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^{1}H AND ^{13}C NMR ANALYSIS OF A 1,2-DIARYL-3-METHYL-4,5-DIHYDRO-1*H*-IMIDAZOLIUM SALTS SERIES

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Abstract – A study of the ^{1}H and ^{13}C NMR spectra of a 1,2-diaryl-3-methyl-4,5-dihydro-1*H*-imidazolium salt series (**1**) and a comparison with their 4,5-dihydro-1*H*-imidazole precursors (**2**) are presented. Signal assignments follow the analysis of two dimensional HMQC, HMBC, HETCOR, COSY and NOESY spectra. The spectral properties of compounds (**1**) reflect electronic features of the imidazole ring and correlate directly with the contribution of different mesomeric structures to the stabilization of dihydroimidazolium ions. We also report examples of configurationally stable non-biaryl atropisomers, compounds (**1k**) and (**2k**), in which the Ar_1-N bond is the chiral axis. Thus, the stereochemical features of these compounds are readily evaluated on the basis of their spectroscopic data.

INTRODUCTION

N,*N*´-Disubstituted 4,5-dihydro-1*H*-imidazolium salts (imidazolinium salts) are cyclic amidinium compounds that have been used as suitable models of N^5,N^{10}-methenyltetrahydrofolic acid, a coenzyme that participates in the transfer of a formyl unit in several biochemical reactions.[1-3] In order to mimic the biological process by chemically reproducing the transfer of the C2 unit, several groups have studied the reaction of different imidazolinium salts with nucleophilic agents.[4-6] As a result, 4,5-dihydro-1*H*-imidazolium salts have became valuable precursors for the synthesis of cyclic and acyclic compounds containing an ethylenediamine unit.[1,5-9] 4,5-Dihydro-1*H*-imidazolium salts have been also investigated as

surfactants,[10] due to their potential for chiral molecular recognition[11] and as catalysts for several chemical reactions.[12,13] Besides, imidazolinium salts are chemical precursors of imidazolidin- 2-ylidenes, a type of nitrogen heterocycle carbenes (NHC) that, either alone or as metal complexes, are efficient catalysts during important chemical transformations.[14,15]

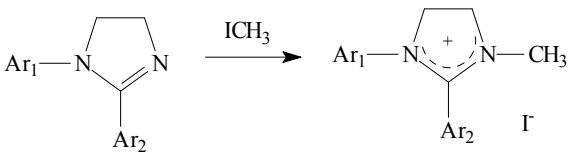
Alkylation of substituted 4,5-dihydro-1*H*-imidazoles (**2**) (2-imidazolines) readily produces the corresponding 4,5-dihydro-1*H*-imidazolium salts. In order to characterize electronic perturbations that result from alkylation of the amidine system, we report here the ^{1}H and ^{13}C NMR spectra of a series of *N,N´*-disubstituted salts (**1**) and compare them with those of their corresponding dihydroimidazole precursors (**2**), either in the absence or the presence of trifluoroacetic acid. The spectral properties reflect the electronic features of the imidazole ring and correlate directly with the contribution of different mesomeric structures to the stability of imidazolinium ions. Furthermore, the analysis of **1j** and **1k** spectra shows that these compounds have particular stereochemical properties.

RESULTS AND DISCUSSION

Reaction of methyl iodide with the corresponding 4,5-dihydro-1*H*-imidazoles (**2**) yielded the 4,5-dihydro-1*H*-imidazolium salts (**1**) studied here (Table 1). Reaction conditions followed established procedures.[8,9]

Tables 2 and 3 list the ^{1}H and ^{13}C NMR parameters of compound (**1**) series. Analysis of HMQC and HMBC spectra of **1d** (as series referent), HETCOR and HMBC spectra of **1j** and HMQC, HMBC, COSY and NOESY spectra of **1k** allowed the unequivocal assignment of proton and carbon signals for the complete series.

