Pergamon

Tetrahedron, Vol. 53, No. 50, pp. 16911-16922, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)10145-4

NMR and Semiempirical Conformational Analysis of the 2-Aryl-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidines

Antônio F. de C. Alcântara[1], Dorila Piló-Veloso[2], Humberto O. Stumpf[2] and Wagner B. de Almeida[2,3] *

[1] Departamento de Química, ICE, Fundação Universidade do Amazonas, Manaus, AM, 69.078-000, BRASIL

[2] Departamento de Química, ICEx, Universidade Federal de Minas Gerais, Belo Horizonte, MG, 31.270-901, BRASIL

[3] Laboratório de Química Computacional e Modelagem Molecular (LQC-MM)

Key words: imidazolidines; magnetic anisotropy; diamagnetic shielding; conformational analysis; semiempirical calculations.

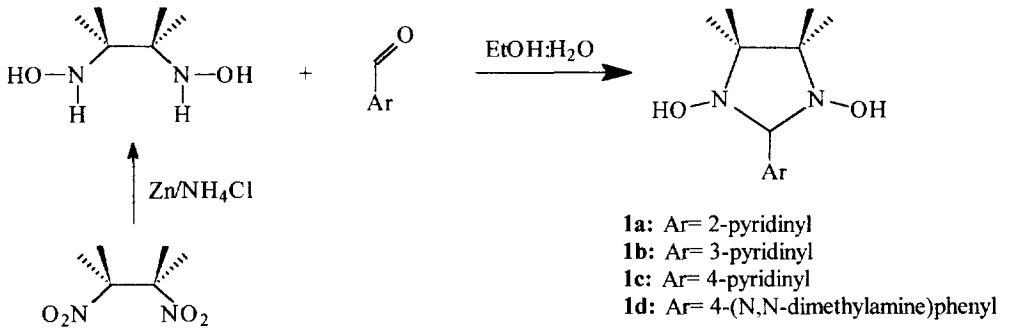
Abstract: 2-Aryl-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidines **(1)** were synthesized and their ^{1}H and ^{13}C NMR spectra recorded. Quantum mechanical semiempirical calculations were also performed, for a better understanding of the signals recorded in the NMR spectra of imidazolidines. The conformation of the imidazolidine ring was initially studied for the 2-methyl-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine **(2)**, used as a model molecule. The results of the calculations obtained for structure **2** showed that the methyl groups are located in axial and equatorial positions. At these positions, the methyl groups are affected by the magnetic anisotropic effects of carbon-nitrogen and carbon-carbon bonds of the imidazolinyl ring with different intensities. Semiempirical calculations for structure **2**, suggested that the effect of the γ-oxygen on the carbon atoms of methyl groups (γ-effect) might lead to an alteration of the electronic charge density and consequently to a change in the diamagnetic shielding on these groups. These data were used for the analysis of the NMR spectra of compound **1**. The diamagnetic shielding effects, estimated from the calculated electronic charge densities on the carbon atoms of methyl groups, are in agreement with the signals observed in the NMR spectra of compound **1**. By combining the contribution of the anisotropic and γ-effects, it appears that the axial methyl groups are located relatively closer to the γ-oxygens in compound **1**. © 1997 Elsevier Science Ltd.

INTRODUCTION

1,3-Dihydroxy-imidazolidines are intermediates in the synthesis of nitronylnitroxide radicals used to obtaining molecular magnets.[1] In spite of their importance, systematic conformational analysis studies involving the imidazolinyl rings have not been reported so far. The only conformational analysis involved various five membered rings[2] and addressed the effect of the eclipsed groups attached to the ring, which favor two non-planar envelope and half-chair conformations[3]. The energy difference between these two conformers is relatively small[4], the interconversion energy barrier (corresponding to a planar structure) for the cyclopentane molecule being estimated[5] at 5.2 kcal mol^{-1}.

Spectroscopic data for tetramethylimidazolidines indicate that the ^1H NMR spectra commonly exhibit two singlets near δ 1.0, which are assigned to the hydrogen atoms of the methyl groups.[6] These results are important since they indicate the existence of two magnetically distinct environments for the methyl groups. Consequently, ^1H and ^{13}C NMR studies can yield important information regarding the imidazolidine conformations. Theoretical calculations, using semiempirical molecular orbital approaches, successfully employed for various molecular systems,[7] can provide a better understanding of the conformational equilibrium.

