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### Vibrational spectroscopic and computational studies on diisopropylammonium bromide

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#### Abstract:

Diisopropylammonium bromide (DIPAB) can be crystallized either in an orthorhombic  $(P2_12_12_1)$  or in a monoclinic  $(P2_1)$  structure at room temperature depending on synthesis The non-polar orthorhombic structure exhibits a subtle, irreversible conditions. transformation into the ferroelectric monoclinic-II (m-II) phase above ~421 K. At a slightly higher temperature of 426 K this m-II (P2<sub>1</sub>) phase reversibly transforms into a disordered, paraelectric monoclinic-I (P21/m) structure. We synthesized DIPAB in the orthorhombic structure, heated it to obtain the m-II phase and carried out a systematic study of their Raman and IR spectra. We obtained the phonon irreducible representations from factor group analysis of the orthorhombic and m-II structures based on the reported structural information. DIPAB is an organic molecular crystal, and the vibrational spectra in the intramolecular region (200-3500 cm<sup>-1</sup>) of the two different phases are identical to each other, indicating weak inter-molecular interactions in both crystalline structures. In the low wavenumber region (10-150 cm<sup>-1</sup>) the Raman spectra of the two phases are different due to their sensitivity to molecular environment. We also carried out first principles calculations using Gaussian 09 and CASTEP codes to analyze the vibrational frequencies. Mode assignments were facilitated by isolated molecule calculations that are also in good agreement with intramolecular vibrations, whereas CASTEP (solid state) results could explain the external modes.

Keywords: Raman spectroscopy, IR spectroscopy, Gaussian 09, CASTEP, Organic ferroelectric

#### **1. Introduction:**

Ever since the discovery of the first ferroelectric Rochelle salt by Valasek in 1920, a huge number of ferroelectric compounds have been synthesized [1]-[3]. Ferroelectric materials find applications in data storage devices, capacitors, piezoelectric, electro optical and pyroelectric devices. Almost all applied ferroelectric materials are inorganic, lead zirconate titanate (PZT) being the most important. BaTiO<sub>3</sub> is another important material with a high spontaneous polarization ( $P_s$ ) that has many applications. Organic ferroelectric materials have drawn attention in recent times due to ease of synthesis, environmentally friendly nature (without lead), and transparency to visible light [2],[3]. Importantly if a material exhibits ferroelectricity at room temperature and has a high Curie temperature ( $T_c$ ), it could be useful for electronic applications.

Recently it was reported that at room temperature monoclinic-II diisopropylammonium bromide (DIPAB) has a high spontaneous polarization  $P_s$ = 23  $\mu$ C/cm<sup>2</sup> and high dielectric constant of 85 (@400 Hz) [4]. These values are comparable to that of BaTiO<sub>3</sub> [3]-[4]. These properties have propelled DIPAB as an important material for possible applications.

At room temperature DIPAB has two polymorphic forms depending on the preparation method, and both crystals are obtained by a solution growth method. It is found that using undistilled methanol-ethanol (1:1) mixture, undistilled methanol, methanol-water (1:1) mixture or water as solvent for recrystallization of diisopropylammonia results in an orthorhombic structure (space group  $P2_12_12_1$ ) and this can be converted to a monoclinic-II (m-II) phase (space group  $P2_1$ ) by heating the material at 428 K for a few minutes (Fig. 2) [4]-[9]. If 12-crown-4 ether is added in undistilled methanol or if anhydrous methanol is used as solvent, DIPAB is recrystallized in the m-II phase itself [6]-[7].

Apart from these two structures DIPAB undergoes a reversible ferroelectric to paraelectric transition at 426 K to a monoclinic-I ( $P2_1/m$ ) [4]-[9] structure. Another low temperature structure (P21/n) at 173 K has also been reported in the literature [10].

Raman spectroscopy is a versatile tool to study phase transformations, especially in ferroelectrics and other inorganic and organic materials [11]-[13]. It can give information that is complementary to x-ray diffraction (XRD), and in recent years, together with first principles calculations, Raman spectroscopy has evolved into an important tool to study phase transformations [14]-[16]. Spectroscopy has also helped resolve the space group structure when diffraction results were ambiguous [17].

Here we report our Raman and IR spectroscopic studies of the orthorhombic and monoclinic-II structures of DIPAB. We carried out group theoretical analysis of the zone centre phonon irreducible representation of both phases. In addition we undertook first principles density functional theory (DFT) calculations of vibrational modes of isolated molecule using Gaussian09 and the crystals using CASTEP module in Material Studio Version 6.0 (Accelrys) package. To our knowledge there are no reports on vibrational property studies on DIPAB crystals.

#### 2. Experimental and computational details:

DIPAB crystal was obtained using solution growth technique by the reaction of diisopropylamine and 48% aqueous hydrobromic acid (molar ratio 1:1). After a few days, a polycrystalline solid white mass was formed by slow evaporation. This was recrystallised in a mixture of methanol and ethanol (1:1) at room temperature, and translucent, block shaped crystals (Phase I) were formed after ~60 days in a Petri dish (Fig. 1).

As prepared (Phase I) crystals were ground into a fine powder in an agate mortar and pestle for 2 hrs; phase identification was carried out by powder XRD technique with a STOE (Germany) diffractometer using CuK $\alpha$  radiation (1.5406 Å) in the 2 $\theta$  range of 7 to 70 with a step size of 0.05. The samples were then annealed at 429 K for 15 minutes and powder XRD pattern was recorded on this Phase II sample. Phase I pattern matches with that reported in the literature as orthorhombic (P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>), and Phase II, monoclinic-II (P2<sub>1</sub>) [5].