Table 1: 4,5-Dihydro-1*H*-imidazolium salts (**1**) and 4,5-dihydro-1*H*-imidazoles (**2**)



2 **1**

Compounds 1,2	Ar_1	Ar_2
a	C_6H_5	C_6H_5
b	4-$CH_3C_6H_4$	C_6H_5
c	4-ClC_6H_4	C_6H_5

d	4-$CH_3OC_6H_4$	C_6H_5
e	3,4-$(CH_3O)_2C_6H_3$	C_6H_5
f	4-$NO_2C_6H_4$	C_6H_5
g	C_6H_5	4-$CH_3OC_6H_4$
h	4-$NO_2C_6H_4$	4-$NO_2C_6H_4$
i	β-$C_{10}H_7$	C_6H_5
j	2-$NO_2C_6H_4$	4-$NO_2C_6H_4$
k	α-$C_{10}H_7$	C_6H_5

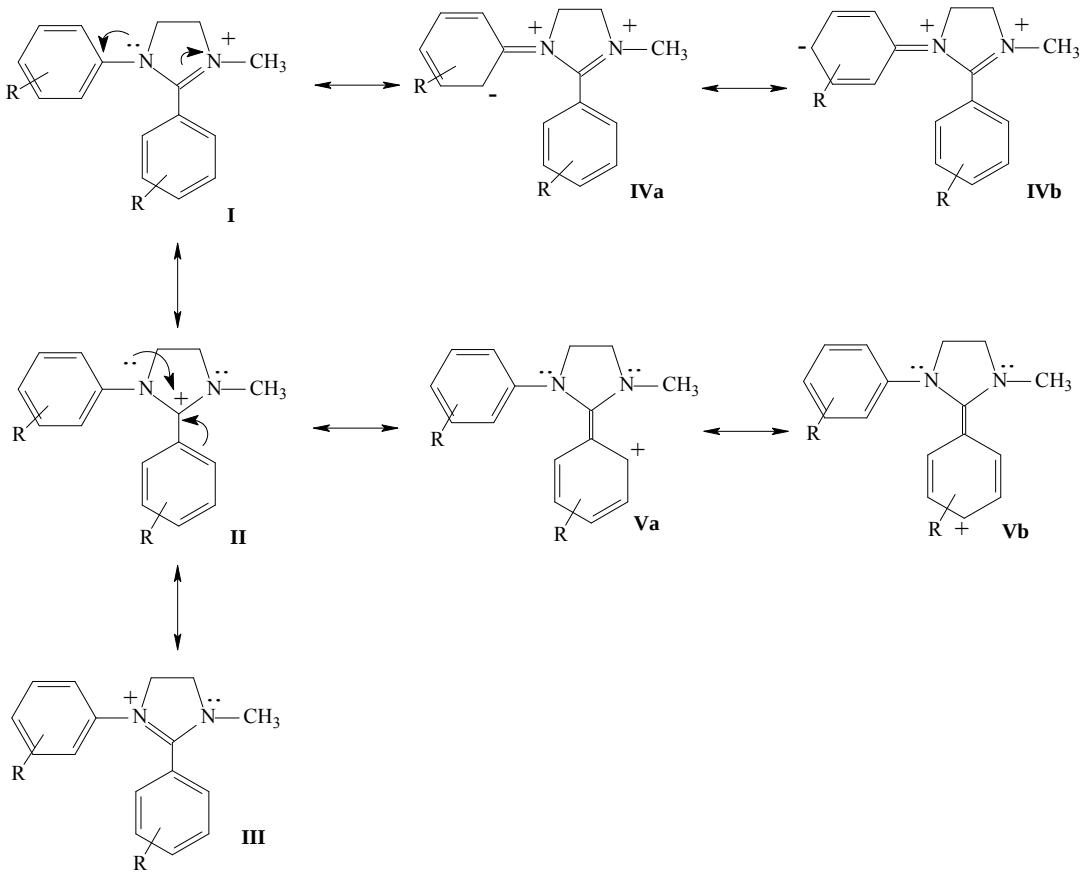
As we reported previously,[16] the ^1H and ^{13}C NMR characteristics of 1,2-diaryl-dihydroimidazoles (**2**) were consistent with the presence of two conjugated systems (Ar_1-N and Ar_2-C=N), competing with the delocalization characteristic of the amidine system. This fact determined shielding of the 1-aryl *ortho* and *para* hydrogens and deshielding of the 2-aryl *ortho* hydrogen. The chemical shift of protons in the ethylenediamine moiety coincidentally overlapped in compounds (**2a-d,g,h,i**) yielding a sharp singlet in the spectra. In contrast they appeared as a center-symmetrical multiplet in compounds (**2e,f**) or as two clear triplets in compound (**2j**).

