

NMR Study of New Ligands as Products of Condensation of 2-Pyridinecarboxaldehyde-*N*-Oxide with Polyamines

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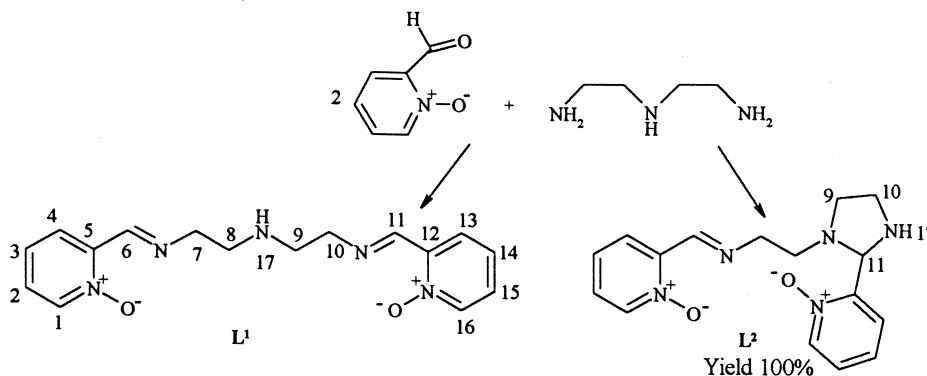
Abstract—New ligands formed as products of the condensation of 2-pyridinecarboxaldehyde-*N*-oxide with polyamines were prepared and characterised by elemental analysis, ¹³C NMR spectroscopy and infrared spectroscopy. Schiff base↔saturated heterocyclic ring isomerization was found to be quite common in this system; the five- and/or six-membered saturated heterocyclic rings containing two nitrogen atoms are more stable. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Carbon atoms of Schiff base moieties are partially positive charged and nucleophilic agents can attack them. An intramolecular nucleophilic attack is possible if the Schiff bases are prepared by the condensation of some aromatic carboxaldehydes with certain polyamines, or amines containing another nucleophilic group, e.g. –SH. The intramolecular nucleophilic attacks in such cases lead to the formation of isomers containing saturated heterocyclic rings. This isomerization is quite common for Schiff bases prepared from 2-pyridinecarboxaldehyde,^{1,2} but not for Schiff bases containing salicylaldehyde moiety.

Our interest in metal complexes with Schiff bases, containing oxygen and nitrogen donor atoms, had led us to synthesise new Schiff base ligands based on the condensation of 2-pyridinecarboxaldehyde-*N*-oxide with polyamines (diethylenetriamine, triethylenetetramine, dipropylenetriamine). According to the literature data^{3–7} the following products can be expected for syntheses **I**, **II** and **III** (see Schemes 1–3).

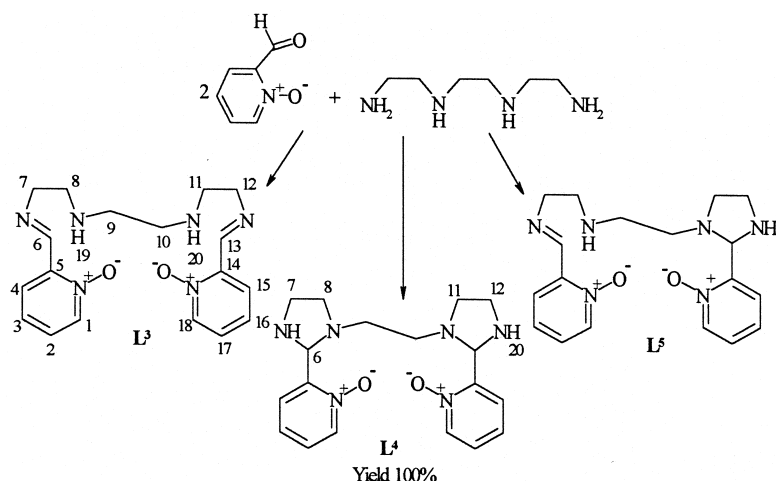
NMR is the most powerful technique to identify the products and to differentiate between the possible isomeric products. Infrared spectra for the above listed products cannot be used for a clear identification of either cyclic secondary amines or aliphatic secondary amines since the



Scheme 1. Possible products of synthesis **I**.

