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SPECTROSCOPIC ANALYSIS OF IMIDAZOLIDINES: PART IV: ^{13}C-NMR SPECTROSCOPY

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Abstract- ^{13}C NMR spectra of a series of 1,3-di- and 1,2,3-trisubstituted imidazolidines with aryl, alkyl and aralkyl groups are analyzed and their spectroscopic parameters correlated with conformational features. Assignments were confirmed by means of two dimensional spectra of heteronuclear correlation HMQC and HMBC. Heterocyclic carbons are highly influenced by the nature of the substituent on adjacent nitrogen. Thus, carbon atoms adjacent to a nitrogen substituted with an alkyl or aralkyl group appear in the spectrum at δ *ca.* 53 ppm as double doublets with $^{1}J_{C\text{-}H}$ 134 and 145 Hz, due to a definite orientation of the substituent. Instead, carbon atoms adjacent to an *N*-aryl group appear at higher fields (δ *ca.* 47 ppm) as triplets with $^{1}J_{C\text{-}H}$ *ca.* 141-143 Hz.

INTRODUCTION

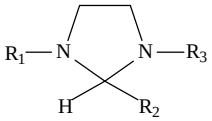
^{1}H NMR spectra of imidazolidines with different substitution patterns and their correlation with conformational features were widely studied by our group[1,2] as well as by other authors.[3-5] However data on ^{13}C NMR studies are scarce in the literature and limited to *N*,*N*´-dimethylimidazolidine,[3] 1,3-diaryl-4-methyl derivatives,[6] 1,3-dihydroxyimidazolidines[7] and 3-alkyl-1,4-dimethyl-5-phenyl derivatives.[4]

Pursuing our research on the spectroscopic properties of imidazolidines,[1,2,8] we present in this work the analysis of ^{13}C NMR spectra of a series of imidazolidines with different substitution patterns (Table 1), specially in regard to the influence of substituents on nitrogen atoms (R_1 and R_3) and C2 (R_2), and discuss their conformational implications.

Chemical shifts of compounds (**1**-**24**) were assigned taking into account the analysis of signal multiplicity and coupling constant values and compairing different terms of the series. Assignments were unequivocally confirmed in some cases by two dimensional spectra of heteronuclear correlation HMQC and HMBC.

Table 1

Imidazolidines (**1-24**)



Compd	R_1	R_2	R_3
1	CH_3	CH_3	CH_3
2	CH_3	C_6H_5	CH_3
3	*p*-$CH_3OC_6H_4CH_2$	CH_3	*p*-$CH_3OC_6H_4CH_2$
4	*p*-$CH_3OC_6H_4CH_2$	$CH{=}CHC_6H_5$	*p*-$CH_3OC_6H_4CH_2$
5	*p*-$CH_3OC_6H_4CH_2$	C_6H_5	*p*-$CH_3OC_6H_4CH_2$
6	*p*-$CH_3OC_6H_4CH_2$	*m*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4CH_2$
7	*p*-$ClC_6H_4CH_2$	*m*-ClC_6H_4	*p*-$ClC_6H_4CH_2$
8	$C_6H_5CH_2$	*p*-$CH_3OC_6H_4$	$C_6H_5CH_2$
9	CH_3	C_6H_5	$CH(CH_3)_2$
10	C_6H_5	H	C_6H_5
11	*p*-ClC_6H_4	H	*p*-ClC_6H_4
12	*p*-$CH_3C_6H_4$	H	*p*-$CH_3C_6H_4$
13	*p*-$CH_3OC_6H_4$	H	*p*-$CH_3OC_6H_4$
14	C_6H_5	CH_3	C_6H_5
15	C_6H_5	C_6H_5	C_6H_5
16	C_6H_5	H	CH_3
17	C_6H_5	C_6H_5	CH_3
18	*p*-$CH_3OC_6H_4$	C_6H_5	CH_3
19	*p*-$CH_3C_6H_4$	C_6H_5	CH_3
20	*p*-ClC_6H_4	C_6H_5	CH_3
21	*p*-ClC_6H_4	H	$CH_2C_6H_5$
22	*p*-ClC_6H_4	C_6H_5	$CH_2C_6H_5$
23	*p*-$NO_2C_6H_4$	*o*-ClC_6H_4	$CH_2C_6H_5$
24	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	$CH_2C_6H_5$

RESULTS AND DISCUSSION

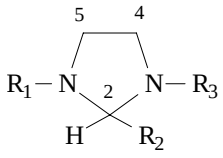
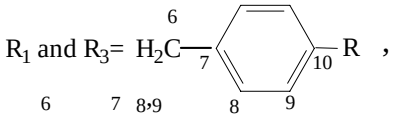
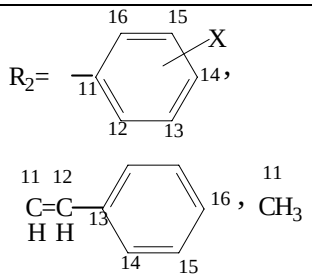
1,3-Dialkyl(or dibenzyl)imidazolidines (Table 2)

