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Nitronyl and Imino Nitroxide Free Radicals as Precursors of Magnetic Phthalocyanine and Porphyrin Building Blocks

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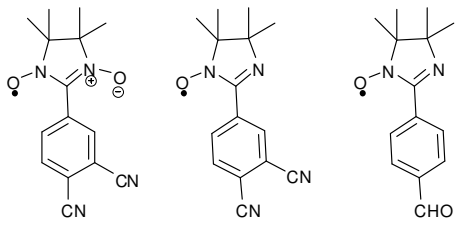
Abstract: Phthalonitrile and benzaldehyde bearing α-nitronyl and α-imino nitroxide free radicals have been synthesized as precursors of nitroxide substituted phthalocyanine and porphyrin macrocycle. To ascertain the structure and radical type they have been characterized by X-ray crystallography on single crystal and by Electron Paramagnetic Resonance spectroscopy (EPR). Their EPR spectrums coincide with those reported for previous nitroxides and are in a good agreement with literature. Electrospray ionization mass spectroscopy (ESI) was used as a complementary and an alternative technique. Depending on the nature of the radical, two ionization behaviors have been underscored; imino radicals were detected as the $[MH_2]^+$ cation ion and nitroxide radicals were detected as the $[MH]^{+\cdot}$ radical cation. This differentiation is pointed as an efficient and rapid method for preliminary characterization of the radical moieties and a judicious technique that allows the prompt detection of radical in low concentration and straightforward confirmation of the structure.

Introduction

The preparation of magnetic metal-organic frameworks, also call hybrid organic-inorganic material, is based on assembling carriers of magnetic moments. These may be the metal ions only, connected by diamagnetic linkers, or the metal ions connected by open-shell organic molecule. The latter case is the so called metal-radical approach[1, 2] which has proved to be particularly efficient for making molecule based magnetic materials.[3]

The building of novel magnetic metal-organic frameworks architectures, following the metal-radical approach, relies on the design of innovative open-shell organic molecular blocks. Following this approach, we focus our strategy on the synthesis of tetrapyrrolic compounds of the phthalocyanine or porphyrins type, incorporating nitroxide free radicals. Indeed, tetrapyrrolic compounds, which are π-conjugated systems, are expected to promote the spin delocalization on the overall macrocycle and further to favor the transmission of the magnetic interactions within the metal-organic frameworks. Several metalloporphyrins or metallophthalocyanines with nitroxide radicals substituted on the macrocycle[4-8] or coordinated on the metal center[9, 10] have been previously reported but generally with 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO).

Due to their excellent stability in a wide variety of chemical environments, and their ability to coordinate with transition metal we privileged α-nitronyl or α-imino nitroxide radicals. To the best of our knowledge there are no previous report on phthalocyanines and porphyrins bearing these radicals. Considering the general synthetic pathway of tetrapyrrolic compounds, the incorporation of nitroxide free radical into the macrocycles may be achieved either by adding them on the precursor of the macrocycle or afterward on the preformed macrocycle. This paper is concerned with the first approach. As phthalocyanines result from the cyclotetramerization of phthalonitrile derivatives and porphyrins from the condensation of pyrrole with benzaldehyde, it seems judicious to introduce the radical moieties on the phthalonitrile and benzaldehyde precursors. Accordingly, we report herein on the synthesis and characterization of 2-(3,4-dicyanophenyl)-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (**4)**, 2-(3,4-dicyanophenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl (**5)** and 2-(4-benzaldehyde)-4, 4, 5, 5-tetramethylimidazoline-1-oxyl (**9)**.



4 **5** **9**

Scheme 1: Targeted molecules

These α-nitronyl and α-imino nitroxide (**Scheme 1**) are appropriate precursors and are the first step among the many of the synthesis pathway that leads to nitroxide substituted phthalocyanines and porphyrins. Along the preparation of these precursors, our motivation has also been to find fast and readily characterization tools for the structural identification of the nitroxide free radicals and their synthesis intermediate. Such tools that can be later extended to the more complex systems that are the porphyrins and phthalocyanines bearing one or several nitroxide moieties. The Electron Paramagnetic Resonance spectroscopy (EPR) and X-ray crystallography are techniques of choice that are currently used to study and characterize nitroxide free radicals. However they may be not readily available. We point in this paper that routine Mass Spectrometry (MS) may be a rapid alternative and

complementary approach to obtain straightforward confirmation on the structure of these free radical molecule as has been also previously reported [11, 12] [13-15]

