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Spectral investigations of amino acid picrates

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Abstract

FTIR and laser Raman spectra of β-alanine β-alaninium picrate and DL-phenylalanine DL-phenylalaninium picrate crystals of space group $P\bar{1}(C_i)$ have been me in the 4000–50 $\mathrm{cm^{-1}}$ range, at room temperature. The former crystal consists of β-alanine β-alaninium and the later DL-phenylalanine DL-phenylalaninium as cations. The presence of both carbonyl (C=O) and carboxylate $\mathrm{COO^-}$ groups in these crystals is the evidence for the existence of the zwitterion and the protonated forms. Factor group analysis has been made and the numbers of vibrational modes have been calculated. The tentative assignments of the observed bands are given. Fermi resonance has also been observed in one of the crystal β-alanine β-alaninium picrate. The picrate group forms the anion in both crystals and the characteristic bands $\nu_{as}\mathrm{NO_2}$, $\nu_{s}\mathrm{NO_2}$, and ν_{phen}C–O stretching are observed in the spectra. These suggest that the picrate ion is unaffected by the presence of the cations.

Keywords: β-alanine β-alaninium; DL-phenylalanine DL-phenylalaninium; Picrate; Infrared and Raman spectra; Intermolecular hydrogen Bonding; Factor group analysis; Fermi resonance and group frequencies

1. Introduction

Amino acids are the molecular building blocks of peptides and proteins. Its side chains play fundamental roles in stabilizing protein structures and in catalyzing enzymatic reaction. Both infrared and Raman spectra of a protein provides a lot of information on structure and environment of the protein backbone and of the amino acid side chain. Hence, IR and Raman spectroscopy are the vital tools for the investigation of protein structure.

β-alanine is a mono amino carboxylic amino acid and the amino group is attached with β carbon atom and hence the name β-alanine. There have been a number of reports on L-alanine [1–3] and on β-alanine [4–12] with inorganic acids. Klotz and Green [13] and Thomson et al. [14] have studied the infrared spectrum of crystalline amino acids. Edsall has made extensive spectral measurements on a larger number of amino acids in aqueous solution [15–17]. Further Nabiev et al. [18] have dealt a number of Raman investigations on the aromatic acids. Kim et al. [19] and Cao and Fischer [20] also detected similar spectra and Fisher and Eysel also have done the polarized Raman spectra of aromatic amino acids [21]. Olszynska et al. have studied the effect of pH on L-phenylalanine in aqueous state using the attenuated total reflectance fourier transform infrared (ATR-FTIR) [22]. In addition, there are other investigations also reported on L-phenylalanine [23–29].

Picric acid (2,4,6-trinitrophenol) is an organic acid, which is used, in the dyeing industry and as an explosive. The presence of three electron withdrawing nitro groups makes it as a good π-acceptor for neutral carrier donor molecule [30–32]. The metal derivatives of picric acid are helpful in homeopathy medicine and it shows extraordinary variety in the bonding of metal salts and complexes [33]. Moreover, there have been several spectral analyses done on β-alanine [11,12] and DL-phenylalanine [28,29] with inorganic acids like nitric, perchloric and sulfuric by our group. Because of the biomedicinal importance of picric acid and metal picrate, we were motivated to study the effect of it on these amino acids.

In this work, we have investigated the spectra of β-alanine and DL-phenylalanine with picric acid. By analyzing the FTIR absorption and Raman spectra of both the picrate crystals, in the region 4000–50 $\mathrm{cm^{-1}}$, at room temperature, the dynamics of the mode of vibrations of various functional groups and how

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hydrogen bonding is influencing the molecular vibrations of the crystals can be brought out.

2. Experimental

Taking equivalent molar aqueous solution of β-alanine and picric acid, under slow evaporation method, the title compound β-alanine β-alaninium picrate (β-AAP) was crystallized as a needle shaped yellow coloured triclinic crystal [34]. Similarly block shaped, yellow colour, triclinic crystal of DL-phenylalanine DL-phenylalaninnium picrate (DL-PPP) was also crystallized by the same method [35].

A Bruker IFS 66 V fourier transform infrared (FTIR) spectrometer was used for IR spectral measurements. The samples were prepared by the pellet technique and the spectra were recorded in the range 4000–400 cm^{-1}. Raman spectral measurements were made using the facility available in our laboratory [36]. The excitation source in the Raman measurement was 488 nm radiations from a Spectra Physics model 2020–04S argon-ion laser. A suitable notch filter was placed before the monochromator to suppress the Rayleigh line. The scattered light was dispersed with a grating monochromator and detected with a thermoelectrically cooled RCA GaAs photomultiplier tube. A PC was interfaced through a data acquisition add–on card to record the spectra. The laser power was maintained at 70 mW. This instrument has a resolution of ∼2–3 cm^{-1}. For reliability of the data, Raman spectral measurements were also made with the facility at IIT, Chennai, with FRA 106 Raman module, an air cooled diode pumped Nd:YAG laser operated at 1064 nm and with the laser power output maintained at 200 mW. The spectrum was recorded over the range 3500–50 cm^{-1}. All the experiments were carried out at room temperature.

