

A planar 2,2'-dipyridylammonium salt : Synthesis and structure

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Abstract : Reaction of 2,2'-dipyridylamine (DPA) with hexafluorophosphoric acid (HPF₆) in methanol generates white rod-shaped crystals of H₂DPA.PF₆.H₂O. The salt is characterised by C, H and N analyses, FT-IR, ¹H NMR, mass spectroscopy and molar conductance measurement. The X-ray crystal structure of the salt has been determined. The structure shows that the salt is monomeric. The amine nitrogen is strongly hydrogen bonded with oxygen atom of water. Two pyridyl rings are almost planar which is a rarity in the coordination chemistry of DPA. Semi-empirical AM1 calculation was also performed to delve into the novel situation.

Keywords : 2,2'-Dipyridylamine, hexafluorophosphate salt, planar structure, hydrogen bonding, AM1 calculation.

Introduction

Organic ligands based on pyridine derivatives are important class of ligands. The prospects of coordination of some chelating ligands containing non or weakly conjugated 2-pyridyl groups have been thoroughly reviewed by William R. McWhinnie in 1970¹. 2,2'-Dipyridylamine (DPA), a tailored diimine (-N=C-NH-C=N-), seems to be a potential bidentate ligand among them owing to its ability to form hydrogen bond through active amine (-NH-) hydrogen. Thus it has relevance in supramolecular chemistry as well²⁻⁴. In fact, the acid "DPA" and its "conjugate base" (DPA⁻) have been widely employed in coordination chemistry⁵⁻⁹.

DPA exhibits photoluminescence property¹⁰. Even, DPA had been shown to catenate¹¹. DPA is used as an anti-oxidant in lubricating oil. Though, the preparation of DPA was first reported by Wibacet and Dingemans¹² in 1923, its crystal structure appears only in 1973¹³. In the free DPA structure, DPA exists as intermolecularly doubly hydrogen bonded dimer. Two pyridyl rings are bent at 23° to retrieve the steric hindrance. In all its complexes reported hitherto, the dihedral angle between the two rings is invariably ≥23°. Again, it is pertinent to note that till date no structure of any DPA salt is known with which we can compare the present dihedral angle. Herein we report a monomeric salt of DPA having a planar disposition of the two rings.

Results and discussion

In the course of our ongoing research work with DPA, we have been able to isolate a protonated variety of DPA. This isolation has been made possible with PF₆⁻ as counter anion. The protonation is achieved through the protolysis of HPF₆ in methanol. The yield of the salt is almost quantitative. It is soluble in dimethylformamide (DMF) and partly in dimethylsulphoxide (DMSO). In DMF, it behaves as a 1 : 1 electrolyte with molar conductance (Λ_M) value of 73 cm² Ω⁻¹ mol⁻¹. Geary¹⁴ specified Λ_M range for a 1 : 1 electrolyte in DMF is 65–90 cm² Ω⁻¹ mol⁻¹. While DPA is soluble in acetonitrile, its PF₆⁻ salt H₂DPA.PF₆.H₂O is not. In a non-aqueous medium like CH₃CN, the acid dissociation constant (pK_a) value has been determined recently for the first time through molar conductance measurements. The pK_a value of DPA (for the loss of -NH- proton) in CH₃CN is found to be 6.48⁶. The pK_a value of DPA in H₂O have been shown earlier to be 6.99¹⁵.

In FT-IR spectrum, the free DPA features the vibrations for characteristic stretching and bending modes of the C-C and C-N bonds in the range between 1645–1390 and 1270–750 cm⁻¹ respectively¹⁶. These features are akin to H₂DPA.PF₆.H₂O. A very sharp band at 839 cm⁻¹ with a medium at 557 cm⁻¹ are due to ν(PF₆) vibration. A strong band at 3416 cm⁻¹ is due to ν(O-H) vibration from water. The -NH- band is noticeable at 3072 cm⁻¹.