Assignments of ^{13}C NMR spectra of 1,3-dibenzylimidazolidines were performed on the basis of HMQC and HMBC spectra of compound (**6**). Single-bond and long-range proton-carbon correlations are

presented in Table 3. Such spectra enabled us to unambiguously assign ethylene carbon signal (C4 and C5, δ 50.7 ppm) which directly correlates with hydrogens of the AA´XX´ system (δ 2.55 and 3.15 ppm), and benzyl carbon signal (δ 56.3 ppm) which correlates with diasterotopic benzyl hydrogen doublets (3.27 and 3.62 ppm).[2]

Table 2

^{13}C Chemical Shift Assignments of 1,3-Dialky(or benzyl)imidazolidines (δ: ppm; *J*: Hz)

			
Compd	**C2** **C4** **C5**		
1	82.9, d $^1J_{C-H}$: 134.2 / 53.0, dd $^1J_{C-H}$: 132.2, $^1J_{C-H}$: 143.2 [a]	39.2 (q, $^1J_{C-H}$: 134.3, C6)	15.2 (q,$^1J_{C-H}$: 127.0, C11)
2	92.0, d $^1J_{C-H}$: 134.2 [b] / 52.9, dd $^1J_{C-H}$: 132.1, $^1J_{C-H}$: 143.9 [b]	39.2, (q, $^1J_{C-H}$: 134.2, C6)	139.3 (t, $^3J_{C-H}$: 6.8; C11), 127.2, 128.1 and 128.4 (C12-14) [c]
3	81.0, d $^1J_{C-H}$: 136.0 / 50.1, dd $^1J_{C-H}$: 133.0, $^1J_{C-H}$: 144.3	56.8 (t, $^1J_{C-H}$: 132.2, C6); 130.2 (s, C7); 130.7 (d, $^1J_{C-H}$: 161.6, C8); 113.5 (dd, $^1J_{C-H}$: 158.2, $^3J_{C-H}$: 4.5, C9); 158.5 (s, C10); 55.3 (q, $^1J_{C-H}$: 143.5, OCH_3)	18.1 (q, $^1J_{C-H}$: 128.2, C11)
4	87.8, d $^1J_{C-H}$: 134.7 / 50.3, dd $^1J_{C-H}$: 132.6, $^1J_{C-H}$: 143.7	56.2 (t, $^1J_{C-H}$: 132.7, C6); 131.0 (s, C7); 129.9 (d, $^1J_{C-H}$: 159.2, C8); 113.4 (dd, $^1J_{C-H}$: 158.3, $^3J_{C-H}$: 5.1, C9); 158.5 (s, C10); 55.1 (q, $^1J_{C-H}$: 144.2, OCH_3)	130.3 (d, $^1J_{C-H}$: 154.3, C11); 136.4 (d, $^1J_{C-H}$: 155.1, C12); 135.5 (s, C13); 127.8 and 128.5 (C14,15) [c]; 126.2 (t, $^3J_{C-H}$: 6.2, C16)
5	88.8, d $^1J_{C-H}$: 134.5 / 50.4, dd $^1J_{C-H}$: 133.1, $^1J_{C-H}$: 142.4	56.1 (t, $^1J_{C-H}$: 132.7, C6); 131.2 (s, C6); 129.6 (d, $^1J_{C-H}$: 159.7, C8); 113.4 (dd, $^1J_{C-H}$: 157.2, $^3J_{C-H}$: 4.6, C9); 158.4 (s, C10); 55.2 (q, $^1J_{C-H}$: 144.1, OCH_3)	140.3 (s, C11); 128.1, 128.5 and 129.4 (C12-14) [c]
6 [d]	87.7, d $^1J_{C-H}$: 135.1 / 50.7, dd $^1J_{C-H}$: 132.7, $^1J_{C-H}$: 144.1	56.3 (t, $^1J_{C-H}$: 131.9, C6); 130.5 (s, C7); 129.5 (d, $^1J_{C-H}$: 154.7, C8); 113.5 (dd, $^1J_{C-H}$: 159.0, $^3J_{C-H}$: 4.1, C9); 158.6 (s, C10); 55.2 (q, $^1J_{C-H}$: 143.8, OCH_3)	143.9 (s, C11); 124.4 (d, $^1J_{C-H}$: 156, C12); 148.2 (d, $^3J_{C-H}$: 6.2, C13); 123.4 (d, $^1J_{C-H}$: 159.3, C14); 128.9 (d, $^1J_{C-H}$: 156.2, C15); 135,4 (d, $^1J_{C-H}$: 157.3, C16)
7	88.2, d $^1J_{C-H}$: 136.0 / 50.6, dd $^1J_{C-H}$: 133.2, $^1J_{C-H}$: 144.5	56.1 (t, $^1J_{C-H}$: 133.2, C6); 137.3 (s, C7); 132.5 (s, C10) [e]	142.6 (s, C11); 134.2 (s, C13) [e]

