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Synthesis and Spectral investigations of Pyridinium picrate

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ABSTRACT

This article describes the vibrational spectra of a crystalline compound called "Pyridinium Picrate. The vibrational spectra measurements were recorded as a function of temperature by both FT-IR and Raman spectroscopy. The presence of various functional groups and modes of their vibrations were assigned and followed evolutions. The stability of the crystalline compound arising from has been analyzed using DSC analysis. This crystal composed of two symmetry groups C_{2v} and P_{-1} respectively named phase I and II, this transition was followed by a function of temperature and XRD, is agreement with crystal structure data. In the present investigation, IR and Raman spectroscopy were employed for the identification of the transitions phase of this dimorphic. Essentially studied by Raman low frequency, the shift, disappearance and appearance of the peaks are used for the determination of the phase transition by the characteristic bands NO₂, C–H deformation and C–O stretching, these results reveal a reversibility of this structural transition, depending on the operating conditions.

Keywords: Pyridinium Picrate, phase transition, FT-Raman, FT-IR, XRD, DSC.

1. INTRODUCTION

Many active ingredients have several polymorphic forms, with one of them only being the desired form to be formulated in the drug. It is thus imperative to control within the mixture which form is present. Being non-invasive, and very chemically selective to discriminate polymorphs, Raman spectroscopy is well adapted to determine within tablets or capsules which form(s) are included. The structural phase transitions alter the crystal's vibrational behavior, so that: Raman spectra show changes across those transitions; Raman spectroscopy provides a convenient proxy for structural phase changes. Doubling of features, frequency shifts, line width changes, are the typical signatures of structural transitions (Soft modes signal softening of restoring forces typical of many structural transitions. The pyridinium Picrate properties has allowed to intervene in various fields such as biology, optics, catalysis and as purification in the pharmaceutical industry, hence the importance of knowing the polymorphic behavior of the active substance to optimize operation and storage conditions so that only the desired shape will be present in these processes, or the importance of the thermal stability of this dimorphic compound (two phase).

The work presented in this article is an contribution to the study of phenomena related to dimorphic of an organic salt called $[(C_6H_2N_3O_7)^{-}.(C_5H_6N)^+]$ " Picrate Pyridine ", by comparing the behavior of its two forms, respectively named phase I and II, to provide additional structural and spectral data with previous results of other authors, by monitoring the behavior and activity of any group spectroscopy essential to the understanding of its mechanism of structural changes to tackle the question of reversibility in this transition. To do this, a particular technique was preferred; Raman spectroscopy has the ability to provide guests with information on the molecule structure, its binding mode and the presence or absence of an interaction, which makes particularly interesting target for certain influenced by phase transition phenomena particular groupings. To complete the data structural studies of this dimorphic, because of our knowledge, the vibration spectra of crystals PicPy has never been a comprehensive spectral study. The unusual work is essentially based on the diffraction XRD, on which, we refer in this study.

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2. EXPERIMENTAL DETAILS

2.1. Synthesis

The title's compound is a yellowish crystalline powder which has a molecular formula $C_{11}H_8N_4O_7$ with molecular weight 308.206 g/mol. The saturated solution of the title's compound was prepared at 1:1 stoichiometric ratio the pyridine solution and picric acid with methanol as the solvent. The solubility for 298K was determined by dissolving the picric acid salt in 10 mL of alcohol (The solubility of the crystal was analyzed by three different solvents). A constant weight of 10 mg of the picric acid powdered was used throughout the experiment. The acid picric and pyridinium solutions were mixed together and stirred well using mechanical stirrer for about 30 min to get a homogeneous solution and the resulting solution was filtered into a clean dry beaker using what man filter paper. After filtration at primary vacuum, the filtrate was kept in dust-free and humidity, average dimensions of the grown crystals were 0,9 x 0,8 x 0,04 mm³, the grown crystal is optically transparent as shown in Fig. 1.



Fig. 1. Photograph of as-grown PicPy crystal (yellow).

2.2. DSC Studies

For structural characterization, it is very important to start with the study of the thermal behavior in order to identify areas of stability and transition, highlight thermal anomalies revealing any change in these properties under the influence of the thermal environment. For this purpose, we used the thermal analysis by differential scanning calorimetry.



Fig. 2. DSC Thermograms.