Mass spectral analysis was performed in DMSO with a positive ionization mode. A peak at m/z value of 172.0575 (100%) is due to $[\text{DPA} + \text{H}^+]$.

In ^1H NMR of $\text{HDPA} \cdot \text{PF}_6 \cdot \text{H}_2\text{O}$ in $\text{DMSO}-d_6$ important signals appear in the range of 6–12 ppm (Fig. 3). The chemical shift (δ_{H} ; in ppm) of the NH proton in

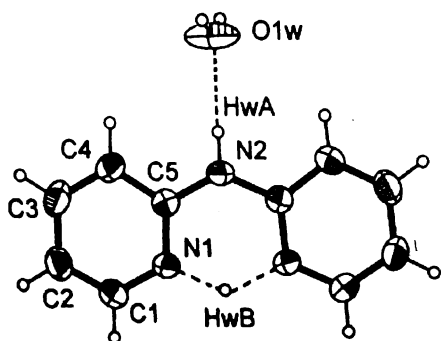


Fig. 1. ORTEP diagram of the cation $[\text{HDPA}] \cdot \text{H}_2\text{O}$ showing the atom labelling scheme with thermal ellipsoids at 50% probability.

$\text{DMSO}-d_6$ of free DPA is 9.9¹⁷. This δ_{H} value of our salt in $\text{DMSO}-d_6$ is 11.64. This considerable downfield shifting is due to the development of positive charge on the proton. The chemical shift of a proton moves more downfield as the positive charge on the proton increases. Expectedly, this situation is a natural consequence of the hydrogen-bonding.

In the electronic spectrum of $\text{HDPA} \cdot \text{PF}_6 \cdot \text{H}_2\text{O}$ in DMF, fully-allowed band at 314 nm with ϵ value of 10,318 $\text{M}^{-1} \text{cm}^{-1}$ is assigned due to $\pi-\pi^*$ transition in DPA moiety.

The ORTEP view of the cation $[\text{HDPA}]^+ \cdot \text{H}_2\text{O}$ in $\text{HDPA} \cdot \text{PF}_6 \cdot \text{H}_2\text{O}$ is shown in Fig. 1. It is a monomeric unit. The C–C bonds adjacent to the bridging pyridyl nitrogen are found to be different, 1.384(6) Å and 1.339(7)

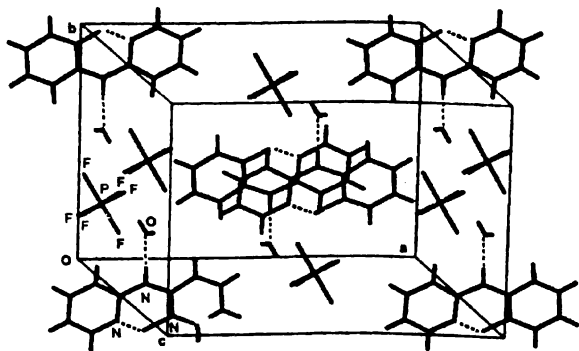
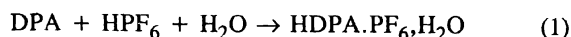


Fig. 2. Packing diagram of the molecule $\text{HDPA} \cdot \text{PF}_6 \cdot \text{H}_2\text{O}$.