The objective of this study was to synthesize the 2-aryl-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidines **1**, from the reaction between the 2,3-bis(hydroxylamine)-2,3-dimethylbutane and aromatic aldehydes (see Figure 1) and perform conformational studies using semiempirical molecular orbitals methods in order to explain the assignments of the ^1H and ^{13}C NMR spectra better. By combining NMR spectral and theoretically generated data, the experimentally observed structure of the imidazolidine compounds could be explained.



1a: Ar= 2-pyridinyl
1b: Ar= 3-pyridinyl
1c: Ar= 4-pyridinyl
1d: Ar= 4-(N,N-dimethylamine)phenyl

Figure 1. Synthesis of 2-aryl-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidines **1**.

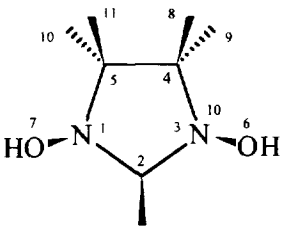
RESULTS AND DISCUSSIONS

Table 1 shows the chemical shifts observed for the hydrogen and carbon atoms of the methyl groups of the imidazolidines **1**. From these data, it can be inferred that two methyl groups magnetically distinct are present. This is in agreement with other studies reported in the literature[6] and indicates that the molecule lies in a conformation in which the methyl groups are in different positions. The two signals observed in the ^1H NMR spectra for the compounds **1b-1d** confirm the fact that the methyl groups are located in magnetically distinct environments. The fact that the ^1H NMR of **1a** shows only one broad singlet indicates that the chemical shifts are very close or the frequency separation of the isochonous sites is too small compared to the exchange rate. On the other hand, the ^{13}C NMR spectra exhibit two signals for the carbon atoms of methyl groups of the imidazolidines **1**. Therefore, it can be said that the methyl groups in **1a** are also situated in magnetically distinct environments, which is evidence for a non-planar structure. For the half-chair conformation, four distinct NMR signals are expected for the methyl groups, independent of the relative spatial orientation of the hydroxyl groups and aromatic substituent of the imidazolidine ring. For the envelope conformation, only two NMR signals are expected for the four methyl groups, if the two hydroxyl groups are in relative *cis* position.

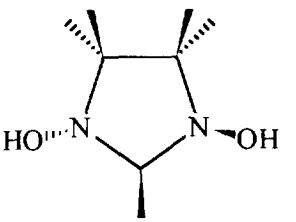
Quantum mechanical semiempirical calculations were carried out in order to relate the results obtained from NMR spectroscopy to conformational analysis of the imidazolidine **1**. The most probable conformations of the 2-methyl substituted imidazolidine ring (structure **2**, Figure 2) were used as initial models in the geometry optimization procedure.

Table 1. Chemical shifts assigned respectively to the hydrogen and carbon atoms of methyl groups of imidazolidines **1**.

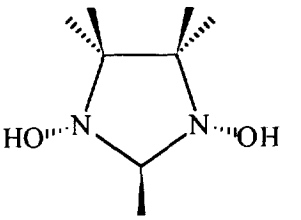
Compound	$\delta\ ^{1}H$	$\delta\ ^{13}C$
1a	1.06	17.9
		24.6
1b	1.04	17.7
	1.07	24.7
1c	1.03	17.3
	1.09	24.1
1d	1.05	17.1
	1.08	24.9



2a



2b



2c

Figure 2. The most probable conformations of the 2-methyl substituted imidazoline ring.

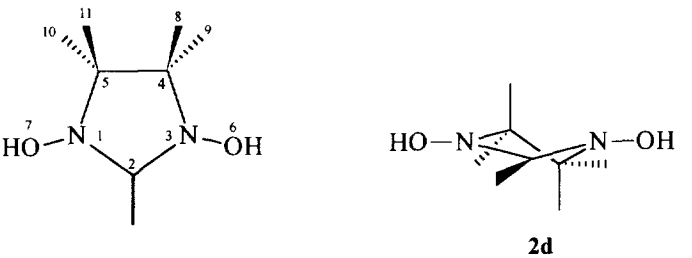
The effect of the 2-methyl substituent group in the imidazoline ring was investigated for the three conformations: **2a**, **2b** and **2c**. Calculated heats of formation (ΔH_f), for structures **2a**, **2b** and **2c** were -38.5 kcal mol^{-1}, -40.4 kcal mol^{-1} and -41.4 kcal mol^{-1} respectively, showing a small difference in the thermodynamic stability of the three conformations. As mentioned, all semiempirical geometries presented two methyl groups in axial positions and other two in equatorial positions for structure **1**.