The curves were obtained on a sail Labsys Evo TG- DSC, with a mass of 35 mg of sample in an aluminum crucible and in a measuring cell with a capsule called a reference, which is subjected to a temperature program ranging from 293 to 424K, as ramps 285, 283 and 281K/min under nitrogen atmosphere (35ml/min). These curves in Fig. 2, shows that at the beginning of a 358K thermal activity gives rise to a first endothermic peak center to 368K, which is the melting start point of the phase I, followed by an exothermic peak intermediate between the two bands endothermic what combines a recrystallization solution phase II with a second endothermic peak

at 383K. The melting peak does not appear on the curve, as in a limited temperature 423K to prevent product degradation in the device and thus damaging its smooth operation (the melting point is confirmed by Kotler banc method).

Both endothermic point of the hypothesis of the formation of phase II, following the merger of Phase I at the same temperature (358K) are find by Koflor Mark Botoshansky [1,3], who gave us an idea of areas in which the temperatures must focus for XRD, IR and Raman records. It is noted that the recordings done by cooling the samples at these speeds, shows no sign of activity.

2.3. X-ray Diffraction analysis

In order to follow the structure, that is to say to ensure that the compounds prepared in the expected crystallize well system (in our conditions), two samples were prepared in one stored at ambient temperature) (293K) and another treated in an oven at a temperature of 368K for 30 min (in order to cause the transition phase), were characterized by X-ray diffraction using a diffract meter operating with copper K α radiation (λ =1.5406 Å), the records obtained are shown in Fig. 3.



Fig. 3. DRX pattern at different temperatures (A):298K, and (B): 368K.

Indexing experimental diffractograms peaks is calculated and performed using the program and Mercury.CCDC [4,5]. The refinement of the cell parameters of phase I (at ambient temperature), shows that it crystallizes in a monoclinic system, space group P2(1)/c, with lattice parameters.

a = 12.122(2) Å; b = 3.7830(10) Å; c = 26.621(3) Å;

$$\alpha = 90^{\circ};\beta = 92.56^{\circ}(5); \gamma = 90^{\circ}, Z=4 \text{ and } Z'=4;$$

And at the processing temperature of 368K for 30 min (the transition stage II) in a triclinic system, space group P-1 with cell parameters:

a = 10.156(2) Å; b = 8.984(2) Å; c = 7.2300(10) Å;
a = 86.38(5) °;
$$\beta$$
 = 80.10(5)°; γ = 89.97(5) °, Z=2 and Z'=0;

3. RESULTS AND DISCUSSION

3.1. SPECTROSCOPIC STUDIES (IR and RAMAN)

The IR spectrum of the grown crystals was recorded using the infrared spectrometer, in the region of 4000 to 400 cm^{-1} . The absorption of IR radiation causes various bands in a spectrum which can be treated as the finger print of different modes of vibration of a molecule, and it clearly exhibits the presence of various functional groups present in a compound. The infrared absorption arises when the vibrational motion produces a change in the permanent dipole moment of the molecule [6]. The recorded IR spectrum is shown in Fig. 4.

The FT-Raman spectral measurements were made with laser beam of wavelength 1.06 μ m (IR), the output power being 60 mw, was used. The spectrum was recorded for a range of 3500 to 200 cm⁻¹ with a spectral resolution of 2 cm⁻¹. Raman spectroscopy is an inelastic photon scattering between a laser beam and a molecule. Raman scattering occurs when the vibrational motion produces an induced dipole moment or change in the polarizability of the molecule [7]. The comparison of FT-Raman and infrared spectral analyses is shown in Fig. 4.



Fig. 4. FT-IR and FT-Raman spectra of PicPy at ambient temperature.

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As with any complex molecules, and for simplicity, vibrational interactions occur and these labels only indicate the predominant vibration, the bands were compared with FTIR spectra of picric acid spectrum. The Pyridinium picrate crystals have functional groups and skeletal groups such as C-H, NO₂ and C-O ring structure. The absence of O-H stretching indicates the presence of picrate ion instead of picric acid. The picrate $(C_6H_2N_3O_7)^-$ forms the nitro group and are twisted out of plane of the ring. Picrate being the trinitrophenolate has the characteristic bands of phenol, the nitro group and the phenoxy group.