8	88.5, d $^1J_{C-H}$: 135.2	50.4, dd $^1J_{C-H}$: 132.9, $^1J_{C-H}$: 144.7		56.8 (t, $^1J_{C-H}$: 132.4, C6); 139.2 (s, C7); 128.0 (d, $^1J_{C-H}$: 155.9 and 128.5 (d, $^1J_{C-H}$:154.8, C8,9); 126.7 (dt, $^1J_{C-H}$:154.8, $^3J_{C-H}$ 6.1, C10)	132 (s, C11); 130.5 (dd, $^1J_{C-H}$: 159.4, $^3J_{C-H}$: 5.1, C12); 113.5 (dd, $^1J_{C-H}$: 159.3, $^3J_{C-H}$: 4.5, C13); 159.8 (s, C14); 55.2 (q, $^1J_{C-H}$: 143.9, OCH_3)
9	86.6, d $^1J_{C-H}$: 134.2	47.9, dd $^1J_{C-H}$: 132.4 $^1J_{C-H}$: 142.9	53.1, dd $^1J_{C-H}$: 132.9 $^1J_{C-H}$: 143.1	38.9 (q, $^1J_{C-H}$: 134.5, C6); 43.6 (d, $^1J_{C-H}$: 131.2, C7); 15.5 (q, $^1J_{C-H}$: 132.1 and 22.0, $^1J_{C-H}$: 131.3, C8,9)	141.8 (t, $^3J_{C-H}$: 6.8, C11); 127.8, 128.1, 128.6 (C12-14) [c]

[a] Lit. $^1J_{C4,5-H}$: 132.0, 142.9 Hz.[5] [b] Lit. $^1J_{C2-H}$: 134.0 Hz; $^1J_{C4,5-H}$: 132.0, 142.0 Hz.[5] [c] Due to the overlapping of signals in the coupled spectra, coupling constants could not be calculated. [d] Signals were unequivocally assigned by HMQC and HMBC spectra. [e] C8,9,12,14-16: 127.5, 128.3, 128.9, 129.4, 129.5 and 129.7 (not assigned signals).

The C4 and C5 signals in 1,3-dibenzyl derivatives (**3-8**) appear at δ *ca*. 50 ppm, shifted to higher fields than in 1,3-dimethyl derivatives (**1**, **2**) (δ *ca* 53 ppm) and are almost not influenced by the nature of C2 substituents (CH_3, Ar). The observed shielding was attributed to the influence of the aryl group on *gamma* position, and it is similar to that observed in phenylalkanes.[9] In both series, C2 undergoes an expected paramagnetic shift (*ca.* 8 ppm) when C2-methyl is changed by an aryl or substituted vinyl group. However, in compounds (**5-8**) chemical shifts (*ca.* 88 ppm) failed to show substantial variations with the different substituents on the 2-aryl group.

The dependence of the lone-pair orientation on NMR coupling constant renders the $^1J_{C-H}$ values, an important means to obtain conformational information of molecules. Lowest constants (*ca.* 135 Hz) are associated to coupling between carbons and hydrogen atoms which present lone pairs in *trans* to the C-H bond, while values of *ca*. 144 and 154 Hz correspond to coupling with hydrogens having contribution of one or two lone pairs in *cis* to the C-H bond[1,4,5] respectively. For compounds (**1-8**) $^1J_{C2-H}$ were around 134-137 Hz, indicating the influence of two lone pairs trans to C2-H, thus determining for itself the transoid distribution of substituents on N1, C2 and N3 (Scheme 1). This result is coincident with that obtained from NOESY spectrum previously reported by us for 1,3-dibenzyl derivatives.[2] On the other hand, C4,5 appear as double doublets ($^1J_{C-H}$ *ca.* 134 and 145 Hz) corresponding to coupling with hydrogens in *trans* (Hb,d) and *cis* (He,c) to lone pairs respectively (Scheme 1).