In all compounds studied here, *N*-methylation of dihydroimidazoles (**2a-i**) causes a chemical shift increase for the ethylenediamine hydrogens (H4 and H5) which shift from *ca.* 3.98-4.20 ppm in the dihydroimidazol to 4.20-4.80 ppm in the salt (Table 1). These protons appear as a center-symmetrical signal, characteristic of an AA'BB' system, and it is possible to identify two multiplets in the majority of the compounds. Deshielding of H4 and H5 results from electron deficiency of the heterocyclic ring caused by nitrogen methylation and is in full agreement with the cationic character of amidinium system. Similar deshielding has been observed previously by Pugmire on five- or six-member aromatic heterocycles having one or two nitrogen atoms[17] and by Morishima on saturated azaheterocycles.[18] Polarization effects due to the presence of the positively charged nitrogen in these cations are responsible for the observed deshielding.[17]

Upon formation of the imidazolinium salts, there is an increase of the $^3J_{H\text{-}H}$ coupling constant and a paramagnetic shift for all Ar_1 hydrogen signals, which is more pronounced for H2 hydrogens, positioned *ortho* to N1. Compounds (**1f,h,j**), where Ar_1 contains strong electron withdrawing groups, experience the largest shifts. The shielding of those hydrogens, observed in the imidazolines (**2**), is absent in the salts (**1**), indicating the lost of N1 induced protection at this position (Scheme 1, structures IVa,b) and suggesting a larger contribution of structures I and III that have an amidinium ion with the positive charge delocalized between both nitrogen atoms.

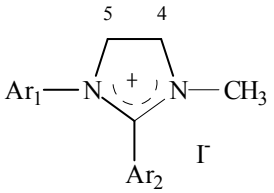
The hydrogen signals of Ar_2 undergo general deshielding that is larger than the one observed for the corresponding base, especially for H2 at the *ortho* position. This property can be related with the positive charge located over C2 of the imidazoline ring and, thus, over H2 and H4 of Ar_2 as seeing in the case of benzyl cations, supporting the contribution of structures Va,b (Scheme 1).

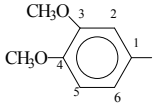
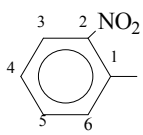
Scheme 1. Mesomeric structures of 1,2-diaryl-3-methyl-4,5-dihydro-1*H*-imidazolium salts (**1**)

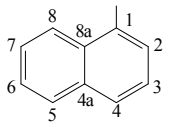


Dissolution of compound (**2c**) in deuterochloroform-trifluoroacetic acid-*d* resolves the ^{1}H NMR signals of the ethylenediamine unit, which now appears as a multiplet, shifted slightly (0.10-0.30 ppm) to the downfield region of the spectrum. These effects are qualitatively similar but of lower magnitude than those observed for the methiodides (**1**), suggesting that protonation causes a smaller cationic character on the amidinium system than *N*-methylation. This observation could be readily explained taking into account that protonation involves a typical acid-base equilibrium that is absent in compounds (**1**) where the methyl group is irreversibly bonded to N3, thus resulting in increased deshielding of those hydrogens located near the basic center.

Table 2: ^{1}H NMR spectra of 1,2-diaryl-3-methyl-4,5-dihydro-1*H*-imidazolium salts (**1a-k**) (δ ppm, *J* Hz)



