Journal of Crystal Growth 401 (2014) 323–326

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Synthesis, growth, structural, optical and thermal properties of a new organic salt crystal: 3-nitroanilinium trichloroacetate

E. Selvakumar [a], A. Chandramohan [a,*], G. Anandha Babu [b], P. Ramasamy [b]

[a] Postgraduate and Research Department of Chemistry, S.R.M.V College of Arts and Science, Coimbatore 20, Tamilnadu, India
[b] Centre for Crystal Growth, SSN College of Engineering, Kalavakkam 603110, Tamilnadu, India

ARTICLE INFO

Available online 20 November 2013

Keywords:
A1. Crystal structure
A2. Growth from solutions
B1. Organic compounds
B2. Nonlinear optic Materials

ABSTRACT

A new organic non-linear optical salt 3-nitroanilinium trichloroacetate has been synthesized and single crystals grown by slow solvent evaporation solution growth technique at room temperature using methanol as the solvent. The ^{1}H and ^{13}C Nuclear magnetic resonance spectra were recorded to establish the molecular structure of the title salt. The crystal structure of the title crystal has been determined by single crystal X-ray diffraction analysis and it belongs to monoclinic crystal system with non-centrosymmetric space group P21. Fourier transform infrared spectral study has been carried out to confirm the presence of various functional groups. The optical transmittance spectrum was recorded in the range 200–2500 nm, to find the optical transmittance window and lower cut off wavelength. The thermo gravimetric and differential thermal analyses were carried out to establish the thermal stability of the title crystal. The second harmonic generation in the title crystal was confirmed by the modified Kurtz–Perry powder test employing the Nd: YAG laser as the source for infrared radiation.

1. Introduction

The design and construction of organic materials for NLO applications have received a great deal of attention owing to their potential applications in the various fields like electro-optic modulation, frequency conversion and optical parametric oscillations [1–4]. The nature of the constituent species and their relative orientations within the solid play a significant role in determining the physical and chemical properties of the organic molecular solids. For instance a material to exhibit non-linear optical property its molecular dipoles should orient in a non-centric manner, which is one of the essential requirements for materials to exhibit second harmonic generation [5]. Majority of the organic molecules crystallize in centrosymmetric space groups and fail to exhibit the non linear optical property. To overcome this issue various molecular engineering strategies like steric hindrance, chirality, electrical poling, dye-polymer blending, co-crystallization, hydrogen bonding etc., have been proposed [6–9]. Among all the strategies hydrogen bonding is a versatile strategy due to its directional nature it can orient the molecules in a head-to tail manner thereby avoiding centrosymmetric packing and thus paves the way for the materials to show SHG [10–14]. This intermolecular hydrogen bonding not only favours the non-centrosymmetric arrangement but also enhances the mechanical and thermal stability of the crystal [15,16]. In organic materials the donor–acceptor o-, p-, and m-disubstituted benzene derivatives are chromophores possessing non-linear optical properties in solutions and in the solid state [17]. Among these 3-nitroaniline is one of the organic compounds which exhibit larger microscopic second order non-linear susceptibilities. Trichloroacetic acid forms crystalline complexes with amines and amino acids [18,19]. In this paper for the first time we report the synthesis, growth, structural and physical properties of the title crystal, 3-nitroanilinium trichloroacetate.

2. Experimental procedure

The title compound 3-nitroanilinium trichloroacaetate (NAT) was synthesized by reacting equimolar quantities of 3-nitroaniline and trichloroaceticacid in methanol solution. Fig. 1 represents the reaction scheme involved in the formation of the title compound. The synthesized salt was purified by repeated recrystallization and used for the growth of single crystals. Single crystals of the title compound were grown from saturated methanol solution of the recrystallized salt by slow solvent evaporation solution growth technique. The crystal size $4\times3\times2\ mm^{3}$ has been obtained within 15 days time and the photograph of as-grown crystals shown in Fig. 2. To confirm the molecular structure of NAT crystal, the ^{1}H and $^{13}CNMR$ spectra were recorded employing a Bruker 500 MHz spectrometer in deuterated methanol solvent using TMS as the internal reference standard. The crystal structure was determined from the single crystal X-ray diffraction data obtained with a Bruker Kappa Apex-II diffractometer (Graphite monochromated,

---

[*] Corresponding author. Tel.: +91 9994283655.
E-mail address: dracmsrmvcas@gmail.com (A. Chandramohan).

0022-0248/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jcrysgro.2013.10.053

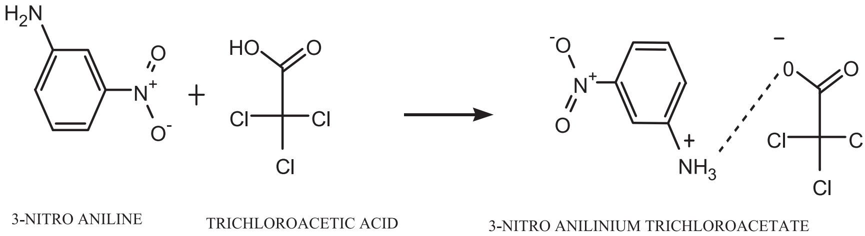

Fig. 1. Reaction scheme of NAT.

