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Crystal structure of 3-methyl 2-vinylpyridinium bromide

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ABSTRACT

Single crystals of 3-Methyl 2-Vinylpyridinium Bromide (MVPB) were grown by slow evaporation method at room temperature. Single crystal x-ray diffraction analysis reveals that MVPB crystallizes in triclinic system with space group Pī and the calculated lattice parameters are a = 7.744(4) Å, b= 7.923(5) Å, c=8.561(5) Å, α=62.483(3)°, β=66.704(3)° and γ= 74.831(3)°. The structure of MVPB shows that the pyridinium moiety is planar. The sum of the bond angles around the protonated nitrogen atom of pyridinium ring is in accordance with sp^2 hybridization.The crystal packing of the pyridinium is through weak N-H...Br, C-H...Br and π …πintermolecular interactions in addition to van der Waals forces.

INTRODUCTION

Pyridinium refers to the cationic form of pyridine. This can either be due to protonation of the ring nitrogen or because of addition of a substituent to the ring nitrogen, via alkylation. The lone pair of electrons on the nitrogen atom of pyridine is not delocalized, and thus pyridine can be protonated easily. Pyridine is often used as an organic base in chemical reactions, thus the pyridinium ion is produced as the counter ion to the leaving group in the reaction. Pyridinium derivatives have been found to have non-linear optical properties [1-4]. Partially fluorinated pyridinium surfactants are used for biomedical applications such as components for novel gene and drug delivery systems [5]. Pyridinium based ionic liquids are used as promissing solvents for the extractive desulfurization of diesel [6]. Pyridinium derivatives find a number of technical and medical uses owing to their adsorption by textiles, bacteria, etc. The adsorption of pyridinium compounds by clay particles affects the water absorption and swelling characteristics of soils [7]. Organic pyridinium salts have been widely used as guest molecules in the construction of supramolecular architecture in the field of chemistry [8]. Numerous inorganic-organic hybrid materials based on bifunctional pyridinium ions have been reported [9,10]. The supramolecular assembly of halide salts of the bifunctional pyridinium ion has also been thoroughly investigated [11,12]. It is well recognized that heterocyclic compounds, especially N-donor ligand systems, participate in numerous biological systems, being a module of several vitamins and drugs [13,14]. Pyridiniumcations are good candidate for second-harmonic generation (SHG) materials because they possess large hyperpolarizabilities irrespective of the short cutoff wavelength. Since pyridinium cations are ionic species, they possess an easy tunability into non-centrosymmetric structures by changing counter anions[15, 16]. The irradiation of pyridinium salts provides the facile, stereo controlled synthesis of a range of molecular architectures such as bicyclic aziridines, fused heterocycles and various functionalized aminocyclopentenes[17]. When pyridinium cations are combined with metal halide anions, the refractive indices of the crystals could be tuned due to exchangeability of metal and halogen species within anions[18]. Halide anions have been reported to

improve the physicochemical stability of 1 -ethyl-2, 6-dimethyl-4-(1H)-pyridinones[19]. The presence of a chloro substituent in different types of pyridinium compounds causes them to exhibit pesticidal activity [20].Pyridinium derivatives exhibit antibacterial and antifungal activities too [21]. In view of the importance of pyridinium derivatives, in the present communication we have synthesized and studied the crystal structure of 3-Methyl 2-Vinylpyridinium Bromide (MVPB).

MATERIALS AND METHODS

1g of freshly distilled 3-methyl 2-vinyl pyridine was dissolved in 5 ml of diethyl ether and kept at -10°C under nitrogen atmosphere. To the above solution, 0.6 ml of HBr in 5 ml of diethyl ether was added drop wise and the solution is allowed to stir continuously for nearly six hours. A pale yellow solid formed after the completion of the reaction was filtered off and washed with diethyl ether. Further it is allowed to dry in vacuum. After recrystallization of salt from methanol, the product 3-methyl 2-vinyl pyridinium bromide was obtained in quantitative yield.