In order to examine the effect of the superimposition of the methyl groups on the conformational stability of the conformers **2**, ΔH_f were calculated varying the C_8-C_4-C_5-C_{11} and C_9-C_4-C_5-C_{10} dihedral angles as shown in Table 2.

Table 2. Calculated heat of formation (ΔH_f) values for several geometries of structure **2**, obtained by fixing the dihedral angles **C_8-C_4-C_5-C_{11}** and **C_9-C_4-C_5-C_{10}** and optimizing the remaining geometrical parameters.

Geometry	Dihedral angle (degrees)		ΔH_f (kcal.mol^{-1})
	C_8-C_4-C_5-C_{11}	C_9-C_4-C_5-C_{10}	
A	35.7	36.0	-40.99
B	26.5	26.2	-41.03
C	20.8	21.0	-40.29
D	15.1	15.0	-39.82
E	9.3	9.6	-39.56
F	3.6	4.2	-39.34

A relative increase of the ΔH_f values can be noticed when the torsion angles approaches to zero, that is, when the methyl groups are eclipsed. On the other hand, a decrease of ΔH_f is observed when the torsion angles tend to 26.5 degrees, which corresponds to a conformer in which the methyl groups are in staggered positions. This can be explained by the smaller steric repulsion between staggered methyl groups than eclipsed ones. The calculated data suggest that the imidazolidine ring preferentially assumes a non-planar geometry, half-chair conformation, as showed in Figure 3 (structure **2d**).



2d

Figure 3. A side view of the non-planar half-chair conformation **2d**.

In this conformation, the two axial methyl groups are situated in a relative *anti*-periplanar position and the two equatorial groups in *syn*-clinal position. These results are in agreement with studies performed for the determination of the most stable conformation of the cyclopentane ring[10] and 3-phenyl-1,2,3-oxathiazolidine-2-oxide heterocyclic systems.[7d]

In order to investigate the influence of the magnetic anisotropy, caused by the N_1-C_5, N_3-C_4 and C_4-C_5 bonds, on the axial and equatorial methyl groups,[11] a study of the variation of the electronic density on the carbon atoms of the methyl groups as a function of the dihedral angles of the imidazolidine ring was carried out. Table 3 gives the calculated semiempirical electronic charge density on the carbon atoms of the methyl groups for the structure **2a** (Figure 2) where the dihedral angle C_2-N_3-C_4-C_8 was fixed at distinct values and the other geometric parameters fully optimized.

Table 3. Calculated electronic density values on the carbon atoms of the methyl groups in structure **2a**, for fixed values of the dihedral angle **C_2-N_3-C_4-C_8**, and optimization of the remaining geometrical parameters.

Geometry	Dihedral angle C_2-N_3-C_4-C_8	Electronic density C_8
A	70	-0.1373
B	75	-0.1353
C	80	-0.1329
D	85	-0.1303
E	90	-0.1276
F	95	-0.1250
G	100	-0.1161
H	105	-0.1146
I	110	-0.1137
J	115	-0.1132

It can be seen that the carbon C_8 in axial position, i.e. C_2-C_3-C_4-C_8 near 90 degrees, has a higher electronic density and consequently higher diamagnetic shielding. On the other hand, when C_8 is in equatorial position, i.e. C_2-C_3-C_4-C_8 near 150 degrees, it has a smaller electronic density and lower diamagnetic shielding. According to the theoretical results obtained for structure **2**, the methyl groups are exposed to two diamagnetically distinct environments, depending whether they are in equatorial position or axial position. Consequently, considering the effects attributed to the magnetic anisotropy on the axial and equatorial methyl groups in the ^{13}C NMR spectra of imidazolidines (Table 1), the larger chemical shifts can be assigned to the carbon atoms of the equatorial methyl and the smaller chemical shifts to the axial methyl groups. This same effect is not observed in imidazolidine rings having sp^2 hybridization of N_1 and C_2 [12] or even in rings having sp^2 hybridization only at C_2[13]. In these compounds the ^1H NMR spectra exhibit only one signal for the hydrogen atoms situated in geminal methyl groups. Consequently, the rings are constrained to assume the envelope conformation, with the methyl groups preferentially eclipsed.

