High resolution ^1H and ^{13}C NMR and mass spectral studies of substituted dipyridylpyridazine

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Abstract. Total assignment of the ^1H and ^{13}C NMR spectra of 3,6-bis(2'-pyridyl)pyridazine derivatives (*n*-dppn) have been recorded at 400 and 100 MHz, respectively.¹ Based on these data, the complete assignment of the ^{13}C NMR chemical shift values was made by a $^{13}\text{C}\{^1\text{H}\}$ decoupling. The spectra clearly show that the *n*-dppn ligands exist in the *cis-cis* conformation at least in solution. Matrix assisted laser desorption ionization (MALDI) and time-of-flight mass spectrometry (TOFMS) are used to record the mass spectra of the *n*-dppn ligands. α -Cyano-4-hydroxycinnamic acid (CHCA) matrix promoted the molecular ion detection when 180 pmol of *n*-dppn is introduced into the TOFMS.

1. Introduction

The tetranitrogenated 3,6-bis(2'-pyridyl)pyridazine (dppn) ligands are widely used to prepare some important complexes especially those of ruthenium(II) and rhodium(III) since these complexes act as photosensitizer for solar energy conversion which exhibit catalytic and biological properties [1–6]. The dppn ligand forms mononuclear and binuclear complexes [7]. In the former, dppn acts as a bidentate chelating ligand, with two neighboring pyridine and pyridazine ring nitrogen atoms bonded to metal ion, while in the later, the ligand adopts a conformation suitable to chelate two metal ions, on the same side, through the four nitrogen donor atoms [7].

Lately, derivatives (*n*-dppn, Fig. 1) of the dppn ligand with electron-releasing cyclic aliphatic groups have been prepared and their complexes with ruthenium(II) and rhodium(III) reported [1,8,9]. The ^1H NMR spectra of some of these ligands have previously been reported [8] but the assignment of the spectral data remained ambiguous; besides, a ^{13}C NMR study has not been described. Very recently, we have reported the ^1H and ^{13}C NMR of some of these ligands and their complexes of rhodium(III) in DMSO- d_6 [9].

In the present study we report and interpret a full ^1H and ^{13}C NMR spectral data of the *n*-dppn ligands as well as the mass spectra.

¹For the *n*-dppn ligands, *n* stands for the size of the cyclic aliphatic ring on position 4 and 5 of the pyridazine ring, *n* = 5, 6, 7, 8, and 12.

Fig. 1. Structure of the *n*-dppn: 5-dppn, $m = 5$; 6-dppn, $m = 6$; 7-dppn, $m = 7$; 8-dppn, $m = 8$; 12-dppn, $m = 12$.

2. Materials and methods

2.1. Synthesis of *n*-dppn ligands and their mass (m/z)

All solvents used were analytical reagent grade. The *n*-dppn ligands ($n = 5, 6, 7, 8$, and 12) were prepared according to the procedure described by Atfah [8]. All MALDI of *n*-dppn were acquired by using α -cyano-4-hydroxycinnamic acid and gave the protonated molecular ion of *n*-dppn ligands. The following m/z data were obtained: (5-dppn) = 275.239, (6-dppn) = 289.132, (7-dppn) = 303.010, (8-dppn) = 317.050, and (12-dppn) = 373.005.

2.2. Sample preparation for MS

Matrix-assisted laser desorption ionization (MALDI); all matrices were acquired from Sigma or Aldrich and used without further purification. Several matrices were tested as vehicles for the desorption and ionization of the diastereomeric tetrols. α -Cyano-4-hydroxycinnamic acid (CHCA) was among the matrices tested. Matrix solutions were prepared by dissolving the desired matrix (10 mg/ml) in a solution of THF. Samples were then prepared by combining 5 μl of ~ 180 pmol/ μl *n*-dppn solution in THF with 5 μl of matrix solution. Next the resulting solution was deposited on the sample probe and allowed to dry under ambient conditions prior to insertion into the mass spectrometer.

2.3. Physical measurements

All ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on a Varian VXR 400 spectrometer using CDCl_3 . Chemical shifts for ^1H and ^{13}C are relative to $(\text{CH}_3)_4\text{Si}$. Measurements were performed at ambient probe temperature using 5 mm o.d. sample tubes. Molecular weight spectra were acquired using a modified Wiley-McLaren design "time-of-flight mass spectrometry" (TOFMS) (model D850, R.M. Jordan, Co., Grass Valley, CA) in the linear mode. A nitrogen laser (337 nm, 5 mW peak laser power, 3 ns pulse width, and a ~ 400 μm^2 spot size) was used to induce desorption (model VSL-337ND, Laser Science, Newton, MA).