RESULTS AND DISCUSSION

Crystal structure analysis

X-raydiffractionintensitydatawerecollectedforMVPBonBrukeraxsKappaApexIIsingle crystalX-raydiffractometerequipped with graphite mono- chromate MoKα(λ=0.7103Å)radiationandCCDdetector.Crystalswerecuttosuitablesizeandmountedonaglassfibreusingcyanoacrylateadhesive.Theunitcellparameters were determined from 36 framesmeasured (0.5° phi-scan) from three different crystallographiczonesandusingthemethodofdifferencevectors.Theintensitydata were collected with an average four-fold redundancy perreflection and optimum resolution (0.75 Å). The intensity data collection, frames integration, Lorentz and polarizationcorrectionanddecaycorrectionweredoneusingSAINT-NT(version7.06a) software.Empiricalabsorptioncorrection(multi-scan)wasperformedusingSADABS[22]program.
Crystalstructures were solved by direct methods using SHELXS-97 [23]. Thestructures werethenrefinedbyfull-matrixleast-squaresmethodusingSHELXL-97[23].TheLauegroupassignment,systematicabsencesandintensitystatisticswereconsistentwith centrosymmetry indicating space group Pīwith lattice parameter a=7.744(4)Å, b= 7.923(5)Å, c=8.561(5)Å, α=62.483(3)°, β =66.704(3)° and γ= 74.831(3).

The crystal data and structure refinement parameters are given in Table 1. The chemical diagram of MVPB is shown in Fig.1. The molecular structure (ORTEP diagram) of (MVPB) is shown in Fig.2. The packing diagram of MVPB is shown in Fig.3. The various hydrogen bond geometrical parameters are presented in table 5 with symmetry codes. Selected bond distances and bond angles are shown in Fig.3 and 4. Theanisotropicdisplacementparametersarelistedin Table3. Theatomiccoordinatesandtheirisotropicdisplacement parameters involving hydrogen atoms are given in Tables 2. Thetorsionanglesinvolvingnon-hydrogenatoms arelistedinTable4 respectively.

The bond lengths and bond angles of the pyridiniumare in good agreement with the values reported in related literature[24,25]. 2-vinylpyridinium is cation, andis found to be neutralized by bromideanions, respectively. The pyridinium ring is essentially planar. The mean value of C-C and N-C bond lengths are 1.391(2)Å and 1.332(2)Å which are between that of a single and a double bond and agree with those in the literature [26]. The short C=C double bond [C6-C7 = 1.296(3)Åfor pyridiniumis an important characteristics of a vinyl linkage, because it is not participating in electron delocalization with the pyridinium ring[27]. The sum of the bond angles around the protonated nitrogen atom of pyridinium ring is in accordance with sp^2 hybridization. Due to protonation of the nitrogen, the C-N-C angle is widened C4-N1-C5 = 124.3(5)°and comparable with the literature value [28].

Packing Features

The packing of the molecules of pyridiniumis viewed down c-axis is shown in Fig.3. The crystal packing of the pyridiniumis through weak N-H...Br, C-H...Br and $\pi \ldots \pi$intermolecular interactions (Table 5) in addition to van der Waals forces. In the crystal structure, anions and cations are connected by intermolecularC4-H4...Br1 and intramolecular N1-H1...Br1 hydrogen bonds.The crystal packing exhibits $\pi \ldots \pi$ interactions with centroid-centroid distance of [Cg(1)-Cg(1)] 3.6193(1)Å, shown in Fig: 3.

Computational detail

Data collection: SMART [22]; cell refinement: SAINT [22]; data reduction: SAINT; program(s) used to solve structure: SHELXS97 [23]; program(s) used to refine structure: SHELXL97 [23]; molecular graphics: PLATON [29]; software used to prepare material for publication: SHELXL97 and PARST [30].

Fig. 1 SchematicDiagram of the pyridinium

Fig. 2 Perspective view of the pyridinium with the atom numbering scheme Displacement ellipsoids are drawn at 30% probability level.
Fig. 3 Bond lengths (Å) of pyridinium
Fig.4 Bond angles (°) of pyridinium
Fig.5Packing of the molecules viewed down the *c-axis* for pyridinium

Table 1 Crystal data for Pyridinium

Parameters	Pyridinium
Empirical formula	$C_8H_{10}BrN$
Formula weight	200.08
Wavelength(Å)	0.71073
Crystal system	Triclinic
space group	Pī
Unit cell dimensions	
a(Å)	7.744(4)
b(Å)	7.923(5)
c(Å)	8.561(5)
α(°)	62.483(3)
β(°)	66.704(3)
γ(°)	74.831(3)
Volume ($Å^3$)	425.95(4)
Z, Calculated density(Mg/m^3)	2, 1.560
Absorption coefficient(mm^{-1})	4.751
F(000)	200
Crystal size(mm)	0.20 x 0.25 x0.25
θ range (°)	2.83 to 26.00
Limiting indices	
	-9<=h<=9
	-9<=k<=9
	-10<=l<=10
Reflections collected / Unique	8124 / 1684 [R(int) = 0.0280]
Refinement method	Full-matrix least-squares on F^2
	1684 / 22 / 101