Comp.	Ar_1	Ar_2	CH_3	CH_2-CH_2	Ar_1	Ar_2
1a	C_6H_5	C_6H_5	3.17 (s)	4.41-4.53 (m) [a]	7.10-7.21 (m, H3 and H4) 7.25-7.40 (m, H2)	7.50 (tt, H4, ^1J= 7.80, ^2J=1.72) 7.69 (dd, H2, ^1J= 8,81, ^2J=1.53) 7.25-7.40 (m, H3)
1b	4-$CH_3C_6H_4$	C_6H_5	3.15 (s)	4.46-4.66 (m) [a]	6.90 (d, H3, *J*= 7.85) 7.17 (d, H2, *J*= 7.85) 2.21 (s, CH_3)	7.37-7.42 (m, H3) 7.45 (m, H4) 7.70 (dd, H2, ^1J=8.21, ^2J=1.14)
1c	4-ClC_6H_4	C_6H_5	3.16 (s)	4.45-4.66 (m) [a]	7.16 (dd, H3, ^1J= 8.70, ^2J=2.32) 7.31 (dd, H2, ^1J= 8.70, ^2J=2.32)	7.30-7.40 (m, H3) 7.50 (m, H4) 7.70 (dd, H2, ^1J= 8.12, ^2J=1.13)
1d	4-$CH_3OC_6H_4$	C_6H_5	3.16 (s)	4.41-4.59 (m) [a]	6.70 (dd, H3, ^1J= 6.96, ^2J=2.12) 7.25 (dd, H2, ^1J= 6.96, ^2J=2.12) 3.76 (s, CH_3O)	7.40 (m, H3) 7.49 (t, H4, *J*= 7.12) 7.70 (dd, H2, ^1J= 6.23, ^2J=1.10)
1e		C_6H_5	3.15 (s)	4.20-4.68 (m) [a]	6.63 (d, H5, *J*= 8.12) 6.80 (dd, H6, ^1J= 8.12, ^2J= 2.53) 7.12 (d, H2, *J*= 2.53) 3.70; 3.76 (s, CH_3O)	7.32-7.49 (m, H3, H4) 7.69 (dd, H2, ^1J= 6.8, ^2J= 1.7)
1f	4-$NO_2C_6H_4$	C_6H_5	3.26 (s)	4.52-4.75 (m) [a]	7.72 (dd, H2, ^1J= 9.02, ^2J=2.24) 8.10 (dd, H3, ^1J= 9.02, ^2J=2.24)	7.43-7.62 (m, H2-H4)
1g	C_6H_5	4-$CH_3OC_6H_4$	3.19 (s)	4.40-4.60 (m) [a]	7.17-7.20 (m, H3, H4) 7.25-7.28 (m, H2)	6.80 (d, H3, *J*= 8.95) 7.54 (d, H2, *J*=8.95) 3.75 (s, CH_3O)
1h	4-$NO_2C_6H_4$	4-$NO_2C_6H_4$	3.25 (s)	4.54-4.79 (m) [a]	7.60 (d, H2, *J*=8.79) 8.15 (d, H3, *J*=8.79)	8.33 (d, H2, *J*=8.82) 8.17 (d, H3, *J*=8.82)
1i	β-$C_{10}H_7$	C_6H_5	3.20 (s)	4.50-4.75 (m) [a]	[b]	[b]
1j		4-$NO_2C_6H_4$	3.21 (s)	4.35 (bs, H4) 4.83	7.55 (td, H4, ^1J=7.85, ^2J=1.25) 7.75 (td, H5, ^1J=7.85, ^2J=1.43) 7.95 (dd H6, ^1J=8.10, ^2J=1.43)	8.29 (dd, H3, ^1J=7.83, ^2J=1.54) 7.60-8.82 (bs, H2)

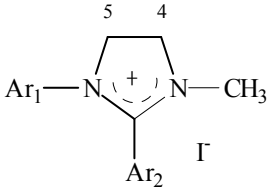
1k		C_6H_5	3.30 (s)	(bs, H5) 4.55-4.60 (m, H4, H5) 4.72-4.80 (m, H5)	8.61 (dd, H3, ^1J=7.9, ^2J=1.52) 7.25 (t, H3, J=7.32) 7.50 (td, H6, ^1J=8.22, ^2J=1.01) 7.65 (t, H7, J= 8.22) 7.75 (d, H4, J= 7.70) 7.80 (d, H5, J=8.22) 7.95 (dd, H2, ^1J=7.32, ^2J=0.85) 8.42 (d, H8, J= 8.22)	7.20 (t, H3, J= 7.55) 7.30 (t, H4, J= 7.24) 7.70 (m, H2)

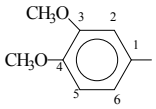
[a] Center-symmetrical signal having two differentiated multiples.
[b] Aromatic protons appear as a non-resolved complex multiplet in the 7.20-7.90 ppm range.

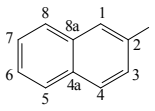
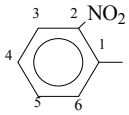
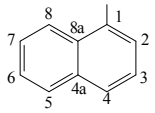
In the ^{13}C NMR spectra, the C2 signal of the imidazolinium ring (**1a-i**) appears between 163.8-166.3 ppm and those of the C4 and C5 do in the 50-52 ppm range (Table 3). The specific assignment of the latter signals follows the analysis of HMQC and HMBC spectra of compound (**1d**), as reference. Its HMQC spectrum correlates the upfield-shifted multiplet at 4.41-4.50 ppm with the 50.8 ppm carbon resonance and the downfield-shifted multiplet at 4.52-4.59 ppm with the 52.8 ppm carbon signal. On the other hand, the HMBC spectrum shows a cross peak between the *N*-methyl protons at 3.16 ppm and the 50.8 carbon signal. Therefore, the upfield-shifted resonance at 50.8 ppm corresponds to the C4 adjacent to the *N*-methyl group while that at 52.8 ppm belongs to C5, adjacent to the *N*-aryl moiety.

