group which causes the delocalization of the electron clouds so as to increase asymmetric unit. Thus we expect the enhancement of dipole moment resulting in the increase of the NLO property of mixed crystal. The SHG efficiency of benzophenone is found to be 81. It is 0.54 times SHG efficient than KDP crystals. The SHG efficiency of mixed crystal is 96. It is found to be 0.64 times efficient than KDP crystals. It is clearly evident that mixed crystals has higher NLO property.

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