Data / restraints / parameters	
Goodness-of-fit on F^2	1.097
Final R indices [I>2σ(I)]	R1 = 0.0177 wR2 = 0.0410
R indices (all data)	R1 = 0.0213 wR2 = 0.0422
Largest diff. peak and hole(eÅ^{-3})	0.182 and -0.193

Table 2 Atomiccoordinates(x10^4)andequivalentisotropicdisplacementparameters(Å^{2}x10^3)forthenon-hydrogenatomsof Pyridinium

Atom	x	y	z	*U(eq)
C1	1097(2)	1978(2)	7077(2)	39(1)
C2	-370(3)	2567(3)	8360(2)	45(1)
C3	-2123(3)	3267(3)	8149(3)	48(1)
C4	-2406(3)	3418(3)	6613(3)	45(1)
C5	747(2)	2133(2)	5538(2)	37(1)
C6	2175(3)	1582(3)	4080(3)	53(1)
C7	2063(3)	1932(4)	2484(3)	60(1)
C8	3004(3)	1227(3)	7324(3)	54(1)
N1	-984(2)	2856(2)	5378(2)	39(1)
Br1	-3006(1)	3890(1)	2431(1)	50(1)

*U_{eq}=(1/3)$\sum_i\sum_j U_{ij}a_i$*a_j***a$_i$.a$_j$**

Table 3Anisotropic displacement parameters (Å^{2}x10^3) for thenon-hydrogen atoms of Pyridinium

Atom	U11	U22	U33	U23	U13	U12
C1	46(1)	32(1)	38(1)	-11(1)	-14(1)	-7(1)
C2	58(1)	44(1)	34(1)	-16(1)	-13(1)	-7(1)
C3	51(1)	50(1)	40(1)	-24(1)	-5(1)	-2(1)
C4	40(1)	42(1)	47(1)	-19(1)	-11(1)	0(1)
C5	41(1)	32(1)	36(1)	-14(1)	-10(1)	-4(1)
C6	44(1)	65(1)	53(1)	-35(1)	-14(1)	8(1)
C7	58(1)	73(2)	49(1)	-37(1)	-10(1)	3(1)
C8	52(1)	60(1)	54(1)	-23(1)	-23(1)	-3(1)
N1	43(1)	41(1)	35(1)	-18(1)	-13(1)	-2(1)
Br1	48(1)	65(1)	45(1)	-30(1)	-18(1)	3(1)

The anisotropic displacement factor takes the form:

$\exp\{-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]\}$

Table 4 Torsion angles (°) involving the non-hydrogen atoms of Pyridinium

Atoms	Angle
C(1)-C(5)-N(1)-C(4)	-0.8(2)
C(3)-C(2)-C(1)-C(5)	0.5(3)
C(3)-C(4)-N(1)-C(5)	0.1(3)
C(3)-C(2)-C(1)-C(8)	179.66(7)
C(4)-C(3)-C(2)-C(1)	-1.3(3)
C(6)-C(5)-C(1)-C(2)	179.39(7)
C(6)-C(5)-N(1)-C(4)	-179.76(6)
C(6)-C(5)-C(1)-C(8)	0.2(3)
C(7)-C(6)-C(5)-C(1)	-169.1(2)
N(1)-C(5)-C(6)-C(7)	9.8(3)
N(1)-C(4)-C(3)-C(2)	1.0(3)
N(1)-C(5)-C(1)-C(2)	0.5(2)
N(1)-C(5)-C(1)-C(8)	-178.63(5)

Table 5 Hydrogen bond interactions for Pyridinium[Å and º]

Compound	D-H…A	D-H	H…A	D…A	D-H…A
Pyridinium	N1-H1...Br1	0.86	2.37	3.1678	154
	C4-H4...Br1[i]	0.93	2.85	3.6320	142
	C7-H7...Br1	0.93	2.91	3.8360	160

Symmetry code:

(i) -x-1,-y+1,-z+1.