The comparison of the ^{13}C NMR spectra of dihydroimidazoles (**2**)[16] and their corresponding salts (**1**) reveals a paramagnetic shift of 3-4 ppm of the C2 signal upon salt formation while, at the same time, the carbon signals of the ethylenediamine unit move in the opposite direction by 2-4 ppm. Shielding of the Cα signal following protonation or quaternization of the heterocyclic nitrogen in five- or six-member rings has been extensively studied by Pugmire et al.[17] The opposing behavior observed for C2 and C4-C5 resonances may correlate with a balance between polarization and bond order effects. Polarization effects prevail in the case of C2, which is bonded to two electron deficient nitrogens, causing the paramagnetic shift seen in the spectrum. On the other hand, C4 and C5 bind to the single heterocyclic nitrogen and the effect of bond order decrease predominates resulting in shielding of these carbons. Low electron density at C2 (Scheme 2, structure II) is in agreement with the high reactivity of the salts towards nucleophilic reagents, which preferentially react at this position yielding imidazolidines or acyclic compounds having an ethylenediamine unit.[1,5-9] On the other hand, the electronic properties of the salts make them behave as weak Lewis acids, explaining recent investigations on their use as catalysts during cycloaddition reactions.[13]

Table 3: ^{13}C NMR spectra of 1,2-diaryl-4,5-dihydro-1*H*-imidazolium salts (**1a-k**) (δ ppm)