3. Results and discussion

The tetranitrogenated dipyridylpyridazine derivatives, namely 5-dppn, 6-dppn, 7-dppn, 8-dppn, and 12-dppn ligands were all prepared in ~ 60 – 92% yield according to the procedure described by Atfah [8]. The ^1H -NMR spectra of some of the *n*-dppn ligands have been recorded earlier using a Bruker WP 80

SY spectrometer [8]. However, no peak assignments and no comments on the exact conformation of these ligands have been made. Recently, we have reported ¹H and ¹³C-NMR of some of *n*-dppn ligands and their complexes with rhodium(III) in DMSO-*d*₆ [9]. In the present study, the ¹H and ¹³C-NMR spectra for some of the isolated ligands were recorded at 400 and 100 MHz, respectively in CDCl₃. The ¹H and ¹³C-NMR results are presented in Tables 1 and 2, respectively.

The numbering scheme of the *n*-dppn ligand protons is given in Fig. 1. The ¹H-NMR spectra for *n*-dppn (*n* = 5, 6, 7, 8, and 12) exhibit four different types of protons for the pyridine hydrogens, as expected for the symmetrical *cis-cis* conformation [9] at least in solution (Fig. 2a). This result may be explained by the presence of cyclic aliphatic carbon ring attached on position 4 and 5 of the pyridazine ring (Fig. 1) which may slow the rotation of the pyridine rings. The (H_{6'}, H_{6''}) protons are expected to be mostly deshielded since they are adjacent to nitrogen atom. The chemical shifts of (H_{6'}, H_{6''}) protons are shown in the range of 8.70–8.80 ppm as a doublet of doublet (*J* = 1.2, 4.8 Hz) through couplings with (H_{4'} or H_{4''}) and (H_{5'} or H_{5''}), respectively. The frequencies for H_{5'} and H_{5''} protons appear in the range 7.36–7.64 ppm as a doublet of doublet of doublet (*J* = 1.2, 4.8, 7.6 Hz) through couplings with (H_{3'} or H_{3''}), (H_{6'} or H_{6''}), and (H_{4'} or H_{4''}), respectively. The two protons doublet of

Table 1
¹H NMR spectral assignments of 3,6-bis(2'-pyridyl)pyridazine derivatives (*n*-dppn)^a

Compound	NMR band shift: δ, ppm (<i>J</i> , Hz)			
	H _{6',6''}	H _{5',5''}	H _{4',4''}	H _{3',3''}
5-dppn ^b	8.74 (dd, <i>J</i> = 1.2, 4.8)	7.36 (ddd, <i>J</i> = 1.2, 4.8, 7.6)	7.88 (dt, <i>J</i> = 1.2, 7.6)	8.60 (dd, <i>J</i> = 1.2, 7.6)
6-dppn ^c	8.71 (dd, <i>J</i> = 1.2, 4.8)	7.37 (ddd, <i>J</i> = 1.2, 4.8, 7.6)	7.89 (dt, <i>J</i> = 1.2, 7.6)	7.94 (dd, <i>J</i> = 1.2, 7.6)
7-dppn ^d	8.73 (dd, <i>J</i> = 1.2, 4.8)	7.38 (ddd, <i>J</i> = 1.2, 4.8, 7.6)	7.88 (dt, <i>J</i> = 1.2, 7.6)	7.94 (dd, <i>J</i> = 1.2, 7.6)
8-dppn ^e	8.80 (dd, <i>J</i> = 1.2, 4.8)	7.64 (ddd, <i>J</i> = 1.2, 4.8, 7.6)	8.15 (dt, <i>J</i> = 1.2, 7.6)	8.46 (dd, <i>J</i> = 1.2, 7.6)
12-dppn ^f	8.70 (dd, <i>J</i> = 1.2, 4.8)	7.39 (ddd, <i>J</i> = 1.2, 4.8, 7.6)	7.87 (dt, <i>J</i> = 1.2, 7.6)	8.04 (dd, <i>J</i> = 1.2, 7.6)

^a¹H NMR were obtained in CDCl₃ with TMS as internal standard, at 400 MHz. d, doublet; dd, doublet of doublet; dq, doublet of quartet; dt, doublet of triplet; br, broad; s, singlet; t, triplet; m, multiplet.

^bAliphatic protons: 2.16 (pentet, 2H; *J* = 7.8), 3.54 (t, 4H; *J* = 7.7).