Scheme 1

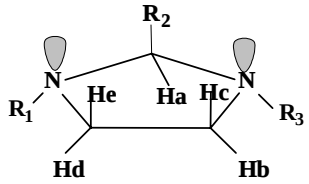
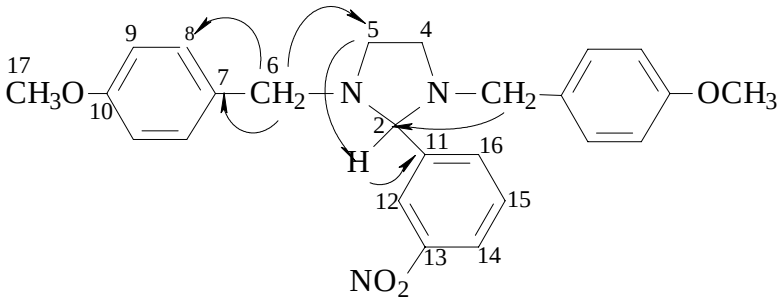


Table 3

HMQC Single-bond and HMBC Long-range Proton-carbon Correlations of Compound (**6**)



C δ (ppm)	**Proton single bond coupling δ (ppm)**	**Proton three bond coupling δ (ppm)**	**Proton two bond coupling δ (ppm)**
50.7 (C4,5)	2.55 and 3.15 (H4,5)	3.27 and 3.62 (H6), 3.92 (H2)	2.55, 3.15 (H4,5)
55.2 (C17)	3.75 (H17)	-	-
56.3 (C6)	3.27 and 3.62 (H6)	2.55 and 3.15 (H4,5), 3.92 (H2), 7.08 (H8)	-
87.7 (C2)	3.92 (H2)	3.27 and 3.62 (H6), 3.15 (H4,5), 8.34 (H12), 7.80 (H16)	-
113.5 (C9)	6.74 (H9)	-	7.08 (H8)
123.4 (C14)	8.12 (H14)	7.80 (H16), 8.34 (H12)	7.49 (H15)
124.4 (C12)	8.34 (H12)	3.92 (H2), 7.80 (H16), 8.12 (H14)	-
128.9 (C15)	7.49 (H15)	-	7.80 (H16)
129.5 (C8)	7.08 (H8)	3.27 and 3.62 (H6)	6.74 (H9)
130.5 (C7)	-	6.74 (H9)	7.08 (H8), 3.27 and 3.62 (H6)
135.4 (C16)	7.80 (H16)	8.12 (H14), 8.34 (H12), 3.92 (H2)	7.49 (H15)
143.9 (C11)	-	7.49 (H15)	3.92 (H2)
148.2 (C13)	-	7.49 (H15)	8.12 (H14), 8.34 (H12)
158.6 (C10)	-	3.75 (H17), 7.08 (H8)	6.74 (H9)

The comparison of the spectra of compounds (**2**) and (**9**) discloses that the substitution of a methyl group on one nitrogen for an isopropyl, induces differentiation between C4 and C5, which appear at 47.9 and 53.1 ppm respectively. C2 chemical shift was the most affected by such change as well as one of the ethylene carbons, which undergo a similar upfield shift (*ca*. 5 ppm). This fact suggests a geometric γ gauche relationship between isopropyl methyl groups and imidazolidine ring carbons bonded to nitrogen carrying the isopropyl group, thus allowing us to assign the signal at 47.9 ppm to C4. However, isopropyl methyl groups do not exert a δ deshielding effect on C5, as it was observed in other imidazolidines.[6] Like

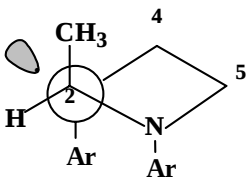
in compounds (**1-8**), $^{1}J_{C\text{-}H}$ coupling constants denote a transoid arrangement between substituents ($^{1}J_{C2\text{-}H}$ 134.2 Hz, $^{1}J_{C4\text{-}H}$ 132.4 and 142.9 Hz, $^{1}J_{C5\text{-}H}$ 132.9 and 143.1 Hz). Characteristically, compound (**9**) presents anisocronous isopropyl methyl groups, being diasterotopicity caused by the presence of the C2- prochiral center.

1,3-Diarylimidazolidines (Table 4)

^{13}C-NMR spectra of C2-unsubstituted 1,3-diarylimidazolidines (**10**-**13**) display C2 at 65.6-67.3 ppm while C4 and C5 appear as a sole signal at 46.4-47.2 ppm, almost independent of the *para* substituent on the aryl group.

The comparison of compounds (**10**) and (**14**), shows that replacement of a hydrogen on C2 by a methyl group induces a downfield shift of C2 signal (2.5 ppm), and an upfield shift of C4 and C5 signals (-3 ppm). Such upfield shift observed for heterocyclic ethylene carbons as well as the deshielding of attached protons (0.10 ppm)[1] is attributed to a γ effect of C2 substituent, and would indicate a preferential gauche arrangement of C2 methyl group and C4 and C5, as it is displayed in the Newman projection seen through C2-N bond (Scheme 2). Instead, in the 1,2,3-triphenylimidazolidine (**15**), C4 and C5 chemical shifts are not significantly modified respect to the C2 unsubstituted compound (**10**).