Finally, the effect of the γ-oxygen atoms on the diamagnetic shielding of the methyl groups (γ-effect) was examined. Table 4 reports the calculated values for the relative variation of the electronic density on the carbon atoms of methyl groups as a function of the dihedral angle C_2-N_3-C_4-$C_{8(9)}$ (or C_2-N_1-C_5-$C_{10(11)}$) and the respective interatomic distances (C···O) in relation to the γ-oxygen, for various geometries of compound **2**. The diamagnetic shielding can be analyzed using these geometrical parameters.

It can be seen that for geometry **A**, the γ- and anisotropic effects offset each other, because C_8 and C_{10} are in equatorial positions and closer to the oxygen atom, causing a small variation in the electronic charge density in relation to C_9 and C_{11}. For the geometry **B**, the γ- and anisotropic effects are additive on C_{10}, producing a high variation of the relative charge density. By comparing the values of the relative variation of the electronic density on C_9 and C_{10} for geometry **C**, the γ-effect predominates over the anisotropic effect, since while C_{10} has the smaller dihedral angle, C_9 is the closest to the oxygen atom. On the other hand, in geometry **D**, C_9 is closer to the oxygen atom (higher γ-effect) but C_{10} has a larger relative variation of electronic charge density due to its smaller dihedral angle, which shows the predominance of the anisotropic effect. It can be seen (Table 4) that the calculated electronic charge density on carbon atoms of methyl groups is dependent on their position towards the ring (anisotropic effect) and on the distance to the oxygen atom (γ-effect). In some cases, these two effects can combine in an additive way, increasing considerably the electronic density on the carbon atoms of the methyl groups. In other cases, they are opposed, producing a small relative variation of the electronic charge density on the methyl carbon atoms. For the geometries considered in the present work, the anisotropic effect contributes more significantly to the electronic charge density than the γ-effect. Thus, through the study of the structures **2** it was possible to establish a relationship between the relative variation of the electronic density on the carbon atoms of methyl groups of the imidazolidines and the anisotropic and γ-effects. However, in order to justify the two singlet signals observed in the NMR spectra of imidazolidines **1b-1d** (Figure 1), a significant difference in the electronic density on the axial methyl carbons and the equatorial carbon atoms is required. The anisotropic and γ-effects should also combine in an additive way. In this case the axial methyl groups of imidazolidines **1** need to be in the vicinity of the γ-oxygen atoms, as shown in conformations **A** and **B** for compound **1c**, resulting from PM3 semiempirical calculations.

Table 4. Calculated electronic density values on the carbon atoms of methyl groups as a function of the dihedral angles C_2-N_3-C_4-$C_{8(9)}$ and C_2-N_1-C_5-$C_{10(11)}$ and the respective interatomic distance to the gamma oxygen atoms calculated for several geometries of structure **2**.

Geometry	Atom	Dihedral angle (degrees)		Interatomic distance (Angstroms)		Relative variation of electronic charge (%)
	C_x	C_2-N_3-C_4-C_x	C_2-N_1-C_5-C_x	O_6	O_7	
A	C_8	143.6		2.77		0.8
	C_9	-98.9		3.65		5.3
	C_{10}		147.1		2.75	0.0
	C_{11}		-95.4		3.64	5.3
B	C_8	148.8		2.76		3.6
	C_9	-93.9		3.66		3.6
	C_{10}		88.1		2.81	22.3
	C_{11}		-149.4		3.19	0.0
C	C_8	151.0		3.21		0.0
	C_9	-88.6		2.78		26.1
	C_{10}		81.4		3.67	5.4
	C_{11}		-156.9		2.78	8.1
D	C_8	149.8		3.22		5.4
	C_9	-90.2		2.80		18.9
	C_{10}		82.3		2.93	35.1
	C_{11}		-155.1		3.13	0.0

Dihedral angle values for the methyl carbons in relation to the ring, their interatomic distances to the γ-oxygen, electronic densities and average electronic densities for the methyl hydrogens calculated for the geometries obtained from the imidazolidines **1** (Figure 1), in the half-chair conformation, are given in Table 5. From the values reported it can be seen that conformations **A** and **B** show a large variation of the relative charge density for the axial carbon atoms of the methyl groups, respectively 15.6% and 23.4% larger than the value for the equatorial methyl carbons. Furthermore, the calculated values for the electronic density on the carbon and hydrogen atoms of the methyl groups are not significantly influenced by the structure or position of the 2-aryl substituent group, situated in a perpendicular plane to the imidazolidine ring.

