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Synthesis, structural, optical and thermal properties of N-methyl–N-aryl benzamide organic single crystals grown by a slow evaporation technique

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ABSTRACT

The organic materials, N-methyl–N-aryl benzamides were synthesized from benzoylation of N-methyl-4-nitrobenzenamine (MNBA) using suitably substituted benzoyl chlorides. The products were purified by recrystallization and their single crystal were grown by a slow evaporation technique. The crystals were characterized by FTIR, UV–Vis–NIR, ^{1}H & ^{13}C NMR, and single & powder X-ray diffraction. Thermal stability of the crystals was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Dielectric and NLO properties of MNPB, FMNPB and MMNPB crystals were studied. The second harmonic generation (SHG) has been confirmed by the Kurtz powder test for all these crystals and the SHG efficiency of MMNPB crystal was found to be 2.25 times higher than that of KDP crystal.

1. Introduction

Molecular engineering is the procedure whereby molecular structure is refined by chemical synthesis to produce desired combination of physical and chemical properties in a given phase for a particular application. The appropriate development of crystal growth is important for materials that exhibit nonlinear optical properties. Organic crystals are often formed by weak van der Waals and hydrogen bonds leading to a high degree of delocalization.

Recent developments in the field of nonlinear optics (NLO) have pushed organic second order nonlinear optical materials into practical applications in the fields of photonics, lasers, electro-optic switches, telecommunication, optoelectronic, frequency conversion and optical information storage devices. During the past decades, numerous organic and inorganic materials with high nonlinear susceptibilities have been synthesized. However, their device applications have been impeded by inadequate optical transmittance, poor optical quality and low laser damage threshold [1–4]. The molecules in pure organic crystals are often bonded by weak van der Waals forces or hydrogen bonds, which result in poor mechanical robustness. Inorganic NLO materials, which have excellent mechanical and thermal properties, suffer relatively modest optical susceptibilities due to the lack of π-electron delocalization.

Organic NLO crystals with high second harmonic generation efficiency and transparency in UV–Vis region are required for numerous device applications [5–7]. In order to exhibit NLO properties the organic material should contain highly conjugated π-electron system affected by electron donor and acceptor groups, and possess increased asymmetric electronic distribution in both the ground and excited states [8]. Some of the advantages of organic NLO materials include flexibility in the method of synthesis, scope for altering the properties by functional group substitution, inherently high nonlinearity, and high damage resistance. Hence it is important to look for new organic NLO materials.

In this work, we report the synthesis, crystal growth and NLO properties of three N-methyl–N-aryl benzamides, N-methyl–N-(4-nitrophenyl)benzamide (MNPB) (**3a**), 4-fluoro-N-methyl-N-(4-nitrophenyl) benzamide (FMNPB) (**3b**) and 4-methoxy-N-methyl-N-(4-nitrophenyl)benzamide (MMNPB) (**3c**).

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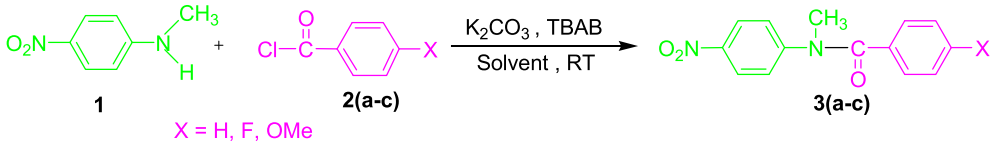

Scheme 1. Synthesis of N-methyl–N-aryl benzamides (**3**).