Å respectively. In the dimeric unit of free DPA¹³, however, the corresponding C–C bonds are of identical in bond length [1.395(5) Å]. The carbon-nitrogen distances in the pyridine rings are almost identical 1.336(6) Å and 1.337(5) Å. This is virtually identical with the C–N distance of 1.340 Å, reported for pyridine¹⁸. The two bridging C–N distances are at 1.362(4) Å. The bond angles within the pyridine ring are not of same values. The values vary between 117.9(5)^o [$\angle\text{C1-C2-C3}$] and 123.2(4)^o [$\angle\text{N1-C1-C2}$]. The bond angles comprising chemically equivalent atoms in the two pyridine rings are equal within the stipulated standard deviations. The observed variations in bonds angles about the ring nitrogen are quite justifiable in the spirit of "conjugative effect" (arising due to attractive and repulsive forces). The geometry about the amine nitrogen is planar. The sum of the three angles surrounding it is 359.2^o. The N–H distance is 0.860 Å. The hydrogen bond length [N2–HwA...O1w] is 2.810(6) Å which is less than the sum of the van der Waals radii of nitrogen (1.5 Å) and oxygen (1.40 Å) atoms¹⁹. The hydrogen bonding pattern of the compound is shown in Fig. 2. This situation is comparable to copper(II)²⁰ and zinc(II)¹⁰ complexes of DPA. In every case the donor atom in the hydrogen bonding is invariably the amine nitrogen. For Cu^{II} , the hydrogen bond, N–H...O (from acetate) is 2.833(2) Å. In Zn^{II} , the acceptor atom is also oxygen but in contrast to acetate, now it is from nitrate. It is of 2.939(3) Å, a little bit longer. The length of the present hydrogen bond in our case indicates that it is not so weak. The shortest known hydrogen bonds are of the order of 2.43 Å¹⁹. No where in the above cited examples the bond is perfectly linear. Here, the hydrogen bond is exactly linear with $\angle\text{N2-HwA...O1w} = 180^\circ$. HwB (arising out of protonation) is placed (Fig. 1) equidistant from two chemically equivalent pyridyl nitrogen atoms. N1–HwB distance is 0.79 Å. The dihedral angle between the two pyridyl rings in the salt is only 1.52^o. This results almost coplanarity of the DPA rings in spite of protonation. In free DPA the above angle is, however, 23.0^o. It is most likely that significant hydrogen bonding renders planarity.

In order to rationalize the situation, AM1 method of calculation was performed on $\text{HDPA} \cdot \text{PF}_6 \cdot \text{H}_2\text{O}$. This semi-empirical quantum mechanical method was developed by Dewar²¹. It is found that in the gas phase protonation of the pyridyl nitrogen of DPA is favourable owing to the hydrogen bonding of -NH- moiety. The following reaction has been considered for the AM1 calculation.



The calculated enthalpy change for the eq. (1) in the gas phase by AM1 method comes out to be $-56.6 \text{ kcal mol}^{-1}$. The hydrogen bonding seems to sacrifice this favourable enthalpy change.

In summary, a new salt of 2,2'-dipyridylamine (DPA) has been synthesized and successfully characterized. Importantly, this type of ligand contains functional groups capable of supporting π - π and N-H...O hydrogen bonds interactions that support supramolecular structures. The hydrogen bond, here, has absolutely dedicated to the stability and coplanarity of the DPA moiety. Moreover, theoretical calculation results also demonstrated the rationality of the crystal structure.

Experimental

DPA was procured from Aldrich (USA) and HPF_6 from Fluka (Germany). MeOH was of analytical reagent grade and was used without further purification. C, H and N microanalyses were performed by a Perkin-Elmer 2400II elemental analyzer. FT-IR spectra (KBr disc) were recorded with a Shimadzu FT-IR-8400S spectrophotometer. UV/Vis spectra were recorded on a Shimadzu UV-160A spectrophotometer, 300 MHz NMR spectra (in DMSO- d_6 with TMS as the reference) on a Bruker DPX300 spectrometer. Purified dimethylformamide (DMF) was used for conductance measurements, which were made by a Systronics (India) direct-reading conductivity meter (Model 304). The cell constant was calibrated with 0.01 M aqueous KCl solution. ESI mass spectrum was recorded (in DMSO) on a Qtof Micro YA263 spectrometer. AM1 calculations were performed by using HyperChem (version 6.0).

