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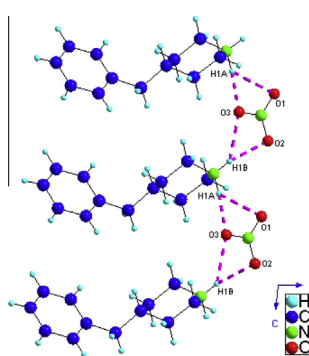
Crystal structure and vibrational spectral studies of a new organic–inorganic crystal: 4-Benzylpiperidinium trioxonitrate

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HIGHLIGHTS

- The 4-BPPN crystallizes in the monoclinic system $P2_1/c$.
- X-ray diffraction, DTA–TG measurements IR and Raman spectral were reported.
- All observed vibrational bands have been discussed and assigned to normal mode on the basis on our DFT calculations.
- The ability of ions to form spontaneous three-dimensional structure through N–H...O hydrogen bond is fully utilized.

GRAPHICAL ABSTRACT



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ABSTRACT

Single crystals of a new organic–inorganic crystal, 4-benzylpiperidinium trioxonitrate (4-BPPN) were grown by slow evaporation at room temperature and were characterized by X-ray diffraction, DTA–TG measurement, FT-IR and FT-Raman spectroscopies. The title compound crystallizes in the monoclinic system $P2_1/c$ at room temperature with the following parameters: $a = 12.787(8)$ Å, $b = 9.007(5)$ Å, $c = 11.120(5)$ Å, $\beta = 95.974(2)^\circ$ and $Z = 4$. Its crystal structure is packing of alternated inorganic and organic layers parallel to (a, c) planes. The different components are connected by a bi-dimensional network of N–H...O hydrogen bonds. The ability of ions to form spontaneous three-dimensional structure through N–H...O hydrogen bond is fully utilized. These hydrogen bonds give notable vibrational effects. The optimized molecular structure and the vibrational spectra were calculated by the Density Functional Theory (DFT) method using the B3LYP function with the 6-31G(d) basis set. All observed vibrational bands have been discussed and assigned to normal mode or to combinations on the basis of our DFT calculations as a primary source of attribution and also by comparison with the previous results for similar compounds. Good consistency is found between the calculated results and the experimental structure, IR, and Raman spectra.

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Introduction

It is well known that the combination of different organic–inorganic components in a single material can lead to new hybrid

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compound, with specific chemical and physical properties. These compounds have been attracted great attention because of their unique opportunity to combine the remarkable features of organic compounds with those of inorganic materials. These have been the subject of intense research to chemists materials scientists and physicists owing to their potential use in a variety of technologies. In particular, hybrid materials based on the nitrates acid have

received much attention in recent years due to their technological interest in several areas [1–7]. On the other hand, the structural and vibrational studies of 4-benzylpiperidinium (4-BPP) derivatives have been published [8–12]. However, in conjunction with some recent works on these hybrids compounds, the crystal structure and vibrational studies of many 4-BPP crystals have been investigated in our laboratory [13–16]. The present work deals with the growth, single X-ray diffraction (XRD) study and detailed vibrational spectral analysis aided by Density Functional Theory (DFT) calculations. In the light of the theoretical calculations, correlation between FT-IR and FT-Raman spectra and computed results help unambiguous identification of vibrational modes and provide deeper insight into the bonding and structural features of the title compound.

Experimental

Crystal growth

Single crystals of 4-BPPN were grown by the slow evaporation solution growth technique. 4-benzylpiperidine (1 ml) dissolved in ethanol (5 ml) was slowly added under stirring of nitric acid (0.37 ml) and mixed well using a magnetic stirrer to ensure homogeneous concentration in the entire volume of the solution. The solution was allowed to evaporate at room temperature a few days until transparent crystalline salt of 4-BPPN were formed. Repeated recrystallization yielded to good quality crystals. The reaction scheme involved in the formation of complex compound is:



Investigation techniques

X-ray data collection was carried out on Enraf-Nonius CAD4 four circle diffractometer using Mo K α radiation. The crystal structure was solved by direct method using SHELXS-97. Successive refinements based on F^2 lead to a reliability factors of $R = 0.0279$. 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 Supplementary Material (Table S1). Supplementary crystallographic data for this article in CIF format are available as Electronic Supplementary Publication from Cambridge Crystallographic Data Centre (CCDC938535). The Fourier transform infrared (FT-IR) spectrum of 4-BPPN was recorded in the range 4000–400 cm^{-1} using PERKIN-ELMER FT-IR spectrometer 100. The resolution of the spectrum is $\pm 2 \text{ cm}^{-1}$. 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 3600–50 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 the spectrum. Thermal analysis was performed using the “multimodule 92 Setaram analyzer” operating from room temperature up to 570 K at an average heating of 5 °C/min. A heating rate of 5 °C/min was selected to measure approximately 10 mg of finely ground sample.