Scheme 2



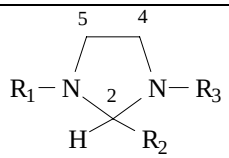
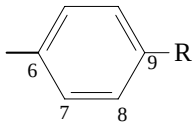
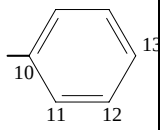
gauche

In comparison to the previous series, all heterocyclic carbon signals of 1,3-diarylimidazolidines are upfield shifted. It could be expected that the decrease in electron density on imidazolidine ring caused by the conjugation of the aniline system (*N*-aryl) would exert a paramagnetic effect. Thus, the observed diamagnetic effect must be associated to a decrease in the C-N bond order, so that the balance between both effects is responsible for the shielding observed in the signal of carbons bonded to nitrogen atoms. A similar effect was reported in other nitrogen heterocyclic systems,[10] when ring electron density decreased and polarization effects were overpassed by a diminution in bond order, leading to an effective upfield shift of the Cα to the heteroatom.

For this series of compounds, C4 and C5 appear in all cases as triplets ($^{1}J_{C\text{-}H}$ 141-145 Hz). This value cannot be associated to a definite orientation of the lone pair, due to the *N*-aryl inversion.[11] It could be better related to the inductive effect resulting from the low electron density on *N*-aryl.

Table 4

^{13}C Chemical Shift Assignments of 1,3-Diarylimidazolidines (δ: ppm; *J*: Hz)

			R_1 and R_3= 	R_2= CH_3, 
Compd	**C2**	**C4,5**		
10	65.6, t $^1J_{C-H}$: 149.2	46.7, t $^1J_{C-H}$: 141.6	146.2 (t, $^3J_{C-H}$: 8.1, C6); 112.3 (dt, $^1J_{C-H}$: 155.8, $^3J_{C-H}$: 6.1, C7); 129.1 (dd, $^1J_{C-H}$: 155.8, $^3J_{C-H}$: 6.1, C8); 117.4 (dt, $^1J_{C-H}$: 161.0, $^3J_{C-H}$: 7.4, C9)	
11	65.7, t $^1J_{C-H}$: 148.7	46.4, t $^1J_{C-H}$: 144.6	144.6 (t, $^3J_{C-H}$: 8.9, C6); 113.3 (dd, $^1J_{C-H}$: 159.9, $^3J_{C-H}$: 5.9, C7); 129.0 (dd, $^1J_{C-H}$: 164.5, $^3J_{C-H}$: 5.7, C8); 122.6 (t, $^3J_{C-H}$: 7.1, C9)	
12	66.3, t $^1J_{C-H}$: 145.5	46.4, t $^1J_{C-H}$: 145.5	144.4 (t, $^3J_{C-H}$: 8.7, C6); 112.4 (dd, $^1J_{C-H}$: 162.1, $^3J_{C-H}$: 5.3, C7); 129.6 (dd, $^1J_{C-H}$: 157.3, C8); 126.6 (t, $^3J_{C-H}$: 6.2, C9); 20.2, q, $^1J_{C-H}$: 128.7, CH_3)	
13	67.3, t $^1J_{C-H}$: 149.5	47.2, t $^1J_{C-H}$: 140.5	141.5 (t, $^3J_{C-H}$: 8.7, C6); 113.6 (dd, $^1J_{C-H}$: 150.1, $^3J_{C-H}$: 5.9, C7); 115.1 (dd, $^1J_{C-H}$: 149.5, $^3J_{C-H}$: 5.0, C8); 152.4 (t, $^3J_{C-H}$: 6.0, C9); 55.7 (q, $^1J_{C-H}$: 142.9, OCH_3)	
14	68.0, d $^1J_{C-H}$: 150.2	43.7, t $^1J_{C-H}$: 141.6	145.4 (t, $^3J_{C-H}$: 8.6, C6); 112.8 (dt, $^1J_{C-H}$: 162.2, $^3J_{C-H}$: 5.5, C7); 129.1 (dd, $^1J_{C-H}$: 157.3, $^3J_{C-H}$: 8.1, C8); 117.0 (dt, $^1J_{C-H}$: 161.2, $^3J_{C-H}$: 7.1, C9)	15.5 (q, $^1J_{C-H}$: 126.7, C10)
15	75.4, d $^1J_{C-H}$: 148.5	45.9, t $^1J_{C-H}$: 141.3	145.6 (t, $^3J_{C-H}$: 8.4, C6); 113.6 (dt, $^1J_{C-H}$: 155.9, $^3J_{C-H}$: 6.5, C7); 129.0 (dd, $^1J_{C-H}$: 157.2, $^3J_{C-H}$: 7.1, C8); 117.8 (dt, $^1J_{C-H}$: 168.8, $^3J_{C-H}$: 7.1, C9)	141.2 (t, $^3J_{C-H}$: 7.0, C10); 127.6, 127.9, 128.3 (C11-13) [a]

[a] Due to the overlapping of signals in the coupled spectra, coupling constans could not be calculated.