X-ray crystallography :

Data for $\text{HDPA.PF}_6.\text{H}_2\text{O}$ were collected at 293 K with a Bruker SMART 1K CCD diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal and experimental data are tabulated in Table 1. Intensity data were corrected for absorption effects. An empirical absorption correction was carried out using DIFABS²². The structure was solved using direct methods with the SHELX97 programs²³. All non-hydrogen atoms were refined anisotropically. H atoms were geometrically fixed and allowed to ride on the parent atoms. The structure was refined²⁴ by least squares method on F^2 using SHELXTL-PC. Selected bond distances, bond angles and hydrogen bonds are given respectively in Tables 2 to 4 respectively.

Table 1. Crystallographic data for $\text{HDPA.PF}_6.\text{H}_2\text{O}$

| | |
|---|--|
| Formula | $\text{C}_{10}\text{H}_{12}\text{N}_3\text{OPF}_6$ |
| Formula weight | 335.20 |
| Crystal system | monoclinic |
| Space group | $C2/c$ |
| Unit cell dimensions | |
| a (\AA) | 15.623(3) |
| b (\AA) | 12.862(3) |
| c (\AA) | 7.731(2) |
| α ($^\circ$) | 90 |
| β ($^\circ$) | 117.11(1) |
| γ ($^\circ$) | 90 |
| Volume (\AA^3) | 1382.9(5) |
| Z | 4 |
| Temperature (K) | 293 |
| $D_{\text{calcd.}}$ (g cm^{-3}) | 1.610 |
| μ (mm^{-1}) | 0.270 |
| $F(000)$ | 680 |
| λ (\AA) | 0.71073 |
| $\theta_{\text{min}} - \theta_{\text{max}}$ ($^\circ$) | 2.9, 26.0 |
| No. of reflections | 3619 |
| Uniq. data, R (int) | 1352, 0.023 |
| Observed data [$I > 2\sigma(I)$] | 1222 |
| $N_{\text{ref.}}, N_{\text{par}}$ | 1352, 101 |
| R_1 | 0.073 |
| wR_2 (all data) | 0.148 |
| Goodness of fit (S) | 1.02 |
| $w = 1/[S^2(F_o^2) + (0.0377P)^2 + 4.3279P]$, where $P = (F_o^2 + 2F_c^2)/3$. | |

Table 2. Selected bond distances (\AA) for $\text{HDPA.PF}_6.\text{H}_2\text{O}$

| | | | |
|-----------|----------|--------|----------|
| N2-C5_b | 1.362(4) | N1-HwB | 0.7900 |
| N2-HwA | 0.860 | C1-C2 | 1.339(7) |
| C2-C3 | 1.388(7) | C3-C4 | 1.353(7) |
| O1w-HwA | 0.65(6) | C4-C5 | 1.384(6) |
| O1w-HwA_a | 0.65(6) | N1-C1 | 1.336(6) |
| N1-C5 | 1.337(5) | N2-C5 | 1.362(4) |

Table 3. Some selected bond angles ($^\circ$) for $\text{HDPA.PF}_6.\text{H}_2\text{O}$

| | | | |
|------------|----------|-------------|----------|
| C5-N2-HwA | 115.00 | C5_b-N2-HwA | 115.00 |
| N1-C1-C2 | 123.2(4) | C1-C2-C3 | 117.9(5) |
| C2-C3-C4 | 120.0(5) | C3-C4-C5 | 119.1(4) |
| N1-C5-C4 | 120.7(4) | N2-C5-C4 | 120.4(4) |
| N1-C5-N2 | 118.9(3) | C1-N1-C5 | 119.1(3) |
| C5-N2-C5_a | 129.2(4) | C5-N1-HwB | 112.00 |