^cAliphatic protons: 1.80 (br.s, 4H), 3.02 (br.s, 4H).

^dAliphatic protons: 1.75 (br.s, 4H), 1.90 (br.d, 2H; *J* = 3.2); 3.06 (t, 4H; *J* = 8.1).

^eAliphatic protons: 1.51 (br.s, 2H), 1.58 (br.s, 2H), 2.04 (m, 4H), 3.17 (br.s, 2H), 3.40 (br.s, 2H).

^fAliphatic protons: 1.18 (m, 6H), 1.28 (br.s, 6H), 1.63 (t, 4H; *J* = 6.4), 2.47 (t, 4H; *J* = 6.4).

Table 2
¹³C NMR spectral assignments of 3,6-bis(2'-pyridyl)pyridazine derivatives (*n*-dppn)^a

Compound	NMR band shift: δ, ppm						
	C ₃ ,C ₆	C _{2',2''}	C _{6',6''}	C ₄ ,C ₅	C _{5',5''}	C _{3',3''}	C _{4',4''}
5-dppn ^b	156.1	155.1	148.8	145.7	136.6	123.6	123.3
6-dppn ^c	158.4	156.7	148.4	137.5	136.8	125.0	123.4
7-dppn ^d	158.4	157.0	148.7	143.0	136.8	125.1	123.1
8-dppn ^e	158.8	155.4	150.8	143.1	137.9	126.5	125.2
12-dppn ^f	158.0	156.2	148.3	140.4	136.6	124.9	123.8

^a¹³C NMR were obtained in CDCl₃ with TMS as internal standard, at 100 MHz.

^bAliphatic carbons: 33.4, 24.2.

^cAliphatic carbons: 26.7, 21.7.

^dAliphatic carbons: 31.8, 29.7, 26.2.

^eAliphatic carbons: 30.7, 26.5, 25.8.

^fAliphatic carbons: 24.1, 24.0, 23.7, 21.9.

triplet ($J = 1.2, 7.6$ Hz) at 7.87–8.15 ppm are assigned to $\text{H}_{4'}$ and $\text{H}_{4''}$ through couplings with ($\text{H}_{6'}$ or $\text{H}_{6''}$) and $\{(\text{H}_{3'}$ or $\text{H}_{3''})$, and ($\text{H}_{5'}$ or $\text{H}_{5''})\}$, respectively. The resonance signals at 7.94–8.60 ppm as doublet of doublet ($J = 1.2, 7.6$ Hz) are assigned to ($\text{H}_{3'}$, $\text{H}_{3''}$) protons through couplings with ($\text{H}_{5'}$ and $\text{H}_{4'}$) or ($\text{H}_{5''}$ and $\text{H}_{4''}$), respectively. The spectra also exhibit peaks characteristic of aliphatic protons [10] in the range of 1.51–3.54 ppm range (Table 1).

Fig. 2. Conformation of n -dppn ligands.

The ^{13}C NMR spectra for n -dppn ($n = 5, 6, 7, 8$, and 12) are presented in Table 2. The spectra show seven different peaks for seven different carbons of the heterocyclic pyridine and pyridazine rings as expected for the symmetrical *cis-cis* conformation [9] at least in solution (Fig. 2a). The quaternary carbons namely (C_3 , C_6) and ($\text{C}_{2'}$, $\text{C}_{2''}$) are the most deshielding carbons and their resonance appears in the range of 158.8–155.1 ppm, respectively. While, the resonance signals at 137.5–145.7 ppm are assigned to quaternary carbons (C_4 and C_5) in the pyridazine ring. The chemical shift for the other pyridine carbons namely ($\text{C}_{5'}$, $\text{C}_{5''}$, $\text{C}_{3'}$, $\text{C}_{3''}$, $\text{C}_{4'}$, and $\text{C}_{4''}$) are resonate in the range of 123.1–137.9 ppm [10].

All MALDI and TOFMS spectra of the n -dppn ($n = 5, 6, 7, 8$, and 12) were acquired with α -cyano-4-hydroxycinnamic acid (CHCA) matrix. All spectra of n -dppn ligands gave a protonated molecular ion introduced into the mass spectrometer. Representative spectrum with the CHCA matrix and 5-dppn ligand in the presence of potassium and sodium as internal standards are presented in Fig. 3.

Fig. 3. Positive ion MALDI-TOFMS spectrum of 5-dppn acquired with 180 pmol introduced into TOFMS in the CHCA matrix.

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