Infrar	ed /(cm ⁻¹)	Raman /(cm ⁻¹)		n ⁻¹) Assignment	
Phase I	Phase II	Phase I	Phase II		
3204 w	3204w	-	-	-	
3080 <i>ms</i>	3080ms	-	-	C-H stretch	
2920ms	2921 <i>ms</i>	-	-		
2850 ms	2853ms	-	-		
1631 ms	1620w	1634 <i>vw</i>	-	C-C stretch	
1641 ms	1510w	1598w	-		
1592w	-	-	-		
1548w	1553w	1555 <i>s</i>	1553 <i>s</i>	C-NO ₂ stretch	
1522 <i>s</i>	1522 <i>s</i>	-	-	NO ₂ asy. stretch	
1460s	1460 <i>s</i>	1496w	1496w	C-C stretch	
1364 <i>w</i>	1367w	1365 <i>vw</i>	-	C=N stretch	
-	-	1365w	1365w		
-	-	1376 <i>vs</i>	1374 <i>vs</i>	C-C stretch	
1342ms	1345 ms	1346w	1336w	NO ₂ sym. stretch	
-	-	1365 <i>ms</i>	1365 <i>ms</i>		
1330w	1330w	1324 <i>vw</i>	-	C-C stretch	
1266vs	1266 <i>vs</i>	1283 <i>ms</i>	1298 <i>ms</i>	C-N stretch	
1173ms	1172 <i>ms</i>	1176w	1198w		
-	1168 <i>ms</i>	1167 <i>m</i> s	-	C-H ipb	
1084 <i>vs</i>	1085 <i>vs</i>	1086 s	1082 <i>s</i>		
995w	995w	1000w	1020w		
942 <i>ms</i>	942 <i>ms</i>	943w	941 <i>w</i>	C-H opb	
925w	925 w	926 <i>ms</i>	929 <i>ms</i>		
838 <i>vs</i>	837 <i>vs</i>	-	-	NO ₂ in plane deform	
820 <i>ms</i>	819 <i>ms</i>	822w	821 <i>w</i>	C-H oph	
786 <i>ms</i>	786 <i>ms</i>	783w	783w	Споро	
-	-	763 <i>w</i>	-	C-C inh	
741 <i>ms</i>	745 <i>ms</i>	742w	-	C-C 1p0	
679 <i>vs</i>	678 <i>vs</i>	695 <i>vs</i>	-	C-C opb	
606 <i>vs</i>	606 <i>vs</i>	607 <i>ms</i>	605 <i>ms</i>		
550w	550w	548 w	541w	NO meltine C.C.C.inh	
472 <i>s</i>	472 <i>s</i>	550 <i>ms</i>	541 <i>ms</i>	NO ₂ rocking, C–C–C ipb	
-	397w	390w	397w	C-C opb	
-	-	297 <i>ms</i>	295w	C- NO ₂ ipb	
-	-	207 <i>ms</i>	205 <i>ms</i>	C- NO2 opb	
-	-	120 <i>ms</i>	120 <i>ms</i>	NO ₂ torsion	

Tableau 1:	Vibrational	assignments	[7-22]
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Note: ipb - in-plane deformation; opb - out-of-plane deformation;

s- strong; b-broad; v-very; w-weak; m-medium.

3.2. Analysis in Temperature dependence



Fig. 5. *Photos the powder compound at different temperatures:* (*A*): 333K, (*B*): 388K, (*C*): 398, (*D*): 418K, (*X*): With Chalumeau (closed room).

Samples have been heated until they have reached the temperature shown by the thermal analysis was kept constant for a duration of treatment of 30 min, and ambient temperature Fig. 5, illustrates the aspects of powder at different temperature, although we note the color of change with the temperature. He observed Raman and IR bands are assigned in terms of fundamentals, overtones and combination bands. The observed wave numbers along with their relative intensities and probable assignments are given in Table 1. The wave numbers were assigned on the basis of earlier assignments and the literature values.



3.3. Temperature dependence of IR Spectral

Fig. 6. Evolution of the FT-IR spectra of PicPy at different temperatures.

Although the IR spectra (Fig.6) of the two phases are the same at different temperatures, the appearance of the XRD diffractogram of the two different powders: one is of monoclinic structure, the yellowish color and another under a system triclinic, brown color.