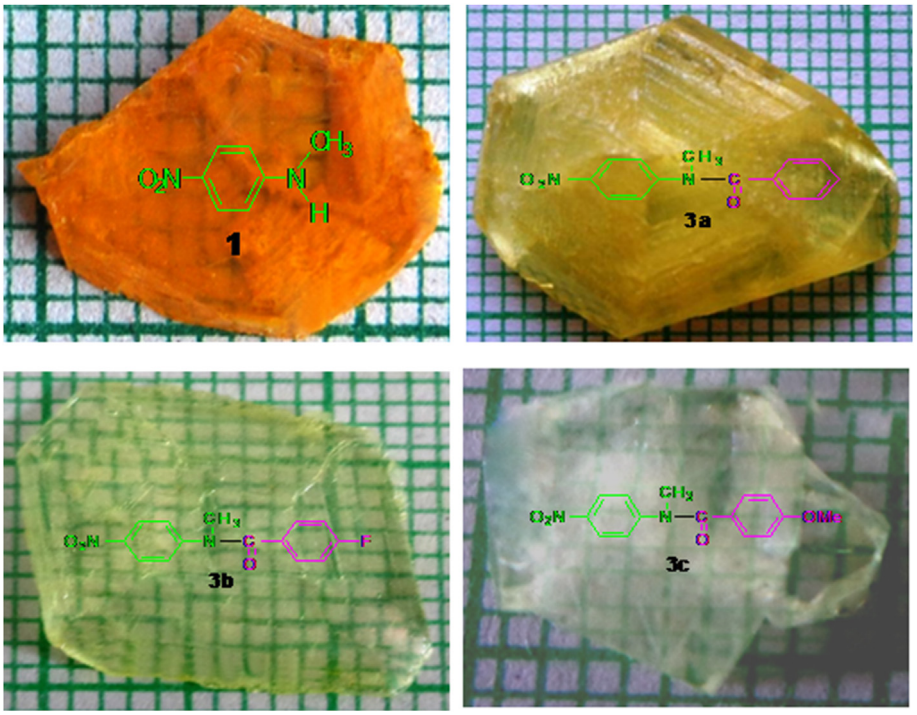

Fig. 1. (a–d) Grown single crystals of (a) MNBA (**1**) (b) MNPB (**3a**) (c) FMNPB (**3b**) and (d) MMNPB (**3c**).

2. Experimental section

2.1. Materials synthesis

All the reagents such as N-methyl-4-nitrobenzenamine, benzoyl chloride, 4-fluoro benzoyl chloride, 4-methoxy benzoyl chloride, tetrabutylammoniumbromide and solvents such as acetonitrile, chloroform, dimethylsulphoxide, ethyl acetate and methanol were purchased as AR grade and used as such without further purification. A modified procedure [9] was used for benzoylation of amine. To synthesize MNPB **3a**, N-methyl-4-nitrobenzenamine 1 (10 mmol), K_2CO_3 (15 mmol), tetrabutylammoniumbromide (TBAB) as catalyst (1 mmol) and benzoyl chloride 2a (12 mmol) in a solvent (20 ml) was stirred at room temperature for 20–30 min. After the completion of reaction (as indicated by the disappearance of starting material on TLC) the mixture was poured into crushed ice (20 g). The separated solid was filtered, washed with water (2 × 10 ml) and dried. The crude product on recrystallization from aq. methanol gave pure MNPB **3a**. Synthesis was carried out in different solvents such as acetonitrile, chloroform, dimethylsulphoxide, ethyl acetate and higher yields were obtained in acetonitrile and chloroform.

Similar procedure was adopted for the synthesis of FMNPB **3b** and MMNPB **3c**. The syntheses of these compounds are illustrated in Scheme 1.

2.2. Crystal growth

The single-crystals of MNBA, MNPB, FMNPB and MMNPB were grown using low temperature solution growth. The saturated solutions of MNBA (**1**), MNPB (**3a**), FMNPB (**3b**) and MMNPB (**3c**) were subjected to slow evaporation at ambient temperature to allow crystal growth. MNBA (**1**) (acetone as solvent) crystal with the dimensions of 12 × 8 × 1 mm^3 was orange in color and MNPB (**3a**), FMNPB (**3b**) and MMNPB (**3c**) (ethyl acetate as solvent) single crystals were transparent yellow, pale yellow and colorless with the dimensions of 20 × 15 × 2 mm^3, 11 × 11 × 1 mm^3 and 10 × 6 × 2 mm^3 respectively. Photographs of the as-grown single crystals of MNBA (**1**), MNPB (**3a**), FMNPB (**3b**) and MMNPB (**3c**) are shown in Fig. 1. The crystal growth pattern was observed by etching method and the results are presented in Supplementary Information.

2.3. Materials and instrumentation

Crystal structures of all the grown crystals were arrived at by single crystal XRD analysis carried out using a Bruker ×8 κ diffractometer with Mo Kα (λ = 0.177 Å) radiation. Diffraction data