Table 5. Calculated dihedral angles in relation to the ring, interatomic distances in relation to the gamma oxygen atom, electronic densities and average electronic densities for the methyl hydrogens, for geometries originated from the imidazolidines **1** in the half-chair conformation.

Compound (conformation)[a]	Atom	Dihedral angle	Interatomic distance (Angstrom)	Relative variation of charge density on C (%)	Relative variation of average charge density on H (%)
1a-A	C_8	-91.4	2.80	22.4	0.0
	C_9	149.1	3.19	0.0	12.3
	C10	-87.9	2.82	15.9	1.2
	C11	152.6	3.18	0.0	13.5
1b-A	C8	-91.6	2.82	21.9	0.0
	C9	148.9	3.18	0.1	12.8
	C10	-87.5	2.81	15.7	2.2
	C11	152.9	3.19	0.0	13.4
1c-B	C8	87.7	2.81	15.6	3.6
	C9	-152.7	3.19	0.0	13.9
	C10	-84.6	2.82	22.3	0.0
	C11	153.2	3.18	0.8	13.9
1d-A	C8	-87.3	2.81	16.1	4.4
	C9	153.0	3.19	0.0	15.0
	C10	-91.5	2.82	23.4	0.0
	C11	149.0	3.18	1.0	15.4

[a] The conformations are depicted in Figure 4, for the imidazolidine **1c**.

On the other hand, it can be seen that carbon atoms with smaller electronic densities are attached to hydrogen atoms with larger electronic densities. This was confirmed by a NMR study using the Heteronuclear Correlation (HETCOR) technique, in which it was shown that signals for hydrogen atoms with larger chemical shifts are connected to the signals of carbon atoms with smaller chemical shifts. Thus, the theoretical results obtained for conformations **A** and **B** proved to be useful for the analysis of the NMR data for the imidazolidines **1**. From various minimum energy structures located on the PM3 potential energy surface of the imidazolidines **1a-1d**, only conformations **A** and **B** (Figure 4) can justify the respective chemical shifts observed for the methyl groups. Although other calculated conformations are energetically lower than **A** and **B**, they cannot explain the NMR chemical shifts.

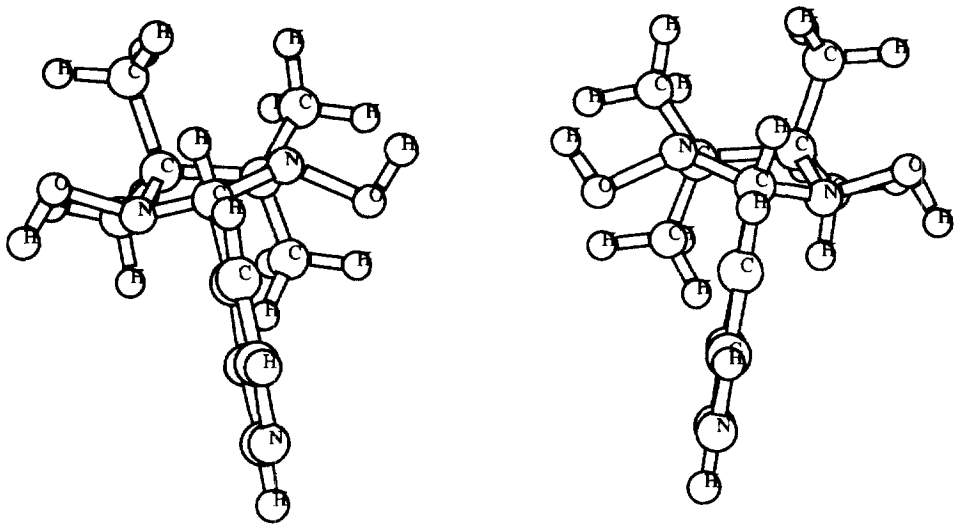


Figure 4. A three-dimensional view of the PM3 fully optimized conformations **A** and **B** for compound **1c**.