***N*-Aryl-*N'*-alkyl(or benzyl)imidazolidines** (Table 5)

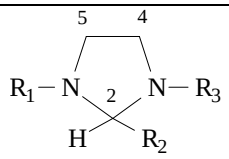
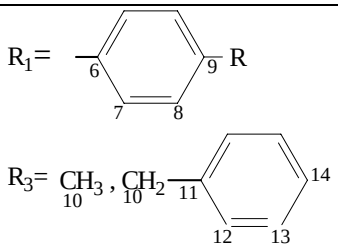
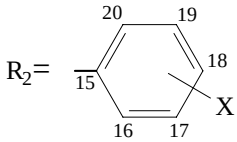
In C2-unsubstituted compounds (**16**,**21**) multiplicity of C2, C4 and C5 signals (triplets) and $^1J_{C-H}$ values indicate that they are not in a preferred conformation, according to results obtained from analysis of the ^{1}H-NMR spectra.[2]

Unequivocal assignment of 1,2-diaryl-3-methyl derivatives (**17-20**) was performed from analysis of HMQC and HMBC spectra of compound (**19**) (Table 6). In these compounds, C2 appear at an intermediate chemical shift value (*ca.* 84 ppm) respect to compounds (**2**) and (**15**), taken as models of the above series. Spectroscopic characteristics (chemical shift, $^1J_{C\text{-}H}$ and multiplicity) of ethylene carbons are related to the nature of adjacent nitrogen and maintain the patrons described for 1,3-diaryl and 1,3-dialkyl compounds. Thus, C4 (δ *ca.* 53 ppm) is presented as a double doublet ($^1J_{C\text{-}H}$ 134 and 145 Hz) resulting from a preferential methyl orientation, and C5 (δ *ca.* 47 ppm) as a triplet ($^1J_{C\text{-}H}$ 142 Hz) which cannot be associated to a particular *N*-phenyl lone pair orientation.

In 1-benzyl-2,3-diarylimidazolidines (**22-24**), C4 and C5 only differ in approximatly 2 ppm, so that assignment was performed exclusively by the observed multiplicity and $^1J_{C\text{-}H}$ values in each case. Thus, triplets at *ca.* 47.0 ppm ($^1J_{C\text{-}H}$ 142 Hz) were assigned to C5, while signals at lower fields (*ca.* 49 ppm dd, $^1J_{C\text{-}H}$ 143 and 135 Hz) were assigned to C4.

Table 5

^{13}C Chemical Shift Assignments of Alkyl(or benzyl)-3-aryl-1- imidazolidines (δ: ppm; *J*: Hz)

