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Synthesis and non linear optical properties of new inorganic–organic hybrid material: 4-Benzylpiperidinium sulfate monohydrate

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ABSTRACT

Single crystals of 4-benzyl-piperidine sulfate monohydrate were grown by slow evaporation method at room temperature. The synthesized compound was characterized by means of single-crystal X-ray diffraction, FT-IR and Raman spectroscopy, UV–visible and photoluminescence studies. The title compound crystallises at room temperature in the non centrosymmetric space group $P2_12_12_1$.The recorded UV–visible spectrum show good transparency in the visible region and indicates a non-zero value of the first Hyperpolarizability. Photoluminescence spectrum shows a broad and intense band at 440 nm and indicates that the crystal emits blue fluorescence. We also report DFT calculations of the electric dipole moments (μ), Polarizability (α), the static first Hyperpolarizability (β) and HOMO–LUMO analysis of the title compound was theoretically investigated by GAUSSIAN 03 package. The calculated static first Hyperpolarizability is equal to 6.4022×10^{-31} esu. The results show that 4-benzyl-piperidine sulfate monohydrate crystal might have important non linear optical behavior and can be a potential non linear optical material of interest.

1. Introduction

There has been an ongoing research in our laboratory on synthesis, crystal structure and vibrational studies of new organic–inorganic compounds which are assumed to show important physical and chemical properties [1–7]. Recently hybrid materials have been attracted great attention because of their unique opportunity to combine the remarkable features of organic compounds with those of inorganic materials, to produce materials having a non-centrosymmetric cell, large polarizabilities and a strong non-linear optical coefficient (first and second Hyperpolarizability) [8–12]. These have been the subject of intense research owing to their potential use in a various fields like laser technology and optical communication. Our last three published papers have been devoted to 4-benzyl-piperidine selinate [1], 4-benzyl-piperidine nitrate [2] and 4-benzyl-piperidine $PbBr_3$ [3] characterized by the X-ray diffraction, thermal study, IR and Raman analysis as well as Density Functional Theory (DFT) calculations. Then, as a continuation of our interest in 4-benzyl-piperidine derivatives, experimental and theoretical analysis of a new organic–inorganic compound was discussed in this paper. The present work deals with the growth, structural characterization; vibrational spectral investigation, optical properties (UV–visible and photoluminescence) as well as the theoretical study of the nonlinear optical properties of the 4-benzyl-piperidine sulfate monohydrate (4-BPPS) aided by Density Functional Theory (DFT) calculations.

2. Experimental

2.1. Crystal growth

The title compound was synthesized by dissolving 1 ml of 4-benzyl-piperidine in ethanol (5 ml) and slowly added under stirring of sulfate acid (0.37 ml). The resulting solution was stirred well and kept at room temperature. After few days of slow evaporation, single transparent crystalline salts of 4-BPPS were formed. Repeated recrystallization decreases the impurity and increases the purity of synthesized compound. After recrystallization, the good optical quality single crystal was obtained at room temperature in solution growth slow evaporation technique over a period of 7 days.

2.2. X-ray data collection

A single crystal of about $0.05 \times 0.1 \times 0.03$ mm^3 was selected for the diffraction experiment. The X-ray data collection was carried

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Table 1
Crystal data and structural refinement for 4-BPPS.

Crystal data	Details
Empirical formula	$C_6H_5CH_2C_5H_9NH_2^+ \cdot HSO_4^- \cdot H_2O$
Formula weight (g/mol)	291.36
Temperature (K)	298
Wavelength (Å)	1.54178
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.3455 (2)
b (Å)	8.6699 (2)
c (Å)	26.2972 (7)
V (Å^3)	1446.74 (7)
Z	4
Density calculated (mg/cm^3)	1.338
Crystal color	Colorless
Crystal size (mm^3)	0.1 × 0.2 × 0.3
Theta range for data collection (°)	3.36–64.88
Index range	$-7 \leqslant h \leqslant 6$
	$-8 \leqslant k \leqslant 10$
	$-30 \leqslant l \leqslant 30$
R_{int}	0.0353
R indices	$R_1 = 0.0229$; $W_{R2} = 0.059$

out on Enraf-Nonus C4D4 four circle diffractometer using Mo Kα radiation at 298 K. The crystal structure was solved by direct method using SHELXS-97. Successive refinements based on F^2 lead to a reliability factors of $R = 0.0229$. Anisotropy thermal displacement parameter refinement was used for all non-hydrogen atoms. Most of the hydrogen atoms attached to carbon and nitrogen were placed at geometrically calculated positions and refined with appropriate riding model. Crystal data and refinement details are given in Table 1.