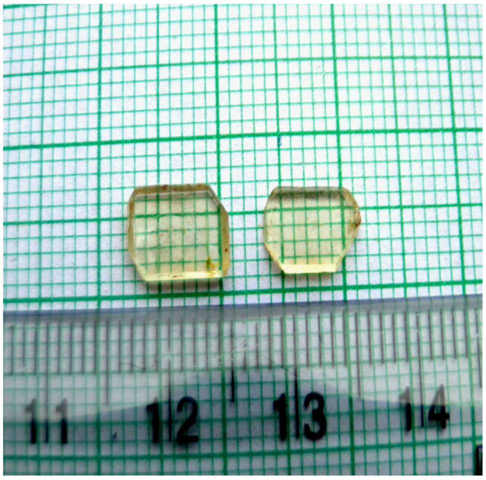

Fig. 2. As-grown crystals of NAT.

MoKα=0.71073 A). The data were collected at 23 °C and the crystal data are given in Table 2. The structure was solved by direct methods using the program SHELXS-97 [20] and refined by full matrix least squares method using SHELXL-97 [21]. The *R*-value of the full-matrix least squared refinement is given in Table 2. The H-atoms could all be located in fourier difference maps. Fourier transform infrared (FT-IR) spectrum was recorded using potassium bromide pellet method employing a Perkin Elmer FT-IR spectrometer in the range 4000–450 cm^{-1}. The UV–vis–NIR transmission spectrum of NAT was recorded employing a Perkin Elmer spectrophotometer. The Thermo gravimetric (TG) and Differential thermal analysis (DTA) studies were carried out on a S-II Nanotechnology TG/DTA 6200 thermal analyzer instrument at a heating rate of 10 °C/min in the temperature range from 20 to 600 °C in nitrogen atmosphere. Quantitative estimation of relative SHG efficiency of NAT crystal with respect to KDP was made by employing the modified Kurtz and Perry powder technique.

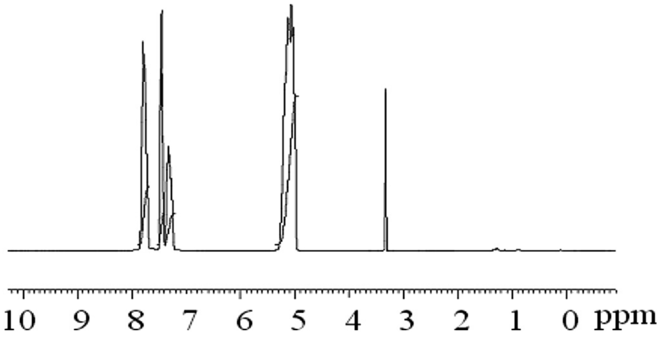

Fig. 3. ^{1}H NMR spectrum of NAT.

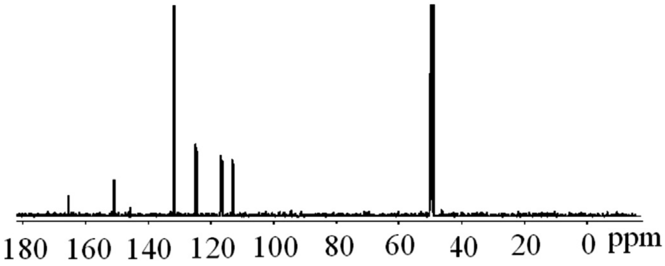

Fig. 4. ^{13}C NMR spectrum of NAT.

Table 1
^{13}C NMR Spectral data of NAT

Chemical shift (ppm)	Assignments
165	Carboxyl carbon of trichloroacetate moiety
150	Chlorine substituted carbon of trichloroacetate moiety
147	C3 Carbon of 3-nitro anilinium moiety
131	C4 Carbon of 3-nitro anilinium moiety
124	C2 Carbon of 3-nitro anilinium moiety
116	C6 Carbon of 3-nitro anilinium moiety
113	C5 Carbon of 3-nitro anilinium moiety
112	C1 Carbon of 3-nitro anilinium moiety

3. Results and discussion

The ^{1}H NMR spectrum of NAT crystal is depicted in Fig. 3. In the ^{1}H NMR Spectrum, the appearance of four distinct proton signals confirms four different proton environments and hence the molecular structure of the title salt. The NH_3^+ protons appear as a singlet at δ 5.066 ppm. The C4 and C6 aromatic protons of the same kind in the m-disubstituted 3-nitroanilinium moiety stand responsible for the doublet signal exhibited at δ 7.762 ppm. The C5 aromatic proton of the same moiety appears as a triplet at δ 7.429 ppm. The singlet proton appearing at δ 7.309 ppm owes to the C2 aromatic proton. The ^{13}C NMR spectrum of NAT crystal is depicted in Fig. 4. In the ^{13}C NMR spectrum the appearance of eight distinct carbon signals in the spectrum explicitly confirms the molecular structure of NAT crystal. The highly deshielded carboxyl carbon of the trichloroacetate moiety appears at δ 165 ppm. The carbon signal at δ 150 ppm is attributed to the chlorine substituted carbon of trichloroacetate moiety, the remaining carbon signals and their respective assignments were given in Table 1. Thus the molecular structure of NAT salt crystal unambiguously confirmed by the ^{1}H and ^{13}C NMR spectral data.

Single crystals suitable for X-ray crystallographic analysis were selected following the examination under a polarizing microscope. X-ray intensity data of 4932 reflections (of which 2567 were unique) were collected on a Bruker Kappa Apex-II CCD Diffractometer equipped with a graphite monochromated MoKα radiation (λ=0.71073 Å). The cell dimensions were determined by least-squares fit of angular settings of 4932 reflections in the θ range 1.80–28.26°. The intensities were measured by ω scan mode for 2θ ranges from 1.80° to 28.26°. The data were collected for Lorentz