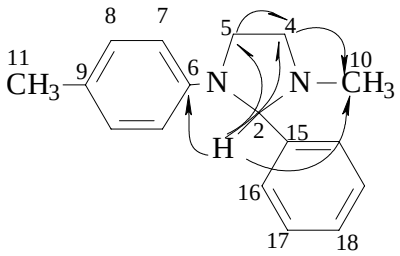
					
Compd	**C2**	**C4**	**C5**		
16	71.0, t $^1J_{C\text{-}H}$: 148.0	53.0, t $^1J_{C\text{-}H}$: 138.4	46.7, t $^1J_{C\text{-}H}$: 140.1	146.1 (t, $^3J_{C\text{-}H}$: 7.9, C6); 112.7 (dd, $^1J_{C\text{-}H}$: 156.1, $^3J_{C\text{-}H}$: 5.8, C7); 128.9 (dd, $^1J_{C\text{-}H}$: 154.9, $^3J_{C\text{-}H}$: 6.0, C8); 116.5 (dt, $^1J_{C\text{-}H}$: 159.0, $^3J_{C\text{-}H}$: 7.0, C8); 38.9 (q, $^1J_{C\text{-}H}$: 134.4, C10)	-
17	84.0, t $^1J_{C\text{-}H}$: 144.0	53.2, dd $^1J_{C\text{-}H}$: 134.5 $^1J_{C\text{-}H}$: 143.2	47.8, t $^1J_{C\text{-}H}$: 142.9	146.3 (t, $^3J_{C\text{-}H}$: 7.9, C6); 112.5 (dd, $^1J_{C\text{-}H}$: 157.0, $^3J_{C\text{-}H}$: 5.7, C7); 129.0 (dd, $^1J_{C\text{-}H}$: 157.0, $^3J_{C\text{-}H}$: 6.0, C8); 116.5 (dt, $^1J_{C\text{-}H}$: 158.0,$^3J_{C\text{-}H}$: 6.9, C9); 39.5 (q, $^1J_{C\text{-}H}$: 134.1, C10)	140.5 (t, $^3J_{C\text{-}H}$: 6.9, C15); 127.7, 128.2 and 128.5 (C16-18) [a]
18	84.2, d $^1J_{C\text{-}H}$: 144.6	53.2, dd $^1J_{C\text{-}H}$: 133.9 $^1J_{C\text{-}H}$: 143.2	48.2, t $^1J_{C\text{-}H}$: 143.1	140.9 (t, $^3J_{C\text{-}H}$: 6.1, C6) [b]; 113.2 (dd, $^1J_{C\text{-}H}$: 158.0, $^3J_{C\text{-}H}$: 5.2, C7) [c]; 114.4 (dd, $^1J_{C\text{-}H}$: 158.9, $^3J_{C\text{-}H}$: 5.2, C8) [c]; 151.0 (s, C9); 39.5 (q, $^1J_{C\text{-}H}$: 134.7, C10); 55.5 (q, $^1J_{C\text{-}H}$: 143.3, OCH_3)	140.5 (t, $^3J_{C\text{-}H}$: 6.7, C15) [b]; 127.4, 127.9 and 128.2 (C16-18) [a]
19 [d]	84.5, d $^1J_{C\text{-}H}$: 145.0	53.7, dd $^1J_{C\text{-}H}$: 134.1 $^1J_{C\text{-}H}$: 142.8	48.4, t $^1J_{C\text{-}H}$: 142.3	144.6 (t, $^3J_{C\text{-}H}$: 7.8, C6); 113.0 (dd, $^1J_{C\text{-}H}$: 157.3, $^3J_{C\text{-}H}$: 5.4, C7); 129.8 (dd, $^1J_{C\text{-}H}$: 156.8, $^3J_{C\text{-}H}$: 5.6, C8); 125.8 (t, $^3J_{C\text{-}H}$: 5.7, C9); 39.8 (q, $^1J_{C\text{-}H}$: 134.4, C10); 20.6 (q, $^1J_{C\text{-}H}$: 126.5, $ArCH_3$)	141.0 (t, $^3J_{C\text{-}H}$: 7.1, C15); 128.0, 128.5 and 128.9 (C16-18) [a]

20	83.8, d $^1J_{C-H}$: 144.1	53.1, dd $^1J_{C-H}$: 133.7 $^1J_{C-H}$: 143.1	47.8, t $^1J_{C-H}$: 142.5	144.6 (t, $^3J_{C-H}$: 7.4, C6); 113.5 (dd, $^1J_{C-H}$: 160.0, $^3J_{C-H}$: 6.0, C7); 128.6 (dd, $^1J_{C-H}$: 163.2, $^3J_{C-H}$: 5.9, C8); 121.1 (t, $^3J_{C-H}$: 5.8, C9); 39.1 (q, $^1J_{C-H}$: 134.0, C10)	139.1 (t, $^3J_{C-H}$: 6.9, C15); 127.5, 128.3 and 128.5 (C16-18) [a]
21	70.1, t $^1J_{C-H}$: 147.5	52.6, t $^1J_{C-H}$: 139.0	45.2, t $^1J_{C-H}$: 139.3	145.0 (t, $^3J_{C-H}$: 8.2, C6); 112.4 (dd, $^1J_{C-H}$: 158.6, $^3J_{C-H}$: 5.9, C7); 128.9 (dd, $^1J_{C-H}$: 163.0, $^3J_{C-H}$: 5.9, C8); 120.9 (t, $^3J_{C-H}$: 5.8, C9); 58.6 (t, $^1J_{C-H}$: 133.1, C10); 138.5 (s, C11); 127,3, 128.8 and 128.6 (C12-14) [a]	-
22	81.2, d $^1J_{C-H}$: 146.1	48.8, dd $^1J_{C-H}$: 135.8 $^1J_{C-H}$: 143.1	47.0, t $^1J_{C-H}$: 142.1	144.8 (t, $^3J_{C-H}$: 7.9, C6); 113.2 (dd, $^1J_{C-H}$: 158.5, $^3J_{C-H}$: 6.0, C7); 121.2 (t, $^3J_{C-H}$: 6.3, C9); 56.8 (t, $^1J_{C-H}$: 133.2, C10); 138.4 (s, C11) [e]	141.1 (s, C15) [e]
23	79.3, d $^1J_{C-H}$: 145.9	48.4, dd $^1J_{C-H}$: 135.6 $^1J_{C-H}$: 144.1	46.9, t $^1J_{C-H}$: 142.3	149.9 (t, $^3J_{C-H}$: 7.5, C6); 111.3 (dd, $^1J_{C-H}$: 157.3, $^3J_{C-H}$: 4.9, C7); 136.2 (s, C9); 57.1 (t, 56.4, t, $^1J_{C-H}$: 132.5, C10); 137.7 (s, C11) [f] [g]	138.5 (s, C15) [f]; 134.2 (s, C16) [g]
24	81.0, d $^1J_{C-H}$: 146.3	49.3, dd $^1J_{C-H}$: 134.9 $^1J_{C-H}$: 144.5	47.0, t $^1J_{C-H}$: 141.9	148.1 (t, $^3J_{C-H}$: 7.9, C6); 111.2 (dd, $^1J_{C-H}$: 156.2, $^3J_{C-H}$: 5.1, C7); 136.5 (s, C_9); 56.4 (t, $^1J_{C-H}$: 132.9, C10); 138.5 (s, C11) [h]	131.8 (s, C15); 114.0 (dd, $^1J_{C-H}$: 159.2, $^3J_{C-H}$: 4.4, C17), 130.2 (dd, $^1J_{C-H}$: 158.2, $^3J_{C-H}$: 4.9, C16), 160.7 (s, C18); 55.3 (q, $^1J_{C-H}$: 142.2, OCH_3) [h]