Raman spectroscopic measurements were carried out on both samples using a micro Raman spectrometer (Renishaw, model inVia) with 514 nm laser excitation from an argon

ion laser. The laser was focused to a spot size of less than 1  $\mu$ m with a 50X microscope objective. Laser power on the sample was kept low (~ 1 mW) to avoid burning of the samples. The resolution of the instrument is ~1.5 cm<sup>-1</sup> per pixel of the CCD detector. The lower wavenumber limit for this instrument is about 70 cm<sup>-1</sup> below which the Rayleigh filters cut off the intensity considerably, with complete cut-off below 30 cm<sup>-1</sup>. Raman spectra below 150 cm<sup>-1</sup> were recorded using a Horiba Jobin-Yvon U1000 high resolution spectrometer with a 532 nm diode pumped solid state laser as excitation source and a photomultiplier tube detector. The entrance and exit slits were set to 200  $\mu$ m, and the spectral band pass with a grating of 1800 lines/mm is ~2 cm<sup>-1</sup>. The infrared absorption spectra of the samples dispersed in CsI and KBr were measured between 150-600 cm<sup>-1</sup> and 350-3500 cm<sup>-1</sup> respectively using a Fourier Transform Infrared spectrometer (Bruker: VERTEX 80V) with a resolution of 2 cm<sup>-1</sup> and 128 scans.

Isolated diisopropylammonium bromide molecule's DFT geometry optimization and normal mode analyses were performed with Gaussian09 [18] package using B3LYP hybrid exchange correlation functional, 6-311++G(d,p) numerical basis set. Solid-state geometry optimizations were performed with plane-wave density functional method within the generalized gradient approximation, using norm-conserving pseudopotentials and the PBE exchange-correlation functional [19] as implemented in the CASTEP code [20] for both structures. Norm conserving pseudopotentials were employed with a plane wave cutoff energy of 800 eV. For the primitive cells of the DIPAB orthorhombic and monoclinic-I structures,  $4 \times 4 \times 2$  and  $4 \times 4 \times 4$  k-point mesh generated by the Monkhorst–Pack scheme [21] were employed for the numerical integrations in the Brilluoin zone. The initial structures were taken from experimentally reported crystal structures in the Cambridge Crystallographic Data Centre (CCDC) website; DIPAB orthorhombic (CCDC-893210) and monoclinic-I (CCDC-893211) [[5]] lattice parameters are: (i) orthorhombic  $(P2_12_12_1)$  a= 8.0233 Å, b=8.308 Å and c= 13.5868 Å (ii) Monoclinc-II (P2<sub>1</sub>) a= 7.8586 Å, b=8.0818 Å and c = 7.8918 Å. The lattice parameters were kept fixed at the experimentally determined values in all the calculations and only the atomic coordinates were optimized using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme such that the interatomic forces between them were lower than 0.001 eV/Å. The self-consistent total energies were obtained

using a density-mixing scheme [22]. Phonon frequency calculations were carried out using the density functional perturbation theory (DFPT) as implemented in CASTEP.

#### 3. Results and Discussion:

As prepared DIPAB (phase-I) crystallizes in an orthorhombic structure with space group  $(P2_12_12_1)$  with four formula units in its primitive cell, whereas annealed samples (phase-II) crystallize in monoclinic-II structure with space group  $(P2_1)$  with two formula units in its primitive cell. Rietveld refinement was carried out on powder XRD data of both phases collected at ambient conditions with CuK $\alpha$  wavelength using Fullprof software. The refined parameters (Table-1) and Figures (Fig.-2a, 2b) are given for both phases showing a good fit to the initial model taken from reported literature [5].

DIPAB structure is composed of hydrogen-bonded zigzag chains. Each bromine anion is attached to two diisopropylammonium cations via hydrogen bonds. The main difference between the two polymorphs (orthorhombic and monoclinic-I) is the substantial reconstruction of cationic sub structure. Diisopropylammonium ions are so arranged that the dihedral angle between two neighboring cations is 85.7<sup>0</sup> in the orthorhombic phase, whereas in the monoclinic-II phase similar cations are oriented parallel to each other [5].

Group theoretical analysis was carried out using Halford-Hornig site group method for both structures to obtain the phonon irreducible representation at the  $\Gamma$  point [23].

#### 3.1 Factor group analysis:

Orthorhombic phase, space group  $P2_12_12_1$ ,  $D_2^4$ : The cation  $C_6H_{16}N^+$  and the Br<sup>-</sup> anion have  $C_1$  site symmetry. To obtain the external lattice vibrations of the cation, the site species A are correlated to the  $D_2$  factor group species of the orthorhombic structure (space group  $D_2^4$ ), resulting in

 $\Gamma_{\text{Cation-Lattice}} = 3A + 3B_1 + 3B_2 + 3B_3 \quad -----(1)$ 

Similarly for the anion,

 $\Gamma_{\text{Anion-Lattice}} = 3A + 3B_1 + 3B_2 + 3B_3 \quad -----(2)$ 

Librations of the cation are again calculated by correlating the  $C_1$  site species with rotation  $(R_x, R_y \text{ and } R_z)$  to the factor group species, obtaining a result identical to eqns. (1) and (2):

$$\Gamma_{\text{Cation}}$$
 (Librations) = 3A+3B<sub>1</sub>+3B<sub>2</sub>+3B<sub>3</sub> ------(3)