CONCLUSION

In this article, a conformational analysis of some imidazolidine compounds was performed by using both experimental spectroscopic data and theoretical quantum mechanical semiempirical results. By combining the anisotropic and γ-effects, it is proposed that the imidazolidines **1** are likely to be found in geometrical forms in which two methyl groups are axial and the other two equatorial. The geometry or position of substitution in the aromatic ring not significantly affects the methyl groups.

Moreover, it is also proposed that the axial methyl carbon atoms are relatively closer to the γ-oxygen atoms, contributing to a significant increase of their electronic densities, independent of the structure of the aryl substituent group which is perpendicular to the plane of the imidazolidine ring. The diamagnetic shielding effect, evaluated from the relative values of the electronic densities, has a bigger influence on the hydrogen and carbon atoms of the axial methyl groups. As a consequence, signals with a smaller chemical shift registered in ^{13}C NMR

spectra and a larger chemical shift in ^{1}H NMR spectra recorded for imidazolidines **1** can be assigned to the axial methyl groups. While signals with a larger chemical shift in ^{13}C NMR spectra and a smaller chemical shift in the ^{1}H NMR can be assigned to the equatorial methyl groups. Finally, it is important to mention that by combining the analysis of the experimental NMR spectra and the results of theoretical quantum mechanical calculations, it is possible to assign structures **A** or **B** (Figure 4) as the most probable conformations of the imidazolidines **1**.

EXPERIMENTAL

Imidazolidines **1** were obtained employing the following standard procedure: To 2,3-dinitro-2,3-dimethylbutane (0.1 mol) in a 1:1 water:ethanol solution, ammonium chloride (0.2 mol) was added, to the mixture cooled at 0°C, zinc powder (0.4 mol) was added in small portions, with stirring. After 2 hours the reaction mixture was filtered. The filtrate containing 2,3-bis(hydroxyamine)-2,3-dimethylbutane was mixed to aldehyde (0.1 mol) with vigorous stirring. After 4 hours, the reaction mixture was filtered and the solid product was rinsed with water, ethanol and acetone.

Infrared spectra were recorded in the 4000 cm^{-1} to 300 cm^{-1} range on a Perkin-Elmer spectrophotometer 283B and Mattson Galaxy Series FTIR 3000. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 and Bruker AC 80 using DMSO-d_6 as solvent and TMS as the internal reference.

Yields and properties (melting points, elemental analysis, NMR and IR spectra) of the products obtained are given below:

2-(2-pyridinyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (**1a**): **Yield** 31%; **m.p** 123.2°C (dec.); **Anal.** Calcd: %C 60.74, %H 8.07, %N 17.71. Found: %C 60.72, %H 8.53, %N 17.61; **^{1}H NMR** (DMSO-d_6): δ 1.06 (s, 12H), 4.66 (s, 1H), 7.23-7.27 (m, 1H), 7.60 (d, 7.3Hz, 1H), 7.73-7.77 (m, 1H), 7.76 (s, 2H), 8.46 (d, 4.8Hz, 1H); **^{13}C NMR** (DMSO-d_6): δ 17.9 (CH_3), 24.6 (CH_3), 66.8 (C quaternary), 91.9 (CH), 122.9 (CH), 123.1 (CH), 136.5 (CH), 148.5 (N=CH), 161.9 (N=C); **I.R.** (KBr, ν, cm^{-1}): 3600-3100, 3000-2850, 1590, 1440, 1330, 1310, 1160, 1110, 1070, 990, 870, 830, 765.

2-(3-pyridinyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (**1b**): **Yield** 67%; **m.p.** 141.1°C (dec.); **Anal.** Calcd: %C 60.74, %H 8.07, %N 17.71. Found: %C 59.46, %H 8.24, %N 17.23; **^{1}H NMR** (DMSO-d_6): δ 1.04 (s, 6H), 1.07 (s, 6H), 4.54 (s, 1H), 7.33-7.39 (dd, 7.5 and 4.5 Hz, 1H), 7.81-7.84 (dt, 7.5 and 1.9 Hz, 1H), 7.89 (s, 2H), 8.41-8.44 (dd, 4.5 and 1.9 Hz, 1H), 8.57 (d, 1.9 Hz, 1H); **^{13}C NMR** (DMSO-d_6): δ 17.7 (CH_3), 24.7 (CH_3), 66.7 (C quaternary), 88.7 (CH), 123.5 (CH), 136.5 (C quaternary), 137.6 (CH), 149.0 (N=CH), 150.2 (N=CH); **I.R.** (KBr, ν, cm^{-1}): 3600-3050, 3000-2800, 1595, 1570, 1460, 1380, 1320, 1255, 1245, 1100, 1065, 950, 915, 880, 780, 705.