In general, we observe two sets of parallel spectra with the same rhythm and the same bands, the spectra recorded at 293K and 333K are very similar and they fit perfectly, so we think that there is no change. However, at 358K, the spectra are slightly modified compared to those recorded at lower temperatures, and beyond the 358K sound recordings also almost identical with that recorded at 388, 398 and 418K. However, there are differences between the massive 600 and 800 Cm⁻¹, around 1450 Cm⁻¹ and 1350 Cm⁻¹ and between 1400 and 1750 Cm⁻¹. At 388K, there is a remarkable evolution of the spectra, there is a contrast reversal of intensities between 600 and 400 Cm⁻¹, and between, we note that the number of bands decreased for regions between 850 - 750 Cm⁻¹ and 1350 Cm⁻¹ [7-15].

3.4. Temperature dependence of Raman Spectral



Fig. 7. Evolution of the Raman spectra of PicPy at different temperatures.

The nitro group has characteristic vibrations active in both IR and Raman spectra. Inspection of Raman spectra (Fig. 7) reveals that the NO₂ asymmetric and symmetric stretching vibrations are coupled with CC stretching vibrations and in-plane CH bending, and the associated IR intensities are distributed over a large number of vibrations. It was shown that nitro aromatic compounds can be identified in the FT-IR spectra by the characteristic bands that appear in 1550-1475 cm⁻¹ (v_{asym} (NO)) and 1360-1290 cm⁻¹ (v_{sym} (NO)) regions [15-22]. The bands at 1620 and 1598 cm⁻¹ are assigned to similar complex vibrations consisting of CC stretch, in plane CH bend and NO₂ asymmetric stretch. The CN stretching vibrations is coupled to δ (CH) vibration giving rise to the bands in 1140-1067 cm⁻¹ region that is overlapped by the absorption of (vC-O) constituents. The band at 1548 cm⁻¹ has a major contribution from the asymmetric stretch of the three nitro groups.

The NO₂ out-of plane wag, (scissors) appear at around 780, 853 and 872 cm⁻¹, the peak at 820 cm^{-1} is assigned to C–H out-of-plane bending. The medium band at 935 cm⁻¹ is attributed to

the presence of C–C stretching. The strong peak at 1266 cm⁻¹ illustrates the presence of C–N stretching and at 1167 cm⁻¹ is assigned to C–H in-plane deformation. C–C–C in-plane deformation is located at the weak peak of 550 cm⁻¹ [10-22].

3.5. Vibrational spectral analysis



Variations in the peak positions of the Raman modes Variations in the peak intensities of the Raman modes

Fig. 8. Observed thermally induced variations peak of the IR and Raman modes.

The fig. 8, illustrates the changing frequencies of the lines of the Raman spectra as a function of temperature. It is found the all modes have frequency substantially stable (is insensitive with to temperature). However, the intensity of these bands varies inversely with temperature (attenuation of intensity); these anomalies are indicative of the existence of the structural changes at a temperature of about 345K (phase transition). Other hand, the latter (with Chalumeau in closed room), present signs of Return to the initial state; under the effect of a change in operational terms

4. CONCLUSIONS :

The Raman spectra depend on the vibrations, and structure, they can be used very effectively as a witness for structural changes. The crystals of pyridinium picrate were synthesized by slow evaporation method, and the structure of the compound was confirmed with the help of powder X-ray diffraction pattern. The thermal analysis (differential scanning calorimetry), was carried out to find the thermal stability of the synthesized crystal. The thermal anomalies observed in this curves indicate the title compound shows a first order phase transition. As a result, the non-destructive techniques FTIR and FT-Raman spectra (reveal the mode of vibrations) have been attempted to identify the numbers of the different functional groups in the compound (monitoring of change in with temperature). The presence of picrate ions in the crystal structures is reflected in the highly mixed bands of the C-O stretch, in-plane deformation and together out-of-plane

bending vibrations. The medium to high peak at 820 cm⁻¹ is attributed to CH out-of-plane bending, and also because of the presence of NO₂ out-of-plane deformation, was followed their indicative of a phase transformation in the compound, with signs of realignment of the vibrations, this is purely due to the effect of the reversibility. These results information the favorable conditions for the preservation of phase I (reversibility), when applied in the pharmaceutical industry and provides some insight into the capabilities of Raman spectroscopy for pharmaceutical applications. Stability of products in their real state over time might be evaluated using this technique, without having to transfer a sub sample into any vial – with the risk of transferring a non-representative fraction of the crystals phase or add contamination.

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