Results and Discussion

Synthesis of phthalocyanine and porphyrin precursors

The synthesis of α-nitronyl nitroxide or α-imino nitroxide compounds follows the Ullman[16-18] procedure resulting from the condensation of 2,3-bis(hydroxylamino)-2,3-dimethylbutane with an appropriate aldehyde followed by oxidation of the condensation product. Imino nitroxide are derivatives of nitronyl nitroxide that form through a hydrolysis process, generally favored by acidic conditions and reoxidation.[19] Considering the reaction pathway, we can see that an aldehyde function is a prerequisite for the introduction of a nitronyl and imino nitroxide moieties. In the case of phthalocyanines and porphyrins, the aldehyde group can be incorporated on the phthalonitrile or on the benzaldehyde precursors.

The synthesis of phthalonitrile bearing an aldehyde function[20, 21] requires the protection of the aldehyde group prior to cyanation of the dibrominated benzenic derivatives. Indeed, it is unstable to the severe conditions necessary for the Rosenmund-Von Braun cyanation reaction. To reduce the number of step, we decided to carry out the cyanation on the nitronyl and imino nitroxide of the dibrominated benzenic derivatives. That is to use the radical as a protecting group (see **Figure 1**). Accordingly 2-(3,4-dibromophenyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine **1** was obtained with a good yield and was oxidized by the standard oxidation protocol in a two phases mixture ($NaIO_4$, $NaHCO_3/H_2O//CH_2Cl_2$) to give predominantly nitronyl nitroxide 2-(3,4-dibromo)-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (**2**) with some imino nitroxide derivative 2-(3,4-dibromo)-4,4,5,5-tetramethylimidazoline-1-oxyl (**3**). Further, compounds **2** and **3** were separated and purified by column chromatography and use separately in the cyanation step

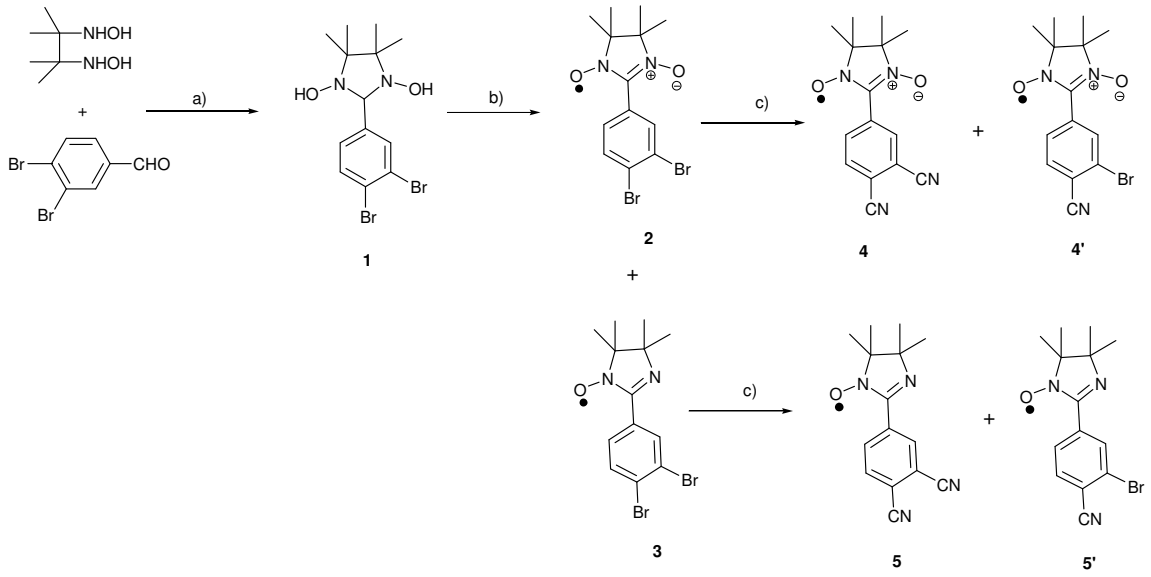


Figure 1: Synthetic pathway to nitronyl and imino nitroxide subtituded phthalonitrile. a) MeOH, reflux; b) $NaIO_4$, $NaHCO_3/CH_2Cl_2$; c)$Zn(CN)_2$, $Pd(PPh_3)_4$, DMF, 85^0C.