Next, intramolecular vibrations of the  $C_6H_{16}N^+$  ion are calculated by correlating the species of the molecular symmetry  $C_2$  [24] to site symmetry of the individual atoms  $C_1$  that is in turn correlated to the  $D_2$  factor group. This exercise gives

 $\Gamma_{\text{Cation-Internal}} = 63\text{A} + 63\text{B}_1 + 63\text{B}_2 + 63\text{B}_3$  ------(4)

Adding the contributions from eqns. (1) to (4), one obtains the total irreducible representation

$$\Gamma_{\text{Total}} = 72A + 72B_1 + 72B_2 + 72B_3 \quad ------(5)$$

including acoustic modes. This accounts for all the degrees of freedom of the orthorhombic crystal of  $C_6H_{16}NBr$  with 4 formula units/primitive cell (Z=4). Acoustic modes are quickly identified by inspection of the character table of the  $D_2$  factor group since they have the same character as the translations:

$$\Gamma_{\text{Acoustic}} = \mathbf{B}_1 + \mathbf{B}_2 + \mathbf{B}_3 \quad -----(6)$$

Subtracting (6) from (5), we obtain

$$\Gamma_{\text{Optical}} = 72 \text{A} + 71 \text{B}_1 + 71 \text{B}_2 + 71 \text{B}_3$$
 -----(7)

Since all modes are Raman active and all except the A species are also IR active (as seen from the Character table of  $D_2$ ), we expect to obtain 285 Raman and 215 IR bands.

A similar exercise for the ferroelectric monoclinic-II phase (space group  $P2_1=C_2^2$ , Z=2) results in the following:

 $\Gamma_{\text{Cation-Lattice}} = 3A + 3B$ 

 $\Gamma_{\text{Anion-Lattice}} = 3\text{A} + 3\text{B}$ 

 $\Gamma_{\text{Cation}}$  (Librations) = 3A+3B

 $\Gamma_{\text{Cation-Internal}} = 64A + 62B$ 

 $\Gamma_{Acoustic} = A + 2B$ 

 $\Gamma_{\text{Optical}} = 71 \text{A} + 70 \text{B}.$ 

Thus, for the ferroelectric monoclinic-II phase we expect to obtain 141 Raman and 141 IR bands since both species are Raman and IR active.

If we consider the diisopropylammonium bromide as an isolated molecule that has  $C_1$  symmetry, we obtain from site group analysis the following irreducible representations:

 $\Gamma_{\text{Total}} = 72A$ ,  $\Gamma_{\text{Translational}} = 3A$ ,  $\Gamma_{\text{Rotational}} = 3A$ 

 $\Gamma_{Vibrational} = 66A$ 

Since the 'A' species is both Raman and IR active, we expect to obtain 66 Raman bands and 66 IR bands from an isolated diisopropylammonium bromide molecule

#### 3.2 Raman and IR Experimental Results:

Raman and IR spectra of the orthorhombic and monoclinic-II phases were recorded in the region 150-3500 cm<sup>-1</sup> [Fig.3 (a)-(c); 4 (a)-(c)]. The whole spectral region was divided into three graphs for clarity and the region 1650-1900 cm<sup>-1</sup> is not shown in the experimental spectra because there were no bands obtained in this region. Group theoretical calculations predict 285 Raman and 241 IR modes for the orthorhombic structure and 141 Raman and 141 IR modes for the monoclinic-II structure. Experimentally we obtained much less number of bands: 54 Raman and 50 IR modes for the orthorhombic and 54 Raman and 50 IR modes for the intramolecular region.

Both Raman and IR spectra of the two phases are identical though we expect a huge difference in the number of modes. The numbers obtained from factor group analysis are correct from a crystallographic point of view because calculations take into account the structure and the number of molecular units in the unit cell, but they are spectroscopically incorrect: the number of Raman and IR bands expected from factor group analysis are far

more than obtained experimentally. DIPAB is a molecular solid in which each bromine atom is attached to two neighbouring cations through hydrogen bonding forming the three dimensional structure. Intramolecular modes correspond to vibrations of atoms within a molecular unit. In the present case the number of molecular units (of diisopropylammonium bromide) in the primitive cell is different from each other: orthorhombic, Z=4; monoclinic-II, Z=2; but the molecular unit is the same for both structures and there is no significant change in the bond length of atoms involved [5] which reflect in the Raman and IR spectra. But the differentiation of the two polymorphic forms was not possible in this region. Close matching of the experimentally obtained number of Raman and IR bands with the results of group theoretical analysis treating diisopropylammonium bromide as an isolated molecule points to the weak nature of intermolecular interactions in DIPAB.

To distinguish between the two different polymorphs we recorded their Raman spectra in the external mode region, 10-120 cm<sup>-1</sup> that arises from lattice and librational modes. There are reports in the literature where the spectra are identical in the intramolecular region for two different polymorphic forms of organic molecular crystals but structure identification was done by recording Raman spectra in the low wavenumber region [25]-[27]. The Raman spectra in the intermolecular region 10-120 cm<sup>-1</sup> are very different for the two phases [Fig.5]. This region corresponds to the lattice phonon modes which are sensitive to differences in molecular packing. Mode assignments could be done with the help of first principles computations that are described in the next Section.