[a] Due to the overlapping of the signals in the coupled spectra, coupling constans could not be calculated. [b] Exchangeable assignment. [c] Exchangeable assignment. [d] Signals were unequivocally assigned by HMQC and HMBC spectra. [e] C8,12-14,16-18: 127.2, 127.7, 127.9, 128.1, 128.3, 128.7 and 128.9 (not assigned signals). [f] Exchangeable assignment. [g]: C8,12-14,17-20: 126.1, 127.1, 127.4, 128.3, 128.5, 128.8, 129.8, 130.0. (not assigned signals). [h] C8,12-14,16: 125.9, 127.4, 127.7, 128.4 and 128.8 (not assigned signals).

Table 6

HMQC Single-bond and HMBC Long-range Proton-carbon Correlations of Compound (**19**)



C δppm	**Proton single bond coupling δ ppm**	**Proton three bond coupling δ ppm**	**Proton two bond coupling δ ppm**
20.6 (C11)	2.20 (H11)	6.90 (H8)	-
39.8 (C10)	2.40 (H10)	4.70 (H2), 2.70 (H4)	-

48.4 (C5)	3.70 and 3.90 (H5)	4.70 (H2)	2.70 and 3.40 (H4)
53.7 (C4)	2.70 and 3.40 (H4)	4.70 (H2), 2.40 (H10)	3.70 and 3.90 (H5)
84.5 (C2)	4.70 (H2)	3.70, 3.90 (H5), 2.70 (H4), 2.40 (H10)	-
113.0 (C7)	6.40 (H7)	-	6.9 (H8)
125.8 (C9)	-	6.40 (H7)	2.20 (H10)
128.0 (C16)	[a]	4.70 (H2)	7.20-7.40 (H17)
128.5 and 128.9 (C17-18)	[a]		
129.8 (C8)	6.90 (H8)	2.20 (H11)	-
141.0 (C15)	-	[a]	4.70 (H2)
144.6 (C6)	-	6.90 (H8), 4.71 (H2)	-

[a] Multiplet corresponding to H16-18 signals.

EXPERIMENTAL

The ^{13}C NMR spectra of compounds (**1-24**) were obtained on a Bruker MSL 300 MHz spectrometer using deuteriochloroform as solvent at rt and the standard concentration of samples was 0.10 M. The HMQC and HMBC spectrum were recorded using a Bruker AVANCE DRX 300 spectrometer. Chemical shifts are reported in ppm (δ) from tetramethylsilane. MS spectra (EI) were recorded using a GC-MS Shimadzu QP-1000 spectrometer operating at 20 eV.

Imidazolidines (**1**-**24**)

Imidazolidines (**1**, **2**),[5] (**3-6**)[12] (**7**, **8**, **23**, **24**)[2] (**9**, **17-20**),[13] (**10**, **12**),[14] (**11**),[15] **13,**[16] (**14, 15**),[17] **21,**[8] and **22**[1] were prepared following literature procedures. Purity was ascertained by TLC experiments on aluminium sheets silica gel 60 F_{254} using five different solvent mixtures.

1-Methyl-3-phenylimidazolidine (16)

Compound (**16**) was synthesized from *N*-phenyl-*N´*-methylethylenediamine (1.5 g, 0.01 mol) and formaldehyde (40% aqueous solution, 1.5 mL, 0.02 mol) in ethanol (10 mL).

The imidazolidine was obtained as an oil (73%) and was purified by silica gel column chromatography eluting with benzene-methanol (9:1). ^{1}H NMR: δ 2.35 (s, 3, CH_3), 3.00 (t, *J*= 6.31 Hz, 2, C*H*$_2$NCH$_3$), 3.50 (t, *J*= 6.31 Hz, 2, C*H*$_2$NC$_6$H$_5$), 4.10 (s, 2, NCH$_2$N), 6.50-7.10 (m, 5, C_6H_5).

ms: *m/z* 162 (M^+).

Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70 ; N, 17.27. Found: C, 74.15; H, 8.63; N, 17.19.

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