Synthesis of phthalonitrile derivatives (**Figure 1**) is always a delicate point. The cyano groups are introduced *via* nucleophilic aromatic substitution of the bromine by the Rosenmund-Von Braun reaction. Here, as the cyanation is carried out on the radical derivatives (**2** and **3**), classical conditions using copper cyanide for one-night refluxing in DMF[22] as well as microwave activation (copper cyanide, NMP, 30 min a 400 watt)[23] were not considered. Indeed, these conditions may kill the radical moiety. Instead, we use zinc cyanide in the presence of $Pd(PPh_3)_4$ in DMF at 85^0C as this was reported to have no interference on the radical moiety.[24] However, following this method compound **4** have been obtained with only 17% of maximum yield, instead of the 95% yield reported in the literature. This may be due to the high air sensitivity of $Pd(PPh_3)_4$ that complicate its use. Compounds 2-(3-bromo-4-cyanophenyl)-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (**4'**) and 2-(3-bromo-4-cyanophenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl (**5')** were isolated as sub-products. The X-ray diffraction single crystal structure of **4'** (**Figure 8**), demonstrates that the cyano group attack at the para position of the benzenic substituent first.

Concerning the benzaldehyde derivatives as precursor of porphyrins, two formyl functions have to be present here on the same molecule; one to be involved in the condensation with pyrrol to form the porphryrin macrocycle and a second one to be further used for the synthesis of the nitronyl niroxide radical. As the two formyl function of the

starting synthon on the 1,4-dibenzaldehyde are equivalent one formyl function was protected selectively with 2,2-dimethylpropane-1,3-diol[25] to obtain 4-(4,4-Dimethyl-2,6-dioxan-1-yl)benzaldehyde [26, 27]. This was reacted with 2,3-bis(hydroxylamino)-2,3-dimethylbutane to obtain (**6**) and then oxidized following the same protocol as for **1** ($NaIO_4$, $NaHCO_3/H_2O//CH_2Cl_2$) to get a mixture of predominant nitronyl nitroxide radical 2-[4-(4,4-dimethyl-2,6-dioxan-1-yl)benzene]-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (**7**) with some imino nitroxide derivative 2-(4,4-dimethyl-2,6-dioxan-1-yl)benzene]-4,4,5,5-tetramethylimidazoline-1-oxyl (**8**).

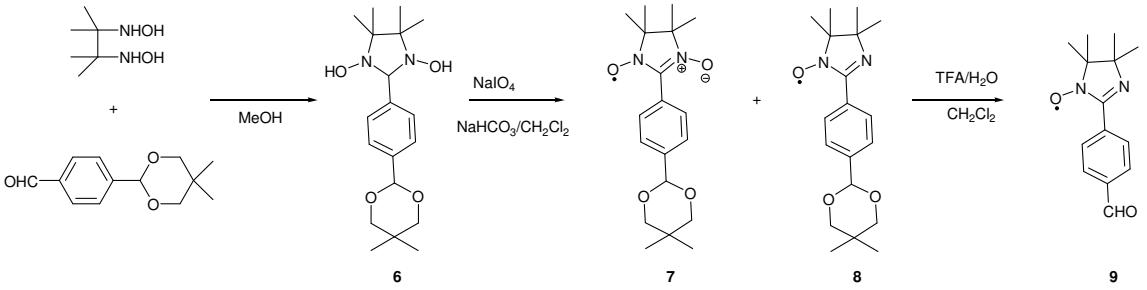


Figure 2: Synthetic pathway to imino nitroxide subtituded p-benzaldehyde. a) MeOH, reflux; b) $NaIO_4$, $NaHCO_3/CH_2Cl_2$; c)TFA/H_2O, CH_2Cl_2.

The non-protected formyl derivative (**9**) was recovered by reacting the raw mixture of (**7**) and (**8**) by trifluoroacetic acid (TFA) as describe for the deprotection of such group[28] and using a biphasic system made of CH_2Cl_2 and water as describe for the synthesis of nitronyl[16-18] and imino nitroxide radical.[19] The reaction was carried out on the raw mixture of (**7**) and (**8**) taking into account that acidic conditions change the nitronyl nitroxide in imino nitroxyde as mention earlier.[19] Accordingly and as expected, only the orange imino derivative was obtained by this way due to treatment by trifluoroacetic acid and further reoxidation by air here. It should be notified that although, 2-(4-benzaldehyde)-4,4,5,5-tetramethylimidazoline-3-Oxide-1-oxyl (**9**) has already been mentioned[12] there were no previous details of the synthesis.