#### 3.3 Computational Results:

We performed DFT calculations on isolated DIPAB molecule and the solid phases (Fig.6 (a) and (b)). In the case of isolated molecule approximation a single DIPAB molecule (Fig. 6 (c)) has considered and vibrational modes were obtained. The main difference in the isolated molecule and the solid state phases are, bromine is attached to two molecules via hydrogen bonding forming 3-dimensional structure. The change in DIPAB geometry from isolated molecule to solid state is that there is a slight shift in the bonds involving hydrogen, nitrogen and bromine atoms. From isolated molecule approach we have assigned the modes by normal vector analysis.

We have performed geometry optimization for isolated molecule and solid structures. The optimized geometry of isolated molecule with lowest energy was obtained with no imaginary frequencies. Optimized bond lengths and bond angles are tabulated in Table-2(a-b) from isolated molecule and solid state calculations.

Frequencies and intensities of Raman spectra were generated from isolated molecular calculations and we obtained the frequencies from solid state calculations also; intensities are not obtained in the solid state due to computational difficulties. Mode assignments in the intramolecular region (150-3500cm<sup>-1</sup>) were done based on isolated molecular calculations. Intramolecular regions are divided into 3 parts: (i) 150- 1260 cm<sup>-1</sup> (ii) 1260-1670 cm<sup>-1</sup> (iii) 1900-3500 cm<sup>-1</sup>. All modes are visualized in the animation window of Chemcraft software, and mode assignments are carried out. IR and Raman spectra for isolated molecule were simulated from the results obtained from Gaussian calculation using SYNSPEC program [28]. The spectra (Fig.7) were generated using a Lorentzian profile with a FWHM of 2 cm<sup>-1</sup>.

#### 3.3a Region I

165- 500 cm<sup>-1</sup> mainly corresponds to isopropyl group libration, CH<sub>3</sub> torsion and the bending vibrations of C-C-C, C-C-N and C-N-C bond. A weak and broad band at ~172 cm<sup>-1</sup> in the Raman spectra that is intense in IR spectra for both phases corresponds to C-N-C in- plane bending and isopropyl group scissoring modes. The broad Raman and IR bands in the region 196-272 cm<sup>-1</sup> of both phases arise from CH<sub>3</sub> torsional modes. In-plane and out of plane bending vibrations of C-C-C, C-C-N and C-N-C are in the range 300-505 cm<sup>-1</sup>.

835 and 837 cm<sup>-1</sup> bands in the orthorhombic and monoclinic-II respectively in the Raman spectra are assigned to C-N-C antisymmetric stretch modes. Bands in the 900-1200 cm<sup>-1</sup> range arise from a combination of CCC, CCN and CNC stretching,  $CH_3$  twisting,  $NH_2$  rocking and  $NH_2$  twisting modes. Detailed assignment of modes and frequencies obtained from experiments and computations are tabulated in Table-3.

#### 3.3b Region II

1270-1650 cm<sup>-1</sup> region includes CH bending,  $CH_3$  wagging,  $CH_3$  twisting,  $NH_2$  rocking,  $NH_2$  wagging, NH bending,  $NH_2$  bending. The band at 1300 cm<sup>-1</sup> corresponds to a

combination of CH<sub>3</sub> twisting and NH<sub>2</sub> rocking modes. 1320-1572 cm<sup>-1</sup> region is related to CH<sub>3</sub> wagging, CH<sub>3</sub> twisting, CH bend, NH bend, NH<sub>2</sub> rocking and NH<sub>2</sub> wagging modes. NH<sub>2</sub> bending modes are located at ~ 1590 cm<sup>-1</sup> for both phases. There is good agreement of modes in this region between experiment and calculations (Table 3).

#### 3.3c Region III

This region is related to stretching vibrations of CH<sub>3</sub>, CH and NH. Here we are able to identify the N-H..Br vibrations from experiments. During the analysis of modes obtained from computation, the one at 2111 cm<sup>-1</sup> is seen to correspond to a N-H..Br vibration. It is clearly seen from the computed IR spectrum (Fig.7) that this band is of the highest intensity. The corresponding band in the experimental results is not intense, but we could detect the N-H..Br vibration in both IR and Raman spectra. N-H...Br vibration was also reported in the literature where the computed IR intensity for N-H...Br vibration at 2700 cm<sup>-1</sup> is high [29]. The deviation in the number is because in the case of isolated molecule the N-H<sub>5</sub>...Br bond contracts and the angle between H5-N-H4 is increases, implying that H5 hydrogen is closer to bromine. Interestingly, we did not obtain this vibrational mode in the solid state computational calculations, and this is consistent with the low intensity of this band in experimental Raman and IR spectra. In the solid this mode is inhibited due to Br<sup>-</sup> ion hydrogen bonding with two cations.

NH stretching frequency also deviates from isolated molecular calculations by 200 cm<sup>-1</sup>. One of the reasons could be that in isolated molecules H4 (Fig. 6c) is a terminal hydrogen: N-H4 bond is free, i.e., it is not attached to bromine or any other atom, but in the case of crystals this hydrogen forms a hydrogen bond with the bromine ion of a neighboring molecule.

The broad Raman bands in the region 2800-3000 cm<sup>-1</sup> arise from C-H vibrations. Due to the different environment of the many C-H vibrations of the isopropyl groups their vibrational frequencies are slightly different from each other, and cumulatively they give rise to broad bands. Some bands in the experimental spectra are not obtained either from isolated molecule or solid state calculation; these can be assigned to combination and overtone bands (Table-4). However, the wavenumber values of some of the non-

fundamental bands are higher than the summation value of the fundamentals from which these bands may originate. This indicates a possibility of Fermi resonance effect in the region 2400-2800 cm<sup>-1</sup> [30]-[33]. Fermi resonance could occur between (a) a fundamental mode and (b) an overtone or combination mode, if they are nearly coincident in energy. In that case the high energy mode would shift to higher energy and the low energy mode to still lower energy. Such an effect occurs for example in amine hydro halide, amides and pyridinium salts [30]-[33].