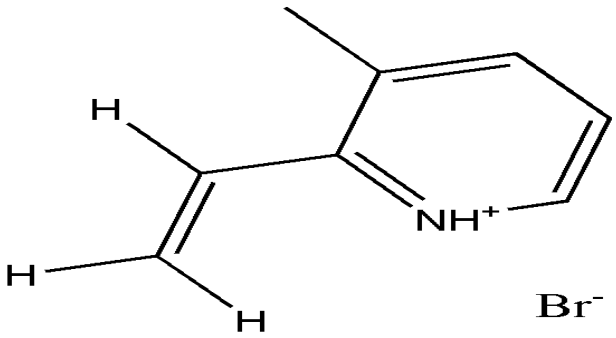

Fig. 1 SchematicDiagram of the pyridinium

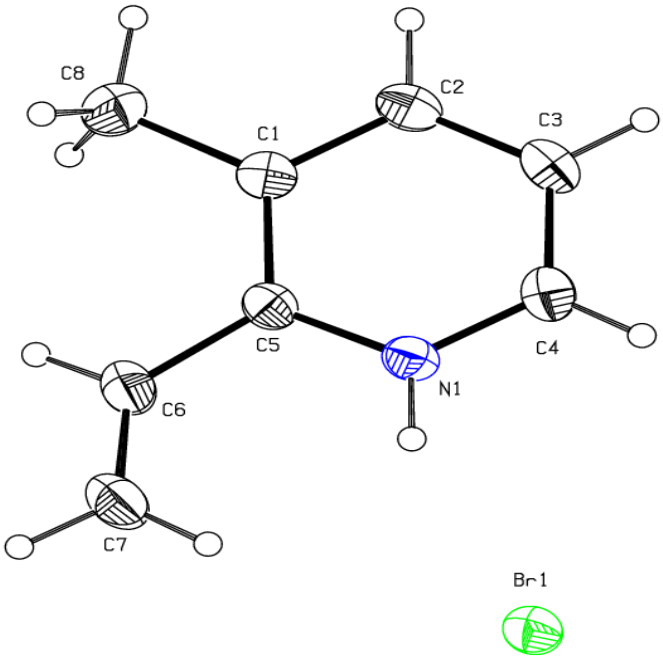

Fig. 2 Perspective view of the pyridinium with the atom numbering scheme Displacement ellipsoids are drawn at 30% probability level.