Structural Characterization

Due to the paramagnetic nature of nitroxide, the use of NMR is precludes for structural characterization. X-ray diffraction on single crystal allows full and unambiguous structural

characterization but this may take time and is futile for non-solid radicals. Moreover this may be of little help during the synthesis process. Thus we were interested on developing a routine set of tools for a rapid and easy complete characterization of such compounds. EPR is of course a technique of choice for free radical but it gives structural information only of the region adjacent to the spin center and nitroxide with similar structure will generally yield identical spectra. Therefore EPR was used mainly in order to ascertain if the nitroxide radical was of nitronyl or imino type. For fully characterization, we found that Mass Spectrometry (MS), as has been also reported by others,[11, 12 13-15] is a complementary and a judicious technique that allows the prompt detection of radical in low concentration.

Electron Paramagnetic Resonance (EPR) Analysis

The X-band EPR measurements were carried out at ambient temperature on chloroform solution of nitronyl and imino nitroxide radicals.

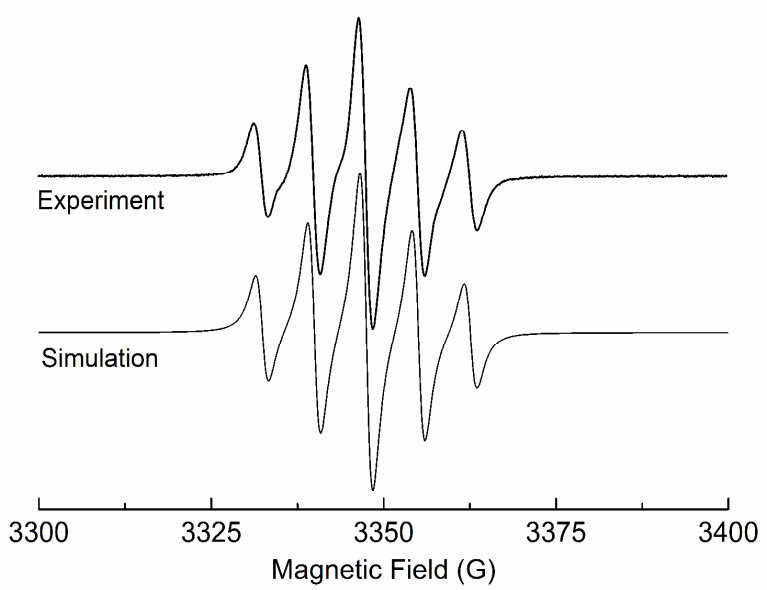


Figure 3: EPR (X-band, 9.404 GHz) spectrum of molecule **7** (10^{-4} M) in chloroform solution at ambient temperature

The EPR spectrum of **7** (**Figure 3**) is characteristic of nitronyl nitroxide monoradicals as it exhibits a quintet hyperfine structure with an intensity distribution in the ratio of 1:2:3:2:1, due to the interaction of the unpaired electron with the two equivalent nitrogen atoms (^{14}N, I = 1) in isotropic media. The nitronyl nitroxide radicals **2** and **4**, also show the similar hyper fine structure (see **supporting information S1**).