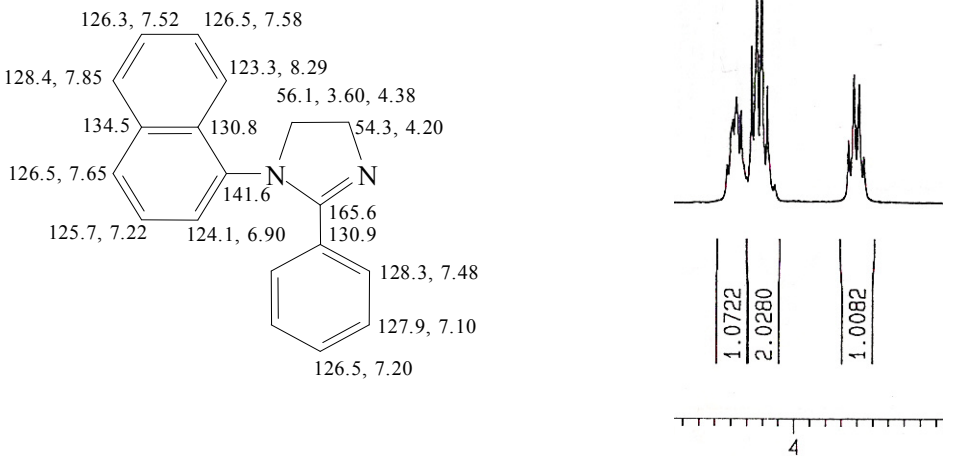


Comp.	Ar_1	Ar_2	CH_3	C2	C4, C5	Ar_1	Ar_2	others
1a	C_6H_5	C_6H_5	34.7	164.2	50.5 (C4) 51.7 (C5)	135.8 (C1); 127.1 (C4); 125.6, 128.2, 128.5, 128.9 (C2, C3, Ar_1 and Ar_2)	131.7 (C4); 121.1 (C1); 125.6, 128.2, 128.5, 128.9 (C2, C3, Ar_1 and Ar_2)	
1b	4-$CH_3C_6H_4$	C_6H_5	35.1	164.9	50.8 (C4) 52.4 (C5)	138.6, 133.5 (C1, C4); 125.6, 128.6, 129.2, 129.7 (C2, C3, Ar_1 and Ar_2)	131.9 (C4); 121.6 (C1); 125.6, 128.6, 129.2, 129.7 (C2, C3, Ar_1 and Ar_2)	20.6 (CH_3)
1c	4-ClC_6H_4	C_6H_5	35.3	165.1	51.2 (C4) 52.4 (C5)	135.0, 134.2 (C1, C4); 127.2, 128.1, 129.3, 129.5 (C2, C3, Ar_1 and Ar_2)	132.5 (C4); 127.2, 128.1, 129.3, 129.5 (C2, C3, Ar_1 and Ar_2); 122.3 (C1)	
1d	4-$CH_3OC_6H_4$	C_6H_5	34.8	164.7	50.8 (C4) 52.3 (C5)	159.8 (C4); 129.6 (C1); 128.4 (C2); 115.4 (C3)	131.7 (C4); 130.0 (C2); 129.5 (C3); 122.4 (C1)	55.8 (CH_3O)
1e		C_6H_5	35.4	165.7	51.2 (C4) 52.9 (C5)	149.0, 149.3 (C3, C4); 129.2 (C1); 119.7 (C6); 110.7, 110.5 (C5, C2)	132.4 (C4); 129.3, 129.1 (C2, C3); 122.0 (C1)	55.8, 56.6 (CH_3O)
1f	4-$NO_2C_6H_4$	C_6H_5	34.7	163.8	50.7, 51.0 (C4, C5)	145.1, 141.2 (C1, C4); 123.5 (C3); 128.5, 128.4, 127.3 (C2, Ar_1; C2, C3, Ar_2)	131.4 (C4); 120.4 (C1); 128.5, 128.4, 127.3 (C2, Ar_1; C2, C3; Ar_2)	
1g	C_6H_5	4-$CH_3OC_6H_4$	35.6	165.1	51.1, 52.2 (C4, C5)	136.9 (C1); 128.3 (C4); 131.7, 129.4, 126.8; (C2, C3, Ar_1; C2, Ar_2)	162.6 (C4); 131.7, 129.4, 126.8; (C2, C3, Ar_1; C2, Ar_2); 114.6 (C3); 113.2 (C1)	55.4 (OCH_3)
1h	4-$NO_2C_6H_4$	4-$NO_2C_6H_4$	36.0	166.3	52.4, 52.5 (C4, C5)	141.0 (C1); 145.1, 147.6 (C4, Ar_1 and Ar_2); 134.0, 133.1, 129.3, 121.2 (C2, C3, Ar_1 and Ar_2)	145.1, 147.6 (C4, Ar_1 and Ar_2); 134.0, 133.1, 129.3, 121.2 (C2, C3, Ar_1 and Ar_2); 120.1 (C1)	

1i		C_6H_5	35.0	164.6	50.9 (C4) 52.2 (C5)	133.4, 132.3, 131.2 (C2, C4a, C8a); 128.9, 127.3, 127.0, 126.5, 126.3 (C4-C8); 124.5, 123.0 (C1, C3)	131.3 (C4); 129.1, 128.5 (C2, C3); 121.4 (C1)	
1j		4-$NO_2C_6H_4$	36.0	164.9	52.4 (C4) 53.1 (C5)	144.8 (C2); 136.1 (C5); 132.7 (C3); 131.7 (C4); 129.2 (C1); 126.0 (C6)	150.1 (C4); 131.0 (C2); 126.9 (C1); 124.4 (C3)	
1k		C_6H_5	35.8	167.1	51.9 (C4) 52.9 (C5)	133.9 (C4a); 132.8 (C1); 130.0 (C4); 129.3 (C8a); 128.6 (C5); 128.1 (C7); 127.5 (C2); 126.8 (C6); 125.6 (C3); 122.1 (C8)	132.4 (C4); 128.9 (C3); 128.8 (C2); 121.8 (C1)	

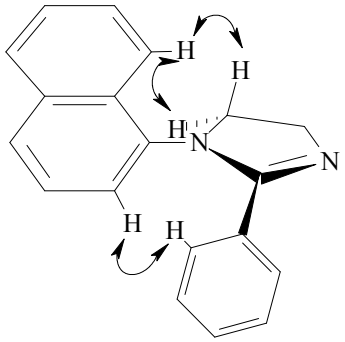
In contrast to the imidazolinium salts analyzed above (**1a-i**) and their corresponding dihydroimidazoles,[16] the four hydrogens of the ethylenediamine moiety of compounds (**1k**) and (**2k**)[19] are magnetically non-equivalent. The spectral pattern for compound (**2k**) is shown in Figure 1. This spectroscopic characteristic indicates that the presence of the α-naphthyl substituent hinders the rotation around the Ar_1-N bond, which now behaves as a stereogenic axis disrupting the magnetic equivalency of the geminal protons. Other examples of configurationally stable non-biaryl atropisomers in heterocycles bearing a naphthyl or an *o*-substituted phenyl group linked to nitrogen have been previously reported.[21]