Keywords: imidazolidines; Schiff bases; 2-pyridinecarboxaldehyde-*N*-oxide; polyamines; ¹³C NMR.

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Scheme 2. Possible products of synthesis II.

valence N–H vibrations are similar. They can, however, identify the –C=N– moiety.

Results and Discussion

NMR spectra

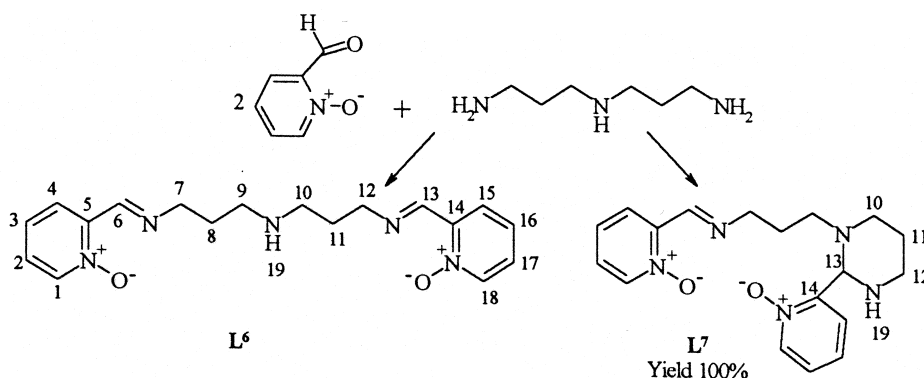
The ^{13}C NMR spectra of ligands L^1 – L^7 were simulated with the products of ACD Labs (ACD/CNMR Spectrum Generator 3.5 and ACD/CNMR Predictor 3.5). Calculated values and measured chemical shifts of ligands L^2 , L^4 and L^7 in ^{13}C NMR spectra are summarised in Table 1. As seen from the table, the simulated and measured values are in very good agreement.

The most significant group for the characterisation of obtained products is the carbon atom directly bonded to the pyridine *N*-oxide fragment in the 2-position. In the case of five- or six-membered saturated rings the above mentioned carbon atom is in the sp^3 hybridisation state which, together with its position between two nitrogen atoms, results in the chemical shift of about 70–90 ppm. The analogous Schiff base carbon atom is of the sp^2 type. For this type of carbon atoms bonded to the nitrogen atoms $\delta \approx 150$ –160 ppm is expected. Chemical shifts of carbon atoms of pyridine-*N*-oxide fragments are expected in the

range of 120–150 ppm and chemical shifts of the carbon atoms of ethylene and propylene bridges are expected in the region for the corresponding sp^3 carbon atoms with respect to their surroundings.

Two products are possible in the case of synthesis I (Scheme 1). The Schiff base product is symmetric, thus a simple spectrum with eight peaks can be expected. The experimental spectrum showed the presence of 16 different values of chemical shift. This number of peaks and their position corresponds with the calculated values for ligand L^2 . It is clear that the carbon atoms of both pyridine-*N*-oxide moieties are not equivalent.

For synthesis II (Scheme 2) three products are possible. For symmetric Schiff base and symmetric imidazolidine ligand relatively simple spectra containing nine peaks can be expected. It is clear that the ligand L^5 is not symmetric and 18 peaks should appear in its spectrum. Experiment showed the presence of nine values of chemical shifts. In order to distinguish between ligands L^3 and L^4 the chemical shift of the group 6 (13) carbons are the most significant. The value of 76.2 ppm with respect to the surroundings of the carbon atom clearly indicates the sp^3 hybridisation of the imidazolidine ring carbon atom. The number of peaks and their position corresponds to the calculated values for the ligand L^4 .



Scheme 3. Possible products of synthesis III.

