Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 120 (2014) 14–18

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Non linear optical analyses of hexamine: Phenol cocrystals based on hydrogen bonding: A comparative study

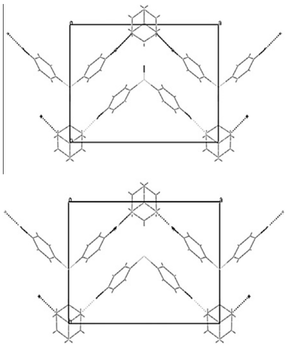
S. Vijayalakshmi, S. Kalyanaraman *

PG & Research Department of Physics, Sri Paramakalyani College, Alwarkurichi 627412, India

HIGHLIGHTS

- Synthesis of similar structures of two hexamine: phenol (1:1) cocrystals.
- Hydrogen bondings are discussed through FT-IR and Raman.
- Charge transfer interaction (CT) is analyzed through hydrogen bonding.
- NLO response analysis through CT.
- Determination of NLO efficiency by Powder Kurtz–Perry method.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 January 2013
Received in revised form 11 May 2013
Accepted 2 October 2013
Available online 12 October 2013

Keywords:
Fourier transform infrared spectroscopy (FTIR)
Raman spectroscopy
Second harmonic generation (SHG)

ABSTRACT

Fourier-Transform Infrared (FT-IR) spectroscopy supported by Raman spectroscopy has been employed to explain the conventional and unconventional hydrogen bonding present in the 4,4′thiodiphenol: hexamine and 4,4′sulfonyldiphenol: hexamine cocrystals. The possible internal and external vibrational modes are predicted through factor group analysis. Influence of intra molecular charge transfer (ICT) interaction caused by the strong ionic ground state hydrogen bonding between charged species, giving rise to a non centro symmetric structure which is a criterion for second harmonic generation (SHG) efficiency has been discussed. Intense low wave number hydrogen bond vibrations in Raman which arise due to electron–phonon coupling are analyzed. Optical quality of adducts is identified through UV–Vis analysis. The second harmonic generation efficiency of both adducts is determined by Kurtz–Perry method.

1. Introduction

Numerous efforts have been devoted over the last decades on cocrystals by developing their design strategies and growing techniques [1–4]. Their importance is greatly emphasized in the last decade as pharmaceutical crystals [5–8] because of their ability to alter the physico-chemical properties without impairing the pharmaceutical activities of ingredients. The idea of cocrystal formation is not restricted to applications in the pharmaceutical industry alone but also finds utility in synthetic chemistry [9], in the generation of optical materials [10].

Hydrogen bond is one of the most important non covalent interactions, which plays key roles in molecular recognition, crystal engineering, supra molecular assembly, materials science, and biological systems [11–14]. Mostly the molecular recognitions are concerned with strong N—H$\cdots$X and O—H$\cdots$X (X = O, N) hydrogen bonds. Besides these conventional hydrogen bonds, unconventional C—H$\cdots$O hydrogen bonds are also involved in the formation of supra molecular assembly [15,16]. Crystallographic and abinitio quantum chemical calculations, over the last decade, have also established the proton donating ability of a methyl group and formation of a weak hydrogen bonding type C—H$\cdots$X (X = O, N) bonds

---

* Corresponding author. Tel.: +91 94438 69658; fax: +91 4634 283560.
E-mail address: mayura_priya2003@yahoo.co.in (S. Kalyanaraman).

1386-1425/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2013.10.006

[17–23]. In the context of supra molecular synthesis, hexamine provides its unique feature for the facile design and isolation of supra molecular complexes using self-assembly of different but complementary supra molecular synthons. Hexamine, a highly symmetrical molecular scaffold, is attractive due to the presence of four equivalent hydrogen bond acceptor nitrogen atoms. At the same time, the methyelene protons of this entity are also involved in the formation of C—H···O and C—H···N unconventional hydrogen bonds to form supramolecular assembly along with the conventional N—H···X (X = O, N) hydrogen bonds in the presence of several appropriate cocrystallizing entities [24]. The hydrogen bonding interaction of hexamine with different types of phenols makes an interesting study and very few of them have been studied in detail [25–27]. The present work describes the vibrational spectroscopic investigations to correlate the NLO response with the hydrogen bonding and intramolecular charge transfer interaction of 4,4′thiodiphenol: hexamine and 4,4′sulfonyldiphenol: hexamine cocrystals.

2. Experimental

All the materials used in the present study were of pure grade procured from Sigma Aldrich. Cocrystals under study were crystallized by slow evaporation method. The two components were separately dissolved in ethanol and the solutions were then mixed to give 4,4′thiodiphenol: hexamine (**1**) and 4,4′sulfonyldiphenol: hexamine (**2**) in the stoichiometric ratios of 1:1 and were allowed to crystallize at room temperature for slow evaporation. The resulting cocrystals were colorless. Crystals suitable for single crystal X–ray diffraction were selected and the lattice parameters were determined using Enraf-Nonius CAD-4 diffractometer. FT-IR spectrum of the crystals were recorded in the wave number range 4000–400 cm^{-1} by KBr pellet technique (Shimadzu Fourier Transform Infrared Spectrometer). Raman spectra of powder samples were measured using a Renishaw Invia micro Raman spectrometer with 514 nm laser excitation from 30 cm^{-1} to 3200 cm^{-1}. No bands were found above 2000 cm^{-1}. The UV–Vis spectra were recorded in the solvent ethanol for better stabilization of excited state using UV–1700 series.