$$a = -x, y, 1/2-z, b = -x, y, 1/2-z$$

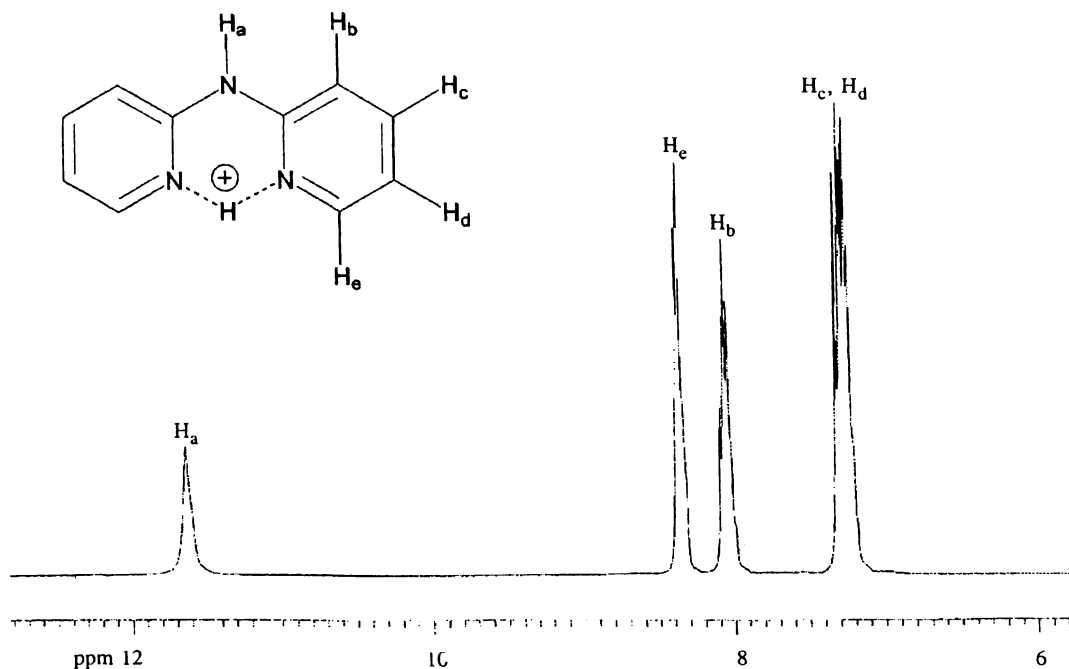


Fig. 3. 300 MHz ^1H NMR spectrum of the molecule HDPA. PF_6 . H_2O in $\text{DMSO-}d_6$.

Table 4. Hydrogen bonds (\AA , $^\circ$) for HDPA. PF_6 . H_2O

| | | | |
|--------------|-------|----------|-----|
| N1-HwB...N1 | 1.950 | 2.627(5) | 144 |
| N2-HwA...O1w | 1.950 | 2.810(6) | 180 |

Synthesis of HDPA. PF_6 . H_2O :

0.1 g (0.59 mmol) of DPA was dissolved in 50 ml of methanol. To it was slowly added dropwise with stirring 0.11 g (0.75 mmol) of HPF_6 . The resulting mixture was left for aerial evaporation. After 10 days, shining white rod-shaped crystals formed thereby was filtered off, washed with 5 ml of ice-cooled methanol and subsequently dried *in vacuo* over fused CaCl_2 . The crystals were fit for X-ray crystallography. Yield : 0.17 g (86%) (Found : C, 35.48; H, 3.72; N, 12.62. $\text{C}_{10}\text{H}_{12}\text{N}_3\text{PF}_6\text{O}$ requires : C, 35.83; H, 3.61; N, 12.54%); FT-IR (KBr) : ν/cm^{-1} 3416(vb) $\nu(\text{OH})$, 3072(m) $\nu(\text{NH})$, 1664(s) $\nu(\text{CN})$, 839(vs) and 557(m) $\nu(\text{PF}_6)$; ^1H NMR ($\text{DMSO-}d_6$) : δ/ppm 7.32 (4H, m), 8.03 (2H, d), 8.37 (2H, d) and 11.64 (1H, s); Λ_M (DMF) : $73 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ (1 : 1 electrolyte); m/z 172.06 [DPA + H^+].

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