Table 1. Calculated and measured chemical shifts for ligands **L**¹–**L**⁷

Group	Predicted/ppm (experimental/ppm)						
	L ¹	L ²	L ³	L ⁴	L ⁵	L ⁶	L ⁷
1	138.3±10.2	138.3±10.2 (139.7)	138.3±10.3	136.1±9.5 (139.8)	138.3±10.2	137.9±9.7	137.9±9.7 (139.9)
2	126.1±3.6	126.0±3.6 (126.5)	126.0±3.6	122.4±– (124.3)	126.0±3.6	126.0±3.6	126.0±3.6 (125.5)
3	133.6±1.8	133.6±1.8 (127.1)	133.6±1.8	127.6±6.3 (126.1)	133.6±1.8	133.2±2.0	133.2±2.0 (126.8)
4	121.2±4.0	121.2±4.0 (124.5)	121.2±4.0	125.2±3.9 (124.6)	121.2±4.0	121.9±4.7	121.9±4.7 (124.3)
5	147.3±7.7	147.3±7.7 (145.3)	147.3±7.7	144.4±12.5 (152.5)	145.2±7.2	147.2±7.7	147.2±7.7 (145.4)
6	156.7±14.7	156.7±14.7 (154.6)	156.7±14.7	84.2±0.8 (76.2)	147.6±9.8	163.8±7.6	163.8±7.6 (153.6)
7	60.1±7.5	63.6±9.4 (61.3)	60.1±7.5	40.0±4.0 (44.4)	53.7±5.1	51.7±13.4	52.2±13.9 (51.5)
8	60.1±7.5	51.3±2.6 (55.1)	45.4±1.3	47.8±5.5 (44.5)	45.4±1.3	24.7±0.5	26.5±0.9 (28.3)
9	60.1±7.5	47.8±5.5 (53.6)	48.1±0.9	52.2±5.4 (54.7)	52.1±5.5	47.1±6.3	51.7±1.5 (51.8)
10	60.1±7.5	40.0±4.0 (44.3)	48.1±0.9	52.2±5.4 (54.7)	51.7±5.0	47.1±6.3	52.6±4.0 (63.9)
11	156.7±14.7	84.2±0.8 (75.9)	45.4±1.3	47.8±5.5 (44.5)	47.8±5.5	24.7±0.5	22.9±4.2 (26.9)
12	147.3±7.7	149.6±3.1 (152.4)	53.7±5.1	40.0±4.0 (44.4)	40.0±4.0	51.7±13.4	48.0±1.4 (59.3)
13	121.2±4.0	125.2±3.9 (124.9)	147.6±9.8	84.2±0.8 (76.2)	84.2±0.8	163.8±7.6	83.8±0.3 (73.2)
14	133.6±1.8	127.6±6.3 (127.1)	145.2±7.2	144.4±12.5 (152.5)	144.4±12.5	147.2±7.7	146.1±12.8 (151.7)
15	126.1±3.6	122.4±– (124.8)	121.2±4.0	125.2±3.9 (124.6)	121.2±3.9	121.9±4.7	125.5±3.9 (125.1)
16	138.3±10.2	136.1±9.5 (139.6)	133.6±1.8	127.6±6.3 (126.1)	127.6±6.3	133.2±2.0	127.2±5.9 (126)
17		–	126.0±3.6	122.4±– (124.3)	122.4±–	126.0±3.6	122.4±– (124.5)
18		–	138.3±10.2	136.1±9.5 (139.8)	136.1±9.5	137.0±3.6	135.6±9.4 (139.7)

There is an analogy of the last synthesis (Scheme 3) to the first one. Two products are possible. It is known that substituted six-membered saturated rings with two heteroatoms are less stable and they are observed only rarely. Experiments showed the presence of 18 different values of chemical shifts. This number of peaks and their position corresponds to the calculated values for the ligand **L**⁷. Both pyridine-*N*-oxide groups are inequivalent.