3. Results and discussion

3.1. Crystal structure

4,4′thiodiphenol: hexamine and 4,4′sulfonyldiphenol: hexamine complexes (adducts) were crystallized in the orthorhombic system of space group Pmn21 with two molecules per unit cell ($Z = 2$). Coupar et al. have reported that the conventional O—H···N hydrogen bonds in both the complexes generate chains in [1 0 0] direction. In addition unconventional C—H···O (short) hydrogen bonds are observed in 4,4′sulfonyldiphenol: hexamine complex only. Besides C—H···π (arene) interactions are also found in both the complexes. These two unconventional hydrogen bonds form a spiral around the 2_1 axis. The basic O—H···N hydrogen bonds are found folded into a zig–zag pattern. This folding of the main O—H···N hydrogen bonds, which forms the basic structure, is stabilized by C—H···π (arene) interactions and the unconventional C—H···O hydrogen bonds. Since 4,4′sulfonyldiphenol: hexamine adduct has unconventional C—H···O═S along with the C—H···π (arene) interactions the zig–zag pattern of the structure was further stabilized by preventing the folding and twisting of main O—H···N hydrogen bond chains when compared with 4,4′ thiodiphenol: hexamine adduct [28]. The lattice parameter values from XRD are in good agreement with the above literature and thus confirm the grown crystal.

3.2. Factor group analysis

The complex of 1:1 mole ratios of 4,4′thiodiphenol:hexamine and 4,4′sulfonyldiphenol: hexamine belongs to the non centro symmetric $Pmn2_1$ space group, with $Z = 2$, which indicates the number of molecules per unit cell. The 47 atoms of hexamine: 4,4′thiodiphenol in the unit cell give rise to a total 282 modes, which can be characterized according to the C_{2V} factor group of the crystal using standard group theoretical methods [29] based on the literature [30]. The representation corresponding to the total degrees of freedom, Γ_{total}, is given by 71 A1 + 70 A2 + 71 B1 + 70 B2 among which the three acoustic modes are 1 A1 + 1 B1 + 1 B2. The 282 total modes are further divided into 210 internal and 72 external modes. Among the 210 internal modes, the irreducible representations for 4,4′thiodiphenol molecule $2[C_{12}H_{10}O_2S]$ is given by 29 A1 + 28A2 + 29 B1 + 28 B2 and the remaining 96 [24 A1 + 24A2 + 24 B1 + 24 B2] for hexamine $2[C_6H_{12}N_4]$ molecule. The total number of atoms (49) in 4,4′sulfonyldiphenol: hexamine give rise to 294 vibrational modes. The modes are distributed as 73 A1 + 73 A2 + 73B1 + 72 B2 for optical modes and 1 A1 + 1 B1 + 1 B2 for acoustic modes. The 294 total vibrational modes are further divided into 222 internal and 72 external modes. Among the 222 internal modes, the irreducible representations for 4,4′sulfonyldiphenol molecule $2[C_{12}H_{10}O_4S]$ is given by 32 A1 + 31A2 + 32 B1 + 31 B2 and the remaining 96 [24 A1 + 24A2 + 24 B1 + 24 B2] for hexamine $2[C_6H_{12}N_4]$ molecule. Compared with adduct **1** we have 12 (3A1 + 3A2 + 3B1 + 3B2) additional vibrational optical modes for adduct **2**. Generally Optical modes, caused by vibrations within unit cells and analogous to intramolecular motions, can exhibit very long wavelengths in the crystal with only small changes in frequency. When intramolecular stretching vibrations are in phase it gives rise to lattice vibrations with longer wavelength. In addition a possibility for lower wavelength mode to appear when the intramolecular stretching vibrations are in out of phase [31]. Unlike adduct **1**, adduct **2** exhibits both these type of optical modes in IR and Raman spectra which arise due to the presence of oxygen atoms. This reveals an effective intramoleclar charge transfer in adduct **2** than adduct **1**. The mode A1 is Raman active only and the modes A2, B1 and B2 are both Raman and IR active.

3.3. FT-IR analysis

The vibrations of both adducts were analyzed on the basis of characteristic vibrations of Hydroxyl, methyelene and sulfone groups and they are enlisted in Table 1 along with assignments for Raman bands. The plot of FT-IR spectra of adducts are shown in Fig. 1. From the spectra, we observe the intense multiplet bands in the region 3470–1910 cm^{-1}; implicate the proton vibrations in all hydrogen bonds. This indicates the non proton transfer of the complexes [32].

3.3.1. Vibrations of hydroxyl group

The non-hydrogen bonded or free hydroxyl group absorbs strongly in the 3700–3584 cm^{-1} region, while the intermolecular hydrogen bond formation can lower the O—H stretching frequency to the 3550–3000 cm^{-1} with an increase in the IR intensity and broadness [33–35].In addition the 3570–3450 cm^{-1} of O—H stretching is assigned to intramolecular hydrogen bonding [36]. The 4,4′thiodiphenol has free O—H stretching vibrations at 3659 cm^{-1}. This is lowered by 185 cm^{-1} and the intermolecular hydrogen bonded O—H stretching frequency occurs at 3474 cm^{-1} in adduct **1**. This red shift indicates the strong intermolecular O—H···N hydrogen bonding. We observe the absence of free O—H stretching vibrations in adduct **2**. The band which arises at 3479 cm^{-1} is assigned to the intermolecular hydrogen bond of