Figure 1. Pattern and complete assignment of ^1H and ^{13}C NMR spectra of compound (**2k**)



The complete assignment of ^{1}H and ^{13}C NMR spectra of α-naphthylimidazoline (**2k**) followed the analysis of one- and two-dimensional (COSY, HMQC, HMBC and NOESY) experiments. Reflecting the characteristic shielding seen on 1-aryldihydroimidazoles, a ^{1}H-COSY spectrum showed that the α-naphthyl H2 neighboring N1 is the most upfield aromatic signal (6.90 ppm). At the other end, largest deshielding occurred for the H8 signal of the same residue, which appears at 8.29 ppm. The HMQC spectrum revealed that the low field carbon signal of the ethylenediamine moiety, located at 56.1 ppm, correlates with the non-equivalent hydrogen signals at 3.60 and 4.38 ppm, while the other carbon signal at 54.3 ppm interacts with the multiplet centered at 4.20 ppm. The HMBC spectrum readily yielded the assignment of all quaternary carbons (at 130.8, 130.9, 134.5, 141.6 and 165.6 ppm) but did not show correlation between these carbon and the ethylenediamine hydrogen signals, thus failing to unequivocally identify C4 and C5. These carbons were tentatively assigned by considering that diastereotopic geminal protons closer to the chiral axis would have the largest chemical shift difference and, consequently, proton signals at 3.60 and 4.38 ppm and the carbon at 56.1 ppm belong to the methylene at the 5-position. The observation of NOE cross-peaks between the α–naphthyl H8 (8.29 ppm) and C5 geminal protons (3.60 and 4.38 ppm) supports this assignment, leaving the 4.20 ppm multiplet and 54.3 ppm carbon signal to the C4 methylene. The NOESY spectrum also showed interaction between the α-naphthyl H2 and the *ortho* proton of the phenyl group, indicating their spatial proximity and suggesting the twisted conformation displayed in Figure 2.

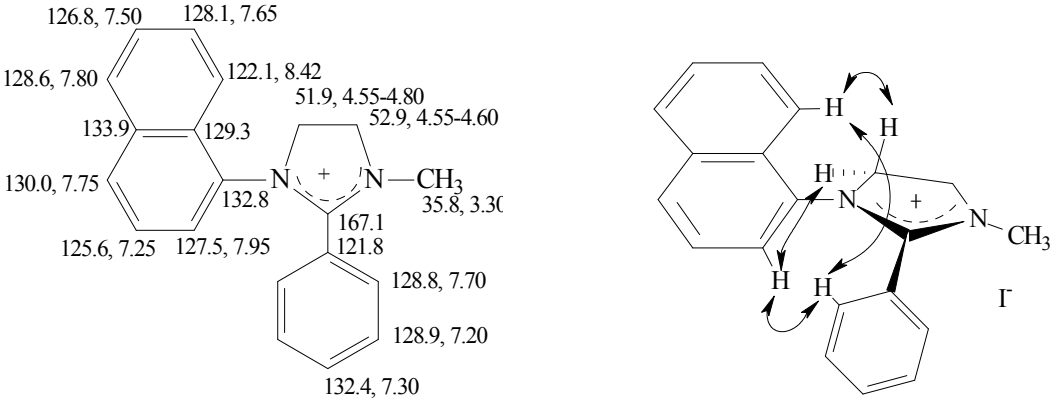
Figure 2. Relevant correlations observed in the NOESY spectrum of **2k**



The full assignment of ^{1}H and ^{13}C NMR signals of the salt (**1k**), shown in Figure 3, followed an identical approach. Comparison of **1k** chemical shift values with those of its corresponding dihydroimidazole (**2k**) reveals the same effects seeing in the whole series, namely, deshielding of all proton and the C2 signals with a concomitant shielding of C4, C5, and the quaternary carbons bound to N1 and C2. The methylene protons of **1k** appear as two multiplets at 4.55-4.60 and 4.72-4.80 ppm. The high field multiplet integrates for three protons that correspond to the C4 and one of the C5 methylene hydrogen, while the low field multiplet belongs to the remaining C5 proton. In the NOESY spectrum of **1k**, the naphthyl H8 signal shows

correlation with only one of the C5 methylene protons (4.72-4.80 ppm) and with the H2 of the Ar_2 group. At the same time, the high field C5 hydrogen signal at around 4.59 ppm interacts with naphthyl H2, which in turn shows correlation with H2 of Ar_2 (Figure 3).