3. Results and discussion

3.1. *Crystal structure and vibrational modes of β-AAP and DL-PPP*

The β-AAP crystal consists of β-alanine β-alaninium $C_3H_7NO_2 \cdot C_3H_8NO_2{}^+$, and DL-PPP consists of DL-phenylalanine DL-phenylalaninium $(C_9H_{11}NO_2)\cdot(C_9H_{12}NO_2)^+$ as cations. The picrate $(C_6H_2N_3O_7)^-$ ion (2,4,6 trinitrophenolate) forms the anion in both the crystals. These crystals β-AAP and DL-PPP belong to the space group $P\bar{1}(C_i)$ and their unit cell contains two molecules. The configurations of the title compounds are shown in Figs. 1 and 2. The structures and information about the hydrogen bonding of both the crystals were determined by X-ray diffraction study [34,35]. The numbers of normal modes of β-AAP and DL-PPP crystals were determined by group theory analysis using the correlation method [37–39]. The results obtained are presented in Table 1. The total set of optic vibrations of β-AAP and DL-PPP crystal lattices are distributed as $\Gamma = 135A_g^{IR,R} + 132A_u^{IR}$ and $\Gamma = 195A_g^{IR,R} + 192A_u^{IR}$ excluding the $3A_u$ species of acoustic modes.

3.2. *Vibrational spectral analysis of β-AAP and DL-PPP*

Both the crystals β-AAP and DL-PPP have many similarities and the general structure of salts of amino acid with the cation having carboxylic and amino groups. The picrate $(C_6H_2N_3O_7)^-$ ion forms the anion in both the crystals. The FTIR and Raman spectra of β-AAP recorded at room temperature are depicted in Figs. 3 and 4, respectively. Similarly for DL-PPP also the above spectra have been presented in Figs. 5 and 6. Assignments of the bands in the vibrational spectra of cation and anion of β-AAP and DL-PPP have been given in Tables 2 and 3, respectively.

3.2.1. *Vibrations of β-AAP and DL-PPP cations*

The functional groups and skeletal groups of both the crystals are similar, such as NH_3^+, O–H, COOH, COO^-, CH_2, C–H, C–N, and C–C–C. Whereas the DL-PPP has another special group the mono substituted benzene. Hence the infrared spectrum from 4000 to 800 cm^{-1} for DL-PPP contains a few bands that are characteristic of the aromatic group.

A careful observation of the spectra of infrared and Raman shows a medium intensity broad band extending from 3400–2300 cm^{-1} (FWHM ∼ 506 cm^{-1}) in β-AAP with peaks at 3216, 3168 and 3078 cm^{-1}. The broad band extends from 3400–2350 cm^{-1} (FWHM ∼ 368 cm^{-1}) with peaks at 3232, 3084 and 3062 cm^{-1} for DL-PPP. The FWHM for DL-PPP is smaller than that of β-AAP indicating the narrowness of the band. Since the DL-PPP consists of three rings (two for cations and one for picrate) the intensity of the C–H ring-stretching mode is more than that of β-AAP, which is having only one ring (due to picrate) in its structure.

The ammonium group NH_3^+ exists with pyramidal symmetry in free state. Its normal modes of vibrations are

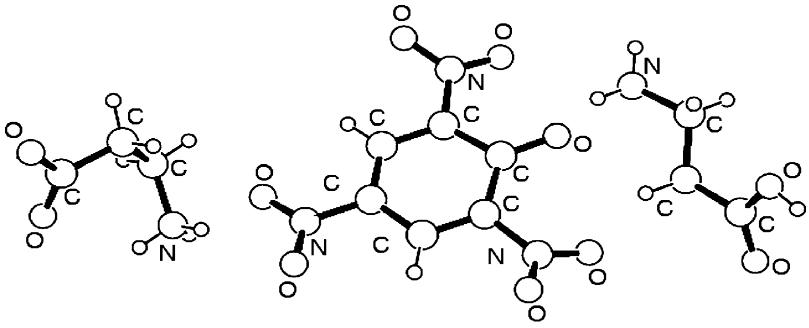

Fig. 1. Structural formula of β-alanine β-alaninium picrate.