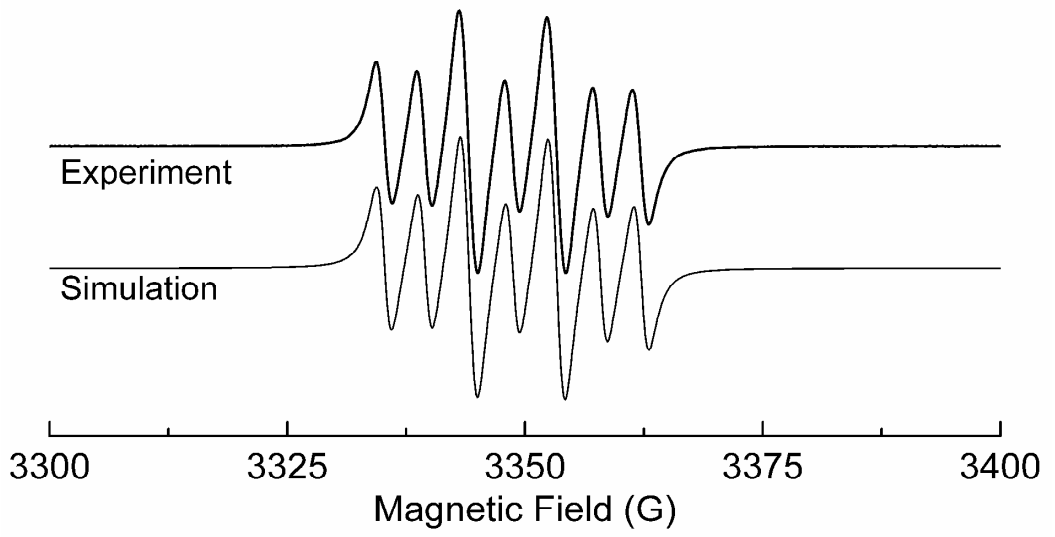


Figure 4: The EPR (X-band, 9.404 GHz) spectrum of Molecule **8** (10^{-4} M) in chloroform solution at ambient temperature.

The EPR spectrum of **8** (**Figure 4**) is meanwhile characteristic of imino nitroxide monoradicals. It has a seven line hyperfine structure with intensities ratio of 1:1:2:1:2:1:1 which arises from the interaction of the unpaired electron with the two non-equivalent nitrogen nuclei. The others imino nitroxide radicals **3**, **5** also show the same hyperfine pattern.

All spectra were simulated using Jeol IsoSimu and Winsim computer programs to extract the value of g, isotropic hyperfine coupling constant (a_N) and linewidth.[29] The best fitting parameters are given for all radicals in **Table 1**. These values are in agreement with those reported for previous nitroxides[17, 18] within the experimental errors.

Table 1. The g values and hyperfine coupling constants (a_N) of the nitronyl nitroxide **2**, **4**, **7** and imino nitroxide **3**, **5**, **8**, **9** radicals.

	Radical	g	a_N (Gauss)	Linewidth (Gauss)
Nitronyl	**2**	2.0078	7.49	1.90
nitroxide	**4**	2.0051	7.36	2.20
	7	2.0070	7.60	1.62
Imino	**3**	2.0071	a_{N1} = 9.15, a_{N2} = 4.32	1.65
nitroxide	**5**	2.0071	a_{N1} = 9.15, a_{N2} = 4.39	1.71
	8	2.0064	a_{N1} = 9.21, a_{N2} = 4.30	1.40
	9	2.0045	a_{N1} = 9.11, a_{N2} = 4.20	1.80

Mass Spectrometry (MS) Analysis

ESI-mass spectra of nitronyl nitroxide (**7, 2, 4**) and imino nitroxide (**8, 9, 3, 5**) radicals have been recorded using a mixture of THF: acetonitrile (3: 2 v/v). All ESI mass spectra were run in the positive ion mode. Molecular ions are, in general, intense and allow a ready mass spectrometric characterization of these compounds. Depending on the nature of the radicals, two different ionization behaviors are observed whose main peaks are gathered in **Table 2**.

Table 2. ESI-MS of nitronyl nitroxide **2**, **4**, **7** and imino nitroxide **3**, **5**, **8**, **9** radicals

	Nitronyl Nitroxide				Imino Nitroxide			
	2	**4**	**7**		**3**	**5**	**8**	**9**
Process	m/z	m/z	m/z	**Process**	m/z	m/z	m/z	m/z
i			259	**a**			218	133
ii			218	**b**			218	133
iii		203	317	**c**		187	251	149
iv		251	259	**d**		253	317	229
v	360	195	233	**e**		195	259	

--------				**f**			233	
MH_2-O^+	372			**MH_2-O^+**	358			
MH^+	389	284	348	**MH^+**				
-------				**MH_2^+**	374	269	333	247

Imino radicals were detected as the $[MH_2]^+$ ion and nitroxide radicals were detected as the $[MH]^{+\cdot}$ radical cation, contrary as it has been previously mentioned[11, 12], where imino as well as nitroxide radicals were detected as the $[MH_2]^+$ ion. Radicals that are substituted by acetal, cyano and aldehyde present fairly extensive fragmentation, whereas the bromine, an electron withdrawing group, exhibit only $[MH]^{+\cdot}$ or $[MH_2]^+$ ions as the major molecular species probably due to its low ionization potential. Such fragmentation behavior can be explained by the redox reaction that can take place in the spray nozzle of the ESI source. Some functional groups are more influenced by the source parameters, i.e. sample flow rate, sample concentration and spray voltage. ESI-MS spectra of **7** and **8** were given as example