On the whole, isolated molecular calculation is in good agreement with experiments in the intramolecular region (150-  $3500 \text{ cm}^{-1}$ ), and hence could be used obtain mode assignments in this region.

#### 3.3d Intermolecular Region:

Phonon modes in the region 10-120 cm<sup>-1</sup> are of special interest. They correspond to lattice and librational modes of the various species in the solid phases. In the experimental spectra, the intense bands at 50 and 60 cm<sup>-1</sup> in the orthorhombic phase are absent in monoclinic-II phase which differentiates clearly between the two phases (Fig. 5). The bands at 33, 40 cm<sup>-1</sup> and 37, 45 cm<sup>-1</sup> in the orthorhombic and monoclinic-II respectively are from the librational motion of DIPAB molecule itself. Raman spectra calculated for isolated molecule are not able to replicate the experimental frequencies in this region, whereas the frequencies obtained from solid state calculations show good agreement with experiments. Assignments in this region are given tentatively (Table-3).

#### 4. Conclusions:

Diisopropylammonium bromide (DIPAB) is an important organic ferroelectric material with potential for applications. We have synthesized DIPAB in a non-polar orthorhombic structure and converted it into a ferroelectric monoclinic-II structure by annealing it at 429 K. We carried out factor group analysis of both structures and obtained the phonon irreducible representation at the Brillouin zone centre; we also carried out Raman and IR spectroscopic measurements on these two samples and find that the spectra are identical to each other in the intramolecular region. In the low wavenumber region the two phases give rise to distinct spectra due to different inter-molecular arrangements. Vibrational

frequencies are obtained from solid state calculations using CASTEP software and for the isolated molecule using Gaussian 09W. There is reasonable agreement between the experimental and computational results. Assignments of intramolecular modes are done from isolated molecular calculations. Plausible assignments of intermolecular modes are also given.

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Table:1 Parameters obtained from Rietveld refinement of XRD patterns for both phases are listed

Fitted parameters Parameters	Orthorhombic P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	Monoclinic-II P2 <sub>1</sub>
R <sub>P</sub>	15.5	18.7
R <sub>WP</sub>	20.1	21.2
<b>R</b> <sub>Exp</sub>	10.86	10.75
χ²	3.41	4.22
Refined Lattice constants	a=8.0189 Å, b=8.3044 Å, c=13.5814 Å	a=7.8547 Å, b=8.0924 Å, c=7.8910 Å
Reported values [Ref.[5]]	a= 8.0233 Å, b=8.308 Å, c= 13.5868 Å	a= 7.8586 Å, b=8.0818 Å, c= 7.8918 Å

#### Table-2(a)

Bond lengths in Å units (excluding C-H bonds) for the optimized isolated molecule (B3YLP/6-311++G(d,p)), solid phases of DIPAB (GGA/PBE), and experimental (XRD). Atomic labels are given in fig 6(c)

							N1-		N1-H4-	N1-H5-
Molecule	C1-C4	C1-C5	N1-C1	N1-C3	C3-C2	C3-C6	H4	N1-H5	Br1	Br1
<b>B3VLP/6</b> -							1 11			
311++G(d,p)	1.528	1.531	1.509	1.513	1.531	1.532	2	1.023	3.049	
Solid -State							N1-		N1-H4-	N1-H5-
(P212121)	C1-C4	C1-C5	N1-C1	N1-C3	C3-C2	C3-C6	H4	N1-H5	Br1	Br1
Experimental						1.503(	0.85(			
[Ref. 5]	1.512(4)	1.514(4)	1.508(3)	1.516(3)	1.507(4)	4)	2)	0.901(3)	3.353(3)	3.334(3)
							1.06			
GGA/PBE	1.519	1.522	1.524	1.527	1.517	1.521	1	1.063	3.348	3.322
		)								
Solid -State (P21							N1-		N1-H4-	N1-H5-
)	C1-C4	C1-C5	N1-C1	N1-C3	C3-C2	C3-C6	H4	N1-H5	Br1	Br1
Experimental						1.525(	0.85			
[Ref. 5]	1.500(5)	1.504(4)	1.497(7)	1.512(6)	1.515(7)	6)	3(3)	0.907(4)	3.335(3)	3.346(3)
							1.05			
GGA/PBE	1.526	1.523	1.524	1.521	1.522	1.526	8	1.057	3.323	3.321

Table-2(b)

Bond angles in degrees for the optimized isolated molecule (B3YLP/6-311++G(d,p)), solid phases of DIPAB (GGA/PBE), and experimental (XRD)