Computational method

Density Functional Theory (DFT) computations were performed by using the Lee–Yang–Parr correlation functional (B3LYP/6-31G*) [17–19] implemented within Gaussian 03 program [20] to derive

the complete geometry optimizations and normal modes analysis. The molecular structure of the title compound was fully optimized without any constraint at the level using. 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 and one nitrate anion linked by N–H \cdots 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 wavenumbers. Prior to compare the calculated vibrational wavenumbers with the experimental counterparts, the former have been scaled by 0.963 scaling factor [21] to correct the evaluated wavenumbers for vibrational anharmonicity and deficiencies inherent to the computational level used. The vibrational modes were made by visual inspection of modes animated by using Molekel program [22] and by comparison with the previous theoretical and experimental results reported in the literature for similar compounds.

Results and discussion

X-ray diffraction study

The title compound crystallizes in monoclinic crystal system, P2₁/c space group with four units in unit cell ($Z = 4$). The following unit cell dimensions were: $a = 12.787(8) \text{ \AA}$; $b = 9.007(5) \text{ \AA}$; $c = 11.120(5) \text{ \AA}$ and $\beta = 95.974(2)^\circ$. The asymmetric unit contains one ionized nitrate anion NO_3^- and one protonated 4-BPP cation $[\text{C}_6\text{H}_5\text{CH}_2\text{C}_5\text{H}_9\text{NH}_2]^+$. Selected bonds length and angles together with the calculated ones are presented in Table 1 in accordance with the atom numbering scheme given in Fig. 1a. Optimized geometry of the title compound model is presented in Fig. 1b. As seen in Table 1, most of the computed bonds are slightly longer than experimental one. This discrepancies can be explained by the fact that the calculations relates to the isolated molecule where the intermolecular Coulombic interaction with the neighboring molecules are absent, whereas the experimental result corresponds to interacting molecules in the crystal lattice. The maximum difference does not exceed 0.04 Å for the bond lengths and 3.85° for the bond angles. This result shows that the cluster approach is sufficient to the analysis of the spectra in the solid state. The structure consists of infinite parallel two-dimensional planes built connected NO_3^- ion and $[\text{C}_6\text{H}_5\text{CH}_2\text{C}_5\text{H}_9\text{NH}_2]^+$ cations. These entities form the atomic arrangement of 4-BPPN which is depicted in Fig. 2. The NO_3^- ions are isolated and arranged in the \bar{c} direction. Between the organic planes, the inorganic species are located such a way to establish multiple hydrogen bonds with the organic cations. This interaction contributes to the cohesion of the structure. The various hydrogen bond parameters are summarized in Table 2. In each anion, the nitrate atom is trihedral coordinated by three distinct oxygen atoms O_1 , O_2 and O_3 . The N–O distances range from 1.207(3) Å to 1.249(3) Å and the O–N–O bond angles ranging from 116.56(3)° to 123.60(3)°. The oxygen atom of the longest N–O bond ($\text{N}_1\text{–O}_3$) is involved in the shorter N–H–O hydrogen bond with a donor–acceptor (N \cdots O) distance of 2.853(3) Å. The molecular arrangement and the hydrogen bonds are presented in Figs. S1 and S2 in supplementary material. The geometrical parameters of the nitrate anion are summarized in Table 3. The 4-BPP cations do not differ significantly and exhibit the characteristic deformation of the aromatic ring from the ideal hexagonal form. The internal C10–N1–C11 angle (111.08(3)°) protonated at the N atom can be considered as regular angle compared with other angles within the piperidine ring: C9–C8–C12 (109.47(2)°), C8–C9–C10 (112.77(2)°), C9–C10–N1 (110.85(3)°), N1–C11–C12 (110.11(3)°) and C8–C12–C11 (112.04(3)°).

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