Figure 3. ^{1}H and ^{13}C NMR spectral assignment of **1k** and relevant NOE correlations



Taken together, these observations suggest that the imidazole ring exhibits a more twisted conformation in the salt (**1k**) than in the corresponding imidazoline (**2k**). This conformational adjustment would probably relieve a larger steric hindrance between the α–naphthyl and Ar_2 groups, which would result from shortening of the C2-N1 bond induced by nitrogen quaternization.

It could be expected that compound (**1j**) having *ortho* nitro groups in Ar_1 would have similar spectroscopic properties. However in this case, the C4 and C5 methylene hydrogens appear as two broad resonances centered at 4.35 and 4.83 ppm, corresponding to two protons each that are characteristic of coalescent signals, suggesting only partial obstruction to the Ar_1-N1 bond rotation. At the same time, the H2 of Ar_2 signal of **1j** is broad generating only weak cross-peaks in the two-dimensional spectra that did not help the conformational analysis of this compound.

EXPERIMENTAL

All melting points were determined using a Büchi capillary apparatus and are informed as uncorrected temperature readings. NMR spectra were recorded on a Bruker MSL spectrometer operating at 7.05 T. In general, samples were dissolved in deuterochloroform to a 0.10 M concentration. Chemical shift values are reported in ppm (δ) relative to internal TMS and scalar coupling constant (J) values are given in Hertz (Hz). Phase-sensitive NOESY (1s mixing time) spectra were recorder at 27ºC in a Varian Inova spectrometer (14.1 T field strength) using the hypercomplex method.[22] Data sets consisted of 4096 and 500 complex points in the t2 and t1 dimensions respectively. Time domain data in both dimensions were multiplied by shifted sine-bell functions. TLC analyses were carried out on aluminum sheets silica gel 60 F_{254} using a 9:1

benzene-methanol mixture as solvent.

Compounds (**1**) were obtained by reaction of the corresponding dihydroimidazoles (**2**) and methyl iodide under reflux until TLC analysis showed the disappearance of the starting material.[8] Synthesis of compounds (**1a,c,d,f,g,i)**[8] and (**1b**)[9] has been previously described.

Physical data and elemental analyses of new compounds are as follows:

1-(3,4-Dimethoxyphenyl)-3-methyl-2-phenyl-4,5-dihydro-1*H*-imidazolium iodide (**1e**)

Yield: 82%. mp 187-189 ºC (2-propanol). Anal. Calcd for $C_{18}H_{21}N_2O_2I$: C, 50.96%; H, 4.99%; N, 6.60%. Found: C, 50.87%; H, 5.11%; N, 6.67 %.

3-Methyl-1,2-di(4-nitrophenyl)-4,5-dihydro-1*H*-imidazolium iodide (**1h**)

Yield: 89%. mp 206-209 ºC (anhyd. 2-propanol). Anal. Calcd for $C_{16}H_{15}N_4O_4I$: C, 42.31%; H, 3.33%; N, 12.33%. Found: C, 42.28%; H, 3.25%; N, 12.42%.

3-Methyl-1-(2-nitrophenyl)-2-(4-nitrophenyl)-4,5-dihydro-1*H*-imidazolium iodide (**1j**)

Yield: 87%. mp 198-199 ºC (anhyd. 2-propanol). Anal. Calcd for $C_{16}H_{15}N_4O_4I$: C, 42.31%; H, 3.33%; N; 12.33%. Found: C, 42.52%; H, 3.29%; N, 12.49%.

3-Methyl-1-(α–naphthyl)-2-phenyl-4,5-dihydro-1*H*-imidazolium iodide (**1k**)

Yield: 80%. mp 224-226 ºC (ethanol). Anal. Calcd for $C_{20}H_{19}N_2I$: C, 57.98%; H, 4.62%; N, 6.76%. Found: C, 57.85%; H, 4.72%; N, 6.83%.

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