Molecule	C6-C3-C2	C2-C3-N1	C6-C3-N1	C <sub>3</sub> -N1-C1	N1-C1-C4	N1-C1-C5	C5-C1-C4	H5-N1-H4
B3YLP/6-								
311++G (d,p)	112.6	110.3	107.4	119.4	112.1	107.69	112.9	106.1
Solid -State					$\bigcirc$			
(P212121)	C6-C3-C2	C2-C3-N1	C6-C3-N1	C <sub>3</sub> -N1-C1	N1-C1-C4	N1-C1-C5	C5-C1-C4	H5-N1-H4
Experimental					9			
[Ref. 5]	112(2)	107.1(2)	109.4(2)	118.1(2)	110.9(2)	107.8(2)	113.1(2)	101.2(8)
GGA/PBE	112.4	107.5	110.5	117.7	110.9	107.7	112.3	106.3
Solid -State	C6-C3-C2	C2-C3-N1	C6-C3-N1	CN1.C1	N1-C1-C4	N1-C1-C5	C5-C1-C4	H5-N1-H4
Experimental	0-05-02	02-05-111	0-05-111	03-111-01	11-01-04	11-01-05	03-01-04	113-111-114
[Ref. 5]	112.2(4)	110.5(6)	108.0(5)	118.1(3)	110.4(4)	106.3(2)	109.4(6)	100(3)
GGA/PBE	112	110.8	107.4	117.8	110.7	107.7	110.1	106.4

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#### Table-3

Vibrational frequencies obtained from isolated molecule and solid state calculations compared with experimental results, with assignments.

Mode	B3YLP/	GGA	/PBE	GGA/P	Experime	ental	Experimental IR		Mode assignments
Numbe	6-	P2 <sub>1</sub>	2121	BE	Raman		Frequency		
r	311++G(	1		P2 <sub>1</sub>	Frequenc	y	1 5		
	<b>d,p</b> )			-	-	·			
	Raman	Raman	IR	Raman	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<b>P2</b> <sub>1</sub>	P212121	<b>P2</b> <sub>1</sub>	
	/IR	frequen	freque	/IR					
	frequenc	cy	ncy	frequen					
	y	-	-	cy					
1	-	35		38	33	37	-		Libration
2	-	39	39	42	40	45	-	-	Libration
3	55	52	52	52	50	-	-		Libration
4	-	60	63	61	60	-	-	-	Libration
5	74	74	74	73	74	73	-	-	Libration
6	100	88	88	87	88	-	-	- )	Isopropyl group Torsion
7	113	96	93	104	96	102	-		Isopropyl Scissor
8	178	172	172	175	172	173	175	171	CNC In plane Bend, isopropyl scissoring
9	217	196	196	192	204	205	203	198	CNC In plane Bend, CH <sub>3</sub> Torsion
10	260	259	259	263	259	257	272	268	CH <sub>3</sub> Torsion
11	315	307	307	308	319	319			CCC Out of plane Bend
12	387	375	375	376	382	382	382	379	CCC + CCN Out of plane Bend
13	400	389	389	392	402	402	-	-	CCC + CCN Out of plane Bend
14	440	458	458	457	442	443	-	-	CCC +CCN In plane Bend
15	474	460	460	491	472	473	472	469	CCC+CNC+ CCN In plane Bend
16	505	495	495	492	502	502	503	498	CCN In plane bend+ CCC Out of plane Bend
17	804	786	786	787	804	804	804	802	CNC Sym Str, CCN Sym Str
18	833	824	824	824	835	837	835	833	CNC Asym Str ,CCC+CCN Sym Str
19	917	917	917	918	915	916	-	-	CNC+ CCC Sym Str, CCN Asym Str
									CNC+CCC Asym Str, CCN Sym Str,CH
20	947	937	937	940	939	938	-	-	Bend,CH <sub>3</sub> Twist
21	953	944	944	943	955	958	953	950	CCC Asym Str, CH Bend,CH3 Twist
22	965	954	954	953	974	976	974	974	CCC+CCN Asym Str, CH Bend,CH <sub>3</sub> Twist
23	984	1087	1086	1086	1091	1094	1089	1087	CCN + CNC+CCC Asym Str, CH <sub>3</sub> Twist
24	1104	1089	1089	1087	1104	1102	1101	1100	CCC Asym Str, CH <sub>3</sub> Twist, NH <sub>2</sub> Twist,
				$\sim$					CNC +CCN+CCC Asym Str, CH <sub>3</sub> Twist, NH
25	1122	1155	1154	1154	1151	1151	1150	1149	Bend
26	1165	1169	1169	1168	1170	1172	1174	1175	CNC +CCN Asym Str, CH3 Twist, NH <sub>2</sub> Rock
27	1193	1186	1186	1186	1185	1185	1184	1183	CNC Sym Str, CCN Asym Str, CH <sub>3</sub> Twist
28	1206	1188	1188	1189	1199	1200	1202	1199	CNC Sym Str, CCC Asym Str, CH <sub>3</sub> Twist
29	1218	1313	1314	1312	1306	1308	1306	1302	CH <sub>3</sub> Twist, NH <sub>2</sub> Rock
30	1329	1330	1331	1330	1330	1331	1329	1326	NH <sub>2</sub> Twist, CH Bend, CH <sub>3</sub> Twist
31	1350	1341	1342	1340	1348	1348	1347	1347	NH <sub>2</sub> Wag, CH Bend, CH <sub>3</sub> Twist
32	1366	1360	1360	1359	1358	1359	1357	1356	CH Bend, CH <sub>3</sub> Twist
33	1383	1376	1376	1373	1379	1382	1381	1382	CH <sub>3</sub> Wag, CH Bend
34	1414	1377	1377	1379	1397	1398	1398	1400	CH <sub>3</sub> Wag, CH Bend
35	1423	1408	1408	1407	1410	1412	-	-	CH <sub>3</sub> Wag, CH Bend
36	1431	1427	1427	1426	1420	1421	1420	1415	CH <sub>3</sub> Wag
37	1447	1430	1430	1430	1436	1440	1439	1434	CH <sub>3</sub> Wag, CH Bend, NH <sub>2</sub> Twist
38	1485	1459	1459	1459	1458	1461	1463	1461	NH <sub>2</sub> Wag, CH <sub>3</sub> Twist
39	1492	1469	1469	1469	1475	1476	1473	1471	CH <sub>3</sub> Twist
40	1524	1576	1576	1470	-	-	1571	1572	NH Bend, CH <sub>3</sub> Twist
41	1527	1587	1587	1576	1581	1582	1580	1581	NH Bend ,CH <sub>3</sub> Twist
42	1580	1588	1588	1587	1591	1592	1590	1589	NH <sub>2</sub> Bend
43	2111	-	-	-	2088	2086	2080	2075	N-HBr vibration
44	3031	2838	2838	2839	2817	2818	2809	2807	CH <sub>3</sub> Sym Str
45	3037	2850	2850	2859	2835	2837	2838	2836	CH <sub>3</sub> Sym Str
46	3042	2872	2862	2877	2879	2873	-	-	CH <sub>3</sub> Sym Str