IR spectra

With the help of valence $\nu(\text{N-H})$ and $\nu(\text{C=N})$ vibrations one can also identify, with some restrictions, the products of the condensation reactions. Valence vibrations of cyclic secondary amines are in the range 3380–3205 cm^{-1} .⁹ The range of valence vibrations of secondary aliphatic amines is rather narrow, at 3330 cm^{-1} . Deformation vibrations of N–H groups are in the range 1608–1530 cm^{-1} . Valence

Table 2. Selected IR data for ligands **L**², **L**⁴ and **L**⁷ (s—strong, w—weak; values in cm^{-1})

Ligand	$\nu_{\nu(\text{N-H})}$	$\nu_{\delta(\text{N-H})}$	$\nu_{\nu(\text{N-O})}$	$\nu_{\delta(\text{N-O})}$	$\nu_{\nu(\text{C=N})}$
L ²	3328s	1553w	1233–1241s 1215–1206s	846s	1630s
L ⁴	3231s	1564w	1239–1234s	839s	–
L ⁷	3260s	1566w	1234s	843s, 855s	1634s

vibrations of C=N groups of Schiff bases are in the range 1695–1585 cm^{-1} .¹⁰ Valence N–O vibrations of pyridine-*N*-oxides can be observed in the range 1300–1200 cm^{-1} and deformation vibrations of this group are around 840 cm^{-1} . Some literature suggests that three or four weak vibrations of the N–O group of pyridine-*N*-oxides can be observed in the range 1630–1450 cm^{-1} . Selected infrared data for ligands **L**², **L**⁴ and **L**⁷ are collected in Table 2.

The infrared spectra without supporting information cannot clearly identify the product of the synthesis **I**. It is not clear if the valence vibration $\nu(\text{N-H})$ belongs to a secondary cyclic or aliphatic amine. Both possible products contain the Schiff base C=N group thus the presence of the valence vibration $\nu(\text{C=N})$ of Schiff base should appear in both cases. The product of synthesis **II** exhibits only one valence $\nu(\text{N-H})$ vibration and its position at 3232 cm^{-1} led us to conclude that a symmetric molecule is formed. Furthermore, the absence of the C=N vibration of a Schiff base proves that the product of this condensation is the ligand **L**⁴. In the case of the third condensation it is clear that the presence of valence $\nu(\text{N-H})$ vibration at 3260 cm^{-1} and valence $\nu(\text{C=N})$ vibration confirm ligand **L**⁷ as a product.

As a result of our experiments we can conclude that the condensation of 2-pyridinecarboxaldehyde-*N*-oxide with polyamines (diethylenetriamine, triethylenetetramine,

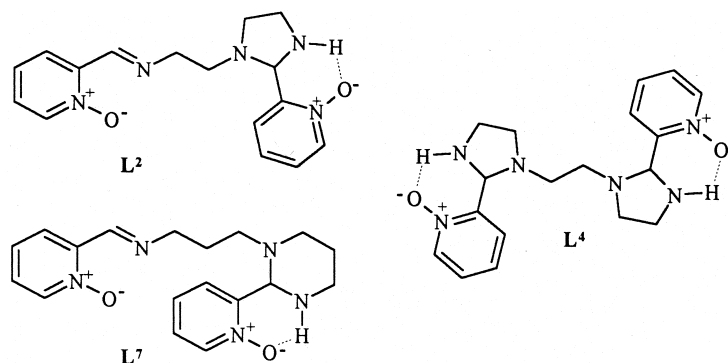


Figure 1. Possible intramolecular hydrogen bonds in obtained ligands.

dipropylenetriamine) instead of Schiff bases predominantly gives the corresponding more stable isomers containing saturated heterocyclic rings. To explain this behaviour in comparison with the condensation of 2-pyridinecarboxaldehyde or salicylaldehyde with polyamines it is necessary to discuss two items: sequence of chemical reactions and different intramolecular hydrogen bonding.

Sequence of chemical reactions. If the first step of the condensation is the formation of the Schiff base then the product is similar in properties to the incoming aldehyde. The reality of this statement can be indicated by values of chemical shifts of C(6) carbons in ^{13}C NMR spectra of three aldehydes and the corresponding Schiff bases. For the 2-pyridinecarboxaldehyde-*N*-oxide the chemical shift of C(6) is 186.4 ppm and for ligands **L**² and **L**⁷ they are 154.6 and 153.6 ppm, respectively. For salicylaldehyde it is 196.2 ppm and for the Schiff base derived from the salicylaldehyde and ethylenediamine the chemical shift is 166.0 ppm. The chemical shift of C(6) for 2-pyridinecarboxaldehyde is 193.0 ppm and for the Schiff base derived from the 2-pyridinecarboxaldehyde and ethylenediamine is 165.5 ppm (theoretical). As we can see, differences among chemical shifts of C(6) of aldehydes and also among Schiff bases are not significant. The result is the formation of the imidazolidine rings. This was observed in our experiments and also reported for the condensation of the 4-nitrobenzaldehyde with diethylenetriamine.¹¹