2-(4-pyridinyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (**1c**): **Yield** 73%; **m.p** 175.5°C (dec.); **Anal.** Calcd: %C 60.74, %H 8.07, %N 17.71. Found: %C 60.01, %H 7.82, %N 16.56; **^{1}H NMR** (DMSO-d_6): δ 1.03 (s, 6H), 1.09 (s, 6H), 4.53 (s, 1H), 7.48 (d, 6.0 Hz, 2H), 7.96 (s, 2H), 8.52 (d, 6.0 Hz, 2H); **^{13}C NMR** (DMSO-d_6): δ 17.3 (CH_3), 24.1 (CH_3), 66.5 (C quaternary), 89.1 (CH), 123.4 (CH), 149.1 (CH), 150.7 (C quaternary); **I.R.** (KBr, ν, cm^{-1}): 3540-3150, 2980-2870, 1640, 1450, 1435, 1415, 1380, 1300, 1255, 1165, 1145, 1120, 1055, 1030, 1000, 925, 820, 790, 745.

2-(4-N,N-dimethylaminephenyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine **(1d): Yield** 12%; **m.p.** 158.9°C (dec.); **Anal.** Calcd: %C 64.49, %H 9.02, %N 15.04. Found: %C 62.90, %H 8.32, %N 13.77; **^{1}H NMR** (DMSO-d_6): δ 1.05 (s, 6H), 1.08 (s, 6H), 2.86 (s, 6H), 4.45 (s, 1H), 6.69 (d, 7.6 Hz, 2H), 7.28 (d, 7.6 Hz, 2H), 7.65 (s, 2H); **^{13}C NMR** (DMSO-d_6): δ 17.1 (CH_3), 24.9 (CH_3), 41.0 (NCH_3), 66.0 (C quaternary), 91.1 (CH), 112.3 (CH), 125.0 (CH), 139.7 (C quaternary), 150.2 (C quaternary); **I.R.** (KBr, ν, cm^{-1}): 3600-3150, 3050-2800, 1615, 1490, 1430, 1410, 1365, 1320, 1235, 1130, 1070, 1040, 870.

Calculations. Theoretical studies for imidazolidines **1** were performed using the PM3 (Parametric Method 3) molecular orbital approximation[8]. Several distinct trial structures were used as initial models in the geometry optimization calculations. The PRECISE and GNORM=0.1 options were used in all calculations for tightening the convergence criteria for all optimizations. The geometry optimizations were carried out at the restricted Hartree-Fock level (RHF). The structures obtained were characterized as true minimum energy in the PES through the frequency calculation (all positive frequencies correspond to minimum energy geometry). The calculations were performed using the MOPAC package Version 6.0.[9]

ACKNOWLEDGEMENTS

A.F.C. Alcântara would like to thank the Departamento de Química, ICEx, UFMG and the Departamento de Química, CCT, UFRR, for support. D. Piló-Veloso, H.O. Stumpf and W.B. De Almeida acknowledge the support from the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), the Fundação de Amparo a Pesquisa no Estado de Minas Gerais (FAPEMIG) and the Pró-Reitoria de Pesquisa da UFMG (PRPq). The authors are also grateful to Hélio F. Dos Santos (LQC-MM, UFMG) for reading the manuscript. Thanks are also due to the referees for their comments and useful suggestions.