47	3049	2895	2895	2895	2893	2892	-	-	CH <sub>3</sub> Sym Str
48	3067	2947	2947	2948	2905	2909	2903	2897	CH Str
49	3094	2948	2948	2956	2921	2924	2918	2919	CH <sub>3</sub> Asym Str , CH Str
50	3108	2955	2955	2957	2947	2943	-	-	CH <sub>3</sub> Asym Str
51	3110	2957	2957	2960	2961	2958	-	-	CH <sub>3</sub> Asym Str
52	3119	2990	2990	2993	2984	2986	2973	2970	CH <sub>3</sub> Asym Str, CH Str
53	3124	3026	3026	3026	-	-	3048	3051	CH <sub>3</sub> Asym Str, CH Str
54	3129	3032	3032	3036	-	-	3142	3142	CH <sub>3</sub> Asym Str
55	3136	3046	3046	3044	3161	3163	3159	3155	CH <sub>3</sub> Asym Str
56	3139	3049	3049	3049	3172	3177	-	-	CH <sub>3</sub> Asym Str
57	3462	3054	3054	3053	3212	3214	-	-	N-H Str

#### Table-4

P212121    P21    IR P2121    P21      -    -    1965    1960    2×Mode22      -    -    2402    2400    2 ×mode28      2417    2417    2415    2411    Mode24+Mode29      -    -    2457    2457    Mode25+mode29      -    -    2467    2467    Mode23+Mode33      2477    2477    2476    Mode25+Mode30      -    -    2537    2531    Mode28+Mode30      -    -    2561    2558    Mode27+Mode33      2610    2611    -    -    2 ×Mode32      2754    2752    2722    2719    2 ×Mode32      2753    2754    2754    2756    Mode31+Mode35      2771    2774    2762    2769    2 ×Mode33	Experimental frequencies	Raman	Experimenta frequencies	ıl IR	Mode description
-    -    1965    1960    2×Mode22      -    -    2402    2400    2×mode28      2417    2417    2415    2411    Mode24+Mode29      -    -    2457    2457    Mode25+mode29      -    -    2467    2467    Mode25+Mode33      2477    2477    2477    2476    Mode25+Mode30      -    -    2537    2531    Mode28+Mode30      -    -    2561    2558    Mode27+Mode33      2610    2611    -    -    2×Mode29      2630    2628    Mode26+mode38      2650    2650    -    -    2×Mode32      2724    2725    2722    2719    2×Mode32      2753    2754    2756    Mode31+Mode35      2771    2774    2762    2769    2×Mode33	P212121	P21	IR P2121	P21	
-    -    2402    2400    2 ×mode28      2417    2417    2415    2411    Mode24+Mode29      -    -    2457    2457    Mode25+mode29      -    -    2467    2467    Mode23+Mode33      2477    2477    2477    2476    Mode25+Mode30      -    -    2537    2531    Mode28+Mode30      -    -    2561    2558    Mode27+Mode33      2610    2611    -    -    2 ×Mode29      2630    2628    Mode26+mode38      2650    2650    -    -    2 ×Mode32      2724    2725    2722    2719    2 ×Mode32      2753    2754    2754    2756    Mode31+Mode35      2771    2774    2762    2769    2 ×Mode33	-	-	1965	1960	2×Mode22
2417    2417    2415    2411    Mode24+Mode29      -    -    2457    2457    Mode25+mode29      -    -    2467    2467    Mode23+Mode33      2477    2477    2477    2476    Mode25+Mode30      -    -    2537    2531    Mode28+Mode30      -    -    2561    2558    Mode27+Mode33      2610    2611    -    -    2×Mode29      2630    2628    Mode26+mode38      2650    2650    -    -    2×Mode30      2724    2725    2722    2719    2×Mode32      2753    2754    2756    Mode31+Mode35      2771    2774    2762    2769    2×Mode33	-	-	2402	2400	2 ×mode28
-    -    2457    2457    Mode25+mode29      -    -    2467    2467    Mode23+Mode33      2477    2477    2477    2476    Mode25+Mode30      -    -    2537    2531    Mode28+Mode30      -    -    2561    2558    Mode27+Mode33      2610    2611    -    -    2×Mode29      2630    2628    Mode26+mode38      2650    2650    -    -    2×Mode30      2724    2725    2722    2719    2×Mode32      2753    2754    2754    2756    Mode31+Mode35      2771    2774    2762    2769    2×Mode33	2417	2417	2415	2411	Mode24+Mode29
-    -    2467    2467    Mode23+Mode33      2477    2477    2477    2476    Mode25+Mode30      -    -    2537    2531    Mode28+Mode30      -    -    2561    2558    Mode27+Mode33      2610    2611    -    -    2 ×Mode29      2630    2628    Mode26+mode38      2650    2650    -    -    2 ×Mode30      2724    2725    2722    2719    2 ×Mode32      2753    2754    2756    Mode31+Mode35      2771    2774    2762    2769    2 ×Mode33	-	-	2457	2457	Mode25+mode29
2477 2477 2477 2476 Mode25+Mode30 2537 2531 Mode28+Mode30 - 2561 2558 Mode27+Mode33 2610 2611 2×Mode29 2630 2628 Mode26+mode38 2650 2650 2×Mode30 2724 2725 2722 2719 2×Mode32 2753 2754 2754 2756 Mode31+Mode35 2771 2774 2762 2769 2×Mode33	-	-	2467	2467	Mode23+Mode33
-    -    2537    2531    Mode28+Mode30      -    -    2561    2558    Mode27+Mode33      2610    2611    -    -    2×Mode29      2630    2628    Mode26+mode38      2650    2650    -    -    2×Mode30      2724    2725    2722    2719    2×Mode32      2753    2754    2754    2756    Mode31+Mode35      2771    2774    2762    2769    2×Mode33	2477	2477	2477	2476	Mode25+Mode30
-      -      2561      2558      Mode27+Mode33        2610      2611      -      -      2×Mode29        2630      2628      Mode26+mode38        2650      2650      -      -      2×Mode30        2724      2725      2722      2719      2×Mode32        2753      2754      2754      2756      Mode31+Mode35        2771      2774      2762      2769      2×Mode33	-	-	2537	2531	Mode28+Mode30
2610    2611    -    -    2 ×Mode29      2630    2628    Mode26+mode38      2650    2650    -    -    2 ×Mode30      2724    2725    2722    2719    2 ×Mode32      2753    2754    2754    2760    Mode31+Mode35      2771    2774    2762    2769    2 ×Mode33	-	-	2561	2558	Mode27+Mode33
2630      2628      Mode26+mode38        2650      2650      -      -      2×Mode30        2724      2725      2722      2719      2×Mode32        2753      2754      2754      2756      Mode31+Mode35        2771      2774      2762      2769      2×Mode33	2610	2611	-	-	2 ×Mode29
2650    2650    -    -    2 ×Mode30      2724    2725    2722    2719    2 ×Mode32      2753    2754    2754    2756    Mode31+Mode35      2771    2774    2762    2769    2 ×Mode33			2630	2628	Mode26+mode38
2724 2725 2722 2719 2 ×Mode32 2753 2754 2754 2756 Mode31+Mode35 2771 2774 2762 2769 2 ×Mode33	2650	2650	-	-	2 ×Mode30
2753 2754 2754 2756 Mode31+Mode35 2771 2774 2762 2769 2 ×Mode33	2724	2725	2722	2719	2 ×Mode32
2771 2774 2762 2769 2 ×Mode33	2753	2754	2754	2756	Mode31+Mode35
REAM	2771	2774	2762	2769	2 ×Mode33
		40			