It is necessary to note that in literature described isomerizations of Schiff bases to imidazolidines, isomerization concerns only complexes of macrocyclic ligands prepared by template reactions.^{12–17} We are aware of only one reference of pure ligand as a product of condensation of salicylaldehyde and diethylenetriamine, but this compound was characterised only by elemental analysis.¹⁸ This cannot distinguish between the Schiff base and the imidazolidine isomer. One more pure macrocyclic Schiff base is discussed by Menif.¹⁹ It was confirmed by NMR that in solution the Schiff base is unstable and the imidazolidine isomer is stabilised.

Hydrogen bonding. We need to consider two kinds of hydrogen bonds in the condensation products. The first kind is between the hydrogen atom of the OH group of salicylaldehyde and the nitrogen atom of C=N group of the corresponding Schiff base forming six-membered ring.

This imine group is stabilised by the hydrogen bond and thus restricted to further intramolecular nucleophilic addition reaction. The second type of intramolecular hydrogen bond is between the oxygen atom of the pyridine-*N*-oxide group and the hydrogen atom of NH group of imidazolidine ring as shown in Fig. 1.

Probably this hydrogen bond, the instability of Schiff bases and the ability of the C=N group to undergo intramolecular nucleophilic addition reaction are the main reasons for the formation of obtained ligands **L**², **L**⁴ and **L**⁷.

One could expect the formation of **1** (Fig. 2) as a product of the condensation of salicylaldehyde with triethylenetetramine, owing to the stabilisation of the C=N bond by the hydrogen bond. Actually, **2** is also formed in the reaction, ratio aldehyde:amine 2:1.²⁰ Two secondary NH groups can react with the aldehyde by forming the imidazolidine ring, according to Chapus.²¹ The imidazolidine ring decomposes after complexation and one salicylaldehyde splits off. On the other hand one could expect the formation of **3** instead of **L**⁴ as a product of the condensation of

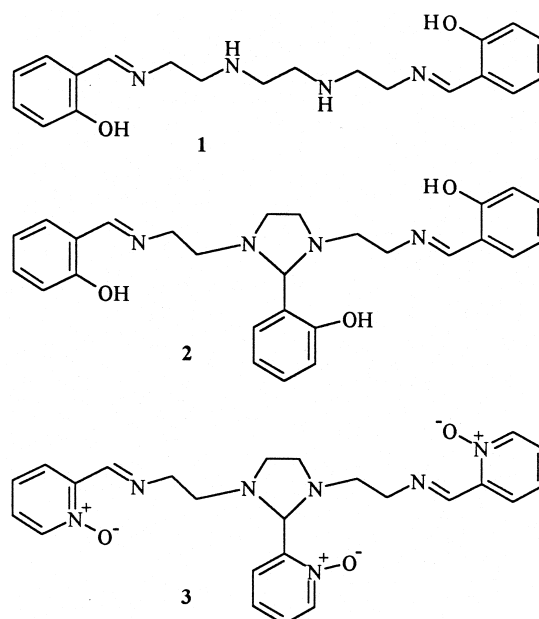


Figure 2. Possible products of condensation of aromatic aldehyde and triethylenetetramine.

2-pyridinecarboxaldehyde-*N*-oxide with triethylenetetramine. Probably, after the formation of Schiff base, further intramolecular nucleophilic addition reaction is preferred instead of an intermolecular attack.

We should point out that we are not aware of any proof that the product of the condensation of the salicylaldehyde and the diethylenetriamine is both-side Schiff base instead of the one-side imidazolidine isomer.

Breaking of the hydrogen bonds in the ligands **L**², **L**⁴ and **L**⁷ by complexation to some metal centres can give complexes containing Schiff base ligands, as has been found in the case of [Cu(**L**⁵)(ClO₄)](ClO₄), [Fe(**L**³)](ClO₄)₂·(MeOH)_{0.5}²² and [Zn(**L**³)](ClO₄)₂ complexes (the last one will be presented elsewhere). These isomerizations have been found to be dependent on the nature of solvent, central atom and character of the counter-anion.