REFERENCES

1. (a) Boocock, D. G. B; Darcy, R.; Ullman, E. F.; *J. Am. Chem. Soc.* **1968**, *90*, 5945-5946. (b) Kopf, P. W.; Kreilick, R.; Boocock, D. G. B.; Ullman, E. F.; *J. Am. Chem. Soc.* **1970**, *92*, 4531-4535. (c) Turek, P.; Nozawa, K.; Shiomi, D.; Awaga, K.; Inabe, T.; Maruyama, Y.; Kinoshita, M.; *Chem. Phys. Lett.* **1991**, *180*, 327-331. (d) Caneschi, A.; Gatteschi, D.; Rey, P.; Sessoli, R.; *Inorg. Chem.* **1988**, *27*, 1756-1761. (e) Stumpf, H, O.; Ouahab, L.; Pei, Y.; Grandjean, D.; Kahn, O.;. *Science*, **1993**, *261*, 447-449. (f) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Bergerat, P.; Kahn, O.; *J. Am. Chem. Soc.* **1994**, *116*, 3866-3874.
2. (a) Fuchs, B.; *Top.Stereochem.* **1978**, *10*, 1-94. (b) Legon, A. C.; *Chem.Rev.* **1980**, *80*, 231-262.
3. Poupko, R.; Luz, Z.; Zimmermann, H.; *J.Am.Chem.Soc.* **1982**, *104*, 5307-5314.
4. (a) Willy, W. E.; Binsch, G.; Eliel, E. L.; *J. Am. Chem. Soc.* **1970**, *92*, 5394-5402. (b) Lipnick, R. L.; *J. Mol. Struct.* **1974**, *21*, 423-429.
5. Carreira, L. A.; Jiang, G. J.; Person, W. B.; Willis, J. N.; *J. Chem. Phys.* **1972**, *56*, 1440-1443.

6. Ullman, E. F.; Osiecki, J. H.; Boocock, D. G. B.; Darcy, R.; *J. Am. Chem. Soc.* **1972**, *94*, 7049-7059.
7. (a) De Almeida, W. B.; O'Malley, P. J.; *J. Mol. Struct.(Theochem)* **1992**, *253*, 349-356. (b) Dos Santos, H. F.; *Msc Dissertation*, Universidade Federal de Minas Gerais, 1994. (c) De Almeida, W. B.; Dos Santos, H. F.; O'Malley, P. J.; *Structural Chemistry* **1995**, *6*, 383-389. (d) Do Val, A. M. G.; Guimarães, A. C.; De Almeida, W. B.; *J. Heterocyc. Chem.* **1995**, *32*, 557-562. (e) Dos Santos, H. F.; Taylor-Gomes, J.; Booth, B. L.; De Almeida, W. B.; *Vib. Spectrosc.* **1995**, *10*, 13-28.
8. Stewart, J. J. P.; *J. Comput. Chem.* **1989**, *10*, 209-220.
9. MOPAC Version 6.0: Stewart, J. J. P.; Frank J.Seiler Research Laboratory, U.S. Air Force Academy, Colorado Springs, CO 80840-6528, USA, 1990.
10. Csonka, G. I.; *J. Comp. Chem.* **1993**, *14*, 895-898.
11. (a) Gil, V. M. S.; Geraldes, C. F. G. C.; *Ressonância Magnética Nuclear - Fundamentos, Métodos e Aplicações*; Fund. Calouse Gulbenkian: Lisboa, 1987, pp. 232. (b) Friebolin, H.; *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH: Weinheim, 1993; pp. 53.
12. (a) Lamchen, M.; Mittag, T. W.; *J. Chem. Soc.*(C) **1966**, 2300-2303. (b) Osiecki, J. H.; Ullman, E. F.; *J. Am. Chem. Soc.* **1968**, *90*, 1078-1079. (c) Kreilick, R. W.; Becher, J.; Ullman, E. F.; *J. Am. Chem. Soc.* **1969**, *91*, 5121-5124. (d) Wittekind, R. R.; Capiris, T.; Fahey, J.; Shavel, J.; *J. Org. Chem.* **1973**. *38*, 1641-1645.
13. (a) Boocock, D. G. B.; Ullman, E. F.; *J. Am. Chem. Soc.* **1968**, *90*, 6873-6874. (b) Kopf, P. W.; Kreilick,R. W.; *J. Am. Chem. Soc.* **1969**, *91*, 6569-6573. (c) Ullman, E. F.; Call, L.; Osiecki, J. H.; *J. Org. Chem.* **1970**, *35*, 3623-3631.

(*Received in USA* 19 *February* 1997; *revised* 26 *September* 1997; *accepted* 29 *September* 1997)