Combination and overtone bands obtained from experiment

#### **Figure Captions**

- 1. Orthorhombic crystals grown by solution growth
- (a) Rietveld refinement of ambient X-ray diffraction data for DIPAB orthorhombic (P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>) structure. Red points are experimental data, continuous line represents the fitted data and the bottom curve is the difference plot

(b) Rietveld refinement of ambient X-ray diffraction data for DIPAB monoclinic-II (P2<sub>1</sub>) structure. Red points are experimental data, continuous line represents the fitted data and the bottom curve is the difference plot

- 3. (a) Raman spectra of orthorhombic and monoclinic-II in  $150-1260 \text{ cm}^{-1}$ 
  - (b) Raman spectra of orthorhombic and monoclinic-II in 1270-1650 cm<sup>-1</sup>
  - (c) Raman spectra of orthorhombic and monoclinic-II in 1900-3500 cm<sup>-1</sup>
- 4. (a) IR absorption spectra of orthorhombic and monoclinic-II in  $150-1260 \text{ cm}^{-1}$ 
  - (b) IR absorption spectra of orthorhombic and monoclinic-II in 1270-1650 cm<sup>-1</sup>
  - (c) IR absorption spectra of orthorhombic and monoclinic-II in 1900-3500 cm<sup>-1</sup>
- 5. Experimental Low wavenumber Raman spectra for orthorhombic and monoclinic-II phase
- 6. (a) Orthorhombic  $(P2_12_12_1)$  unit cell of DIPAB
  - (b) Monoclinic-II (P2<sub>1</sub>) unit cell DIPAB
  - (c) Single molecular unit of DIPAB. Hydrogen atoms are grey
- 7. Computed Raman and IR spectra of DIPAB molecule using B3YLP/ 6-311++G(d,p)



Figure- 2(b)





Figure-5





### **Graphical Abstract:**



#### Highlights:

- Diisopropylammonium bromide samples (orthorhombic (P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>) and monoclinic-II (P2<sub>1</sub>)) were synthesized by solution growth method.
- Raman and IR spectroscopic measurements and factor group analyses were carried out to study vibrational properties.
- Computational DTF calculations using Gaussian 09 and CASTEP codes were performed for mode assignments.
- Low wave number Raman spectra were recorded to distinguish between the two polymorphs.

A CERTINAL