Experimental

NMR measurements

¹H- and ¹³C NMR spectra of ligands were measured using Bruker AC 250 FT spectrometer at 250 MHz in CDCl₃ solution with 1% of TMS as an internal standard.

IR measurements

Infrared spectra of ligands were measured on PU 9800 FTIR spectrometer in Nujol suspension (the range 4000–200 cm⁻¹).

Preparation of ligands

L², **L**⁴, **L**⁷. A solution of polyamine (41 mmol of diethylenetriamine for **L**², triethylenetetramine for **L**⁴, dipropyl-enetriamine for **L**⁷) in methanol (10 cm³) was added to a hot filtered solution of 2-pyridinecarboxaldehyde-*N*-oxide (9.97 g, 81 mmol, prepared according Jerchel⁸) in methanol (75 cm³) with stirring. The mixture was stirred and heated on the water bath for 15 min then cooled to room temperature and left to spontaneously evaporate to the volume of 35 cm³. Diethylether (150 cm³) was added to the reaction mixture dropwise until a white solid began to precipitate. Then additional diethylether (400 cm³) was added with stirring. After 20 min the white product was filtered off (only for ligands **L**² and **L**⁴), washed with ether and air-dried. **L**² (9.0 g, 85%), mp 147–148°C (Found: C, 60.9; H, 6.3; N, 22.2. Calcd for C₁₆H₁₉N₅O₂: C, 61.3; H, 6.1; N, 22.4%); ν_{\max} (Nujol) 3328, 1630, 1480, 1433, 1394, 1350, 1240, 1232, 1215, 1206, 1177, 761 cm⁻¹; δ_C (249.9 MHz, CDCl₃) 154.6, 152.4, 145.3, 139.7, 139.6, 127.1, 126.5, 124.9, 124.8, 124.5, 75.9, 61.3, 55.1, 53.6, 44.3; *m/z* (EI) 280 (11), 162 (29), 148 (27), 146 (12), 133 (31), 131 (17), 119 (52), 107 (53), 105 (22), 92 (98), 78 (100), 71 (12), 56 (42), 44 (64), 28 (61%); **L**⁴ (7.8 g, 53%), mp 166–167°C (Found: C, 60.1; H, 6.6; N, 23.2. Calcd for C₁₈H₂₄N₆O₂: C, 60.6; H, 6.8; N, 23.6%); ν_{\max} (Nujol) 3231, 3114, 1435, 1378, 1366, 1298, 1235, 1071, 839, 783 cm⁻¹; δ_C (249.9 MHz, CDCl₃) 152.5, 139.8, 126.1, 124.6, 124.3, 76.2, 54.7, 44.5, 44.4; *m/z* (EI) 234 (1), 215 (2), 191 (1),

162 (5), 148 (6), 138 (5), 133 (8), 127 (8), 119 (9), 116 (8), 107 (62), 99 (54), 78 (74), 73 (52), 56 (78), 44 (100), 28 (80%). **L**⁷: The product was obtained in an oil form from which a solid precipitated below 4°C after 2 months. (10.1 g, 72%), mp 4°C (Found: C, 52.2; H, 7.4; N, 16.7. Calcd for C₁₈H₃₁N₅O₆: C, 52.3; H, 7.6; N, 17.0%); ν_{\max} (Nujol) 3260, 1634, 1566, 1234, 843, 855 cm⁻¹; δ_C (249.9 MHz, CDCl₃) 153.6, 151.7, 145.5, 139.9, 139.7, 126.8, 126.0, 125.5, 125.1, 124.5, 124.3, 73.2, 63.9, 59.3, 51.8, 51.5, 28.3, 26.9; *m/z* (EI) 202 (15), 162 (91), 147 (11), 133 (10), 119 (31), 107 (57), 105 (42), 92 (72), 78 (100), 70 (11), 58 (20), 56 (14), 51 (44), 44 (11), 28 (35%).

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