2.3. Spectroscopic measurements

The Fourier transform infrared (FT-IR) spectrum of 4-BPPS was recorded in the range 4000–400 cm^{-1} using PERKIN-ELMER FT-IR spectrometer 100. The resolution of the spectrum is ±2 cm^{-1}. The Fourier transform Raman (FT-Raman) spectrum of the same compound was recorded using Horiba Jobin Yvon LabRAM HR 800 Dual Spectrophotometer. The incident laser excitation is 632 nm. The scattered light was collected at the angle of 180° in the region 3600–80 cm^{-1} and the resolution was set up to 2 cm^{-1}. Due to the poor detector response, the Raman counterparts of the infrared bands located above 3200 cm^{-1} are not observed in spectrum. Thin films of 4-BPPS were grown on a quartz substrate by spin coating at 2000 rpm and for 20 s duration. The crystals were first dissolved in aqueous solution and optical absorption spectra of the films were measured at room temperature using a conventional UV–visible absorption spectrometer (Hitachi, U-3300). The room temperature photoluminescence spectrum was recorded using a PerkinElmer LS 55 spectrometer and exciting with 350 nm radiation.

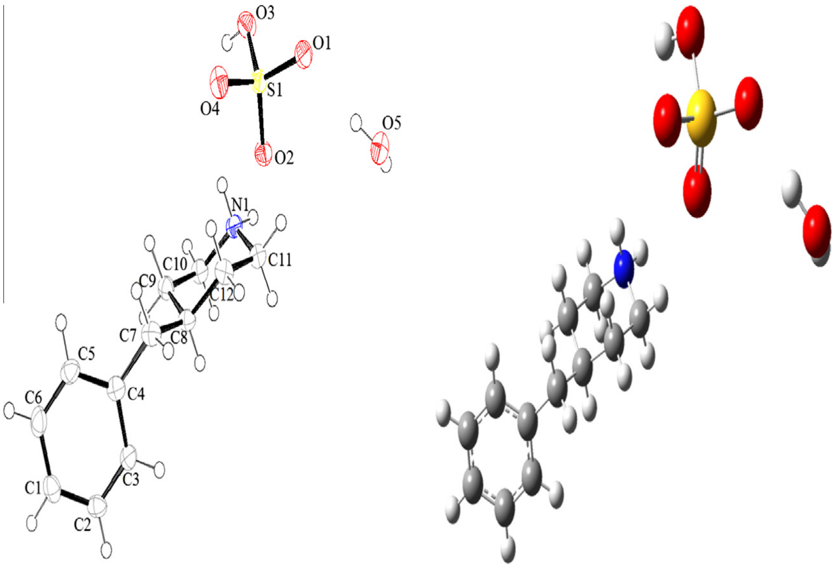
3. Theoretical method

The molecular structure of the title compound was fully optimized without any constraint at the Density Functional Theory (DFT) level using the Lee–Yang–Parr correlation functional (B3LYP/6-31G(d,p)) implemented within Gaussian 03 program [13]. Optimized geometry of the title compound model is presented in Fig. 1b. In order to take into account the effect of intermolecular interactions on geometrical parameters and vibrational spectroscopy, we have considered the cluster built up from one 4-BPP cation, one sulfate anion and one water molecule linked by N–H…O and O–H…O hydrogen bonds. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to an energy minimum as revealed by the lack of imaginary values in the calculated wave numbers.

The total dipole moment (μ), the linear Polarizability (α), the static first Hyperpolarizability (β) and the static second Hyperpolarizability (γ) were calculated using DFT/B3LYP/6-31G(d,p) implemented within Gaussian 03 [13]. The nonlinear optical response of an isolated molecule in an electric field $E_i(\omega)$ can be presented as a Taylor series expansion of the total dipole moment, μ, induced by the field:

$$\mu = \mu_0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l \ldots$$

where μ_0 is the permanent dipole moment, α_{ij} the linear Polarizability, β_{ijk} is the static first Hyperpolarizability tensor components and



(a) (b)

Fig. 1. Atom numbering scheme of 4-BPPS: (a) the experimental results, and (b) the optimized geometry.