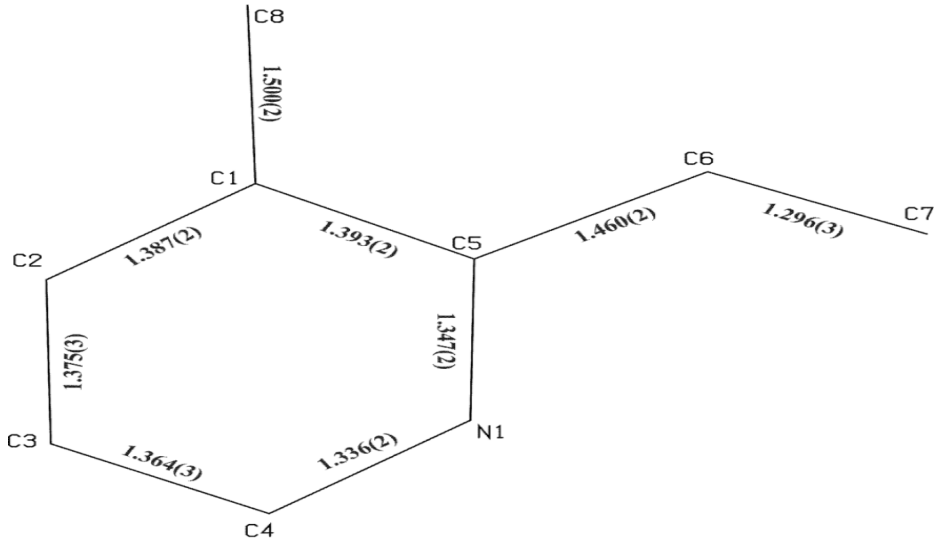

Fig. 3 Bond lengths (Å) of pyridinium

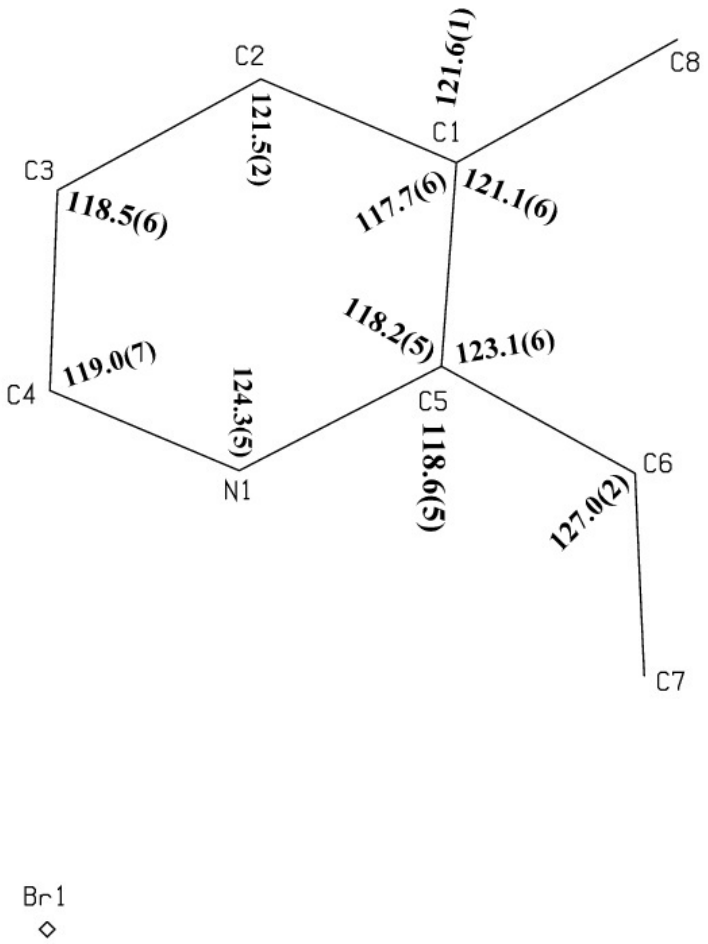

Fig.4 Bond angles (°) of pyridinium

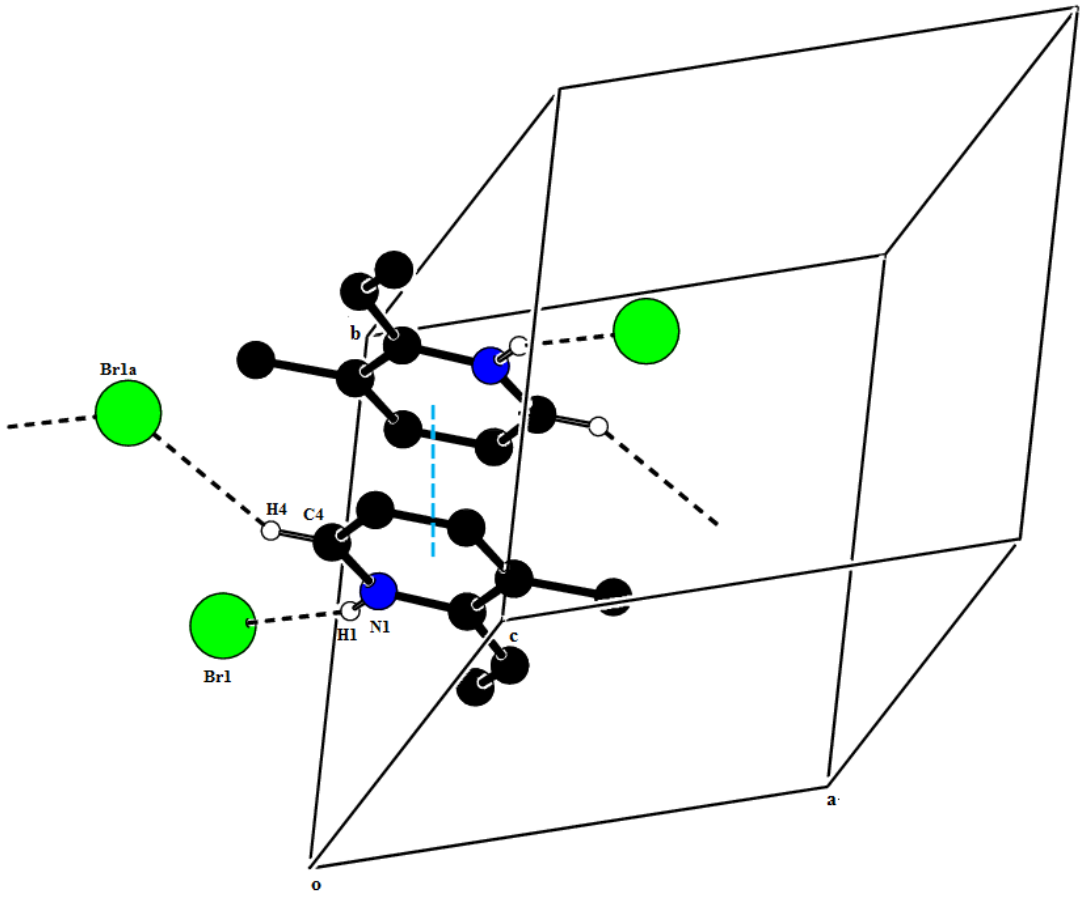

Fig.5Packing of the molecules viewed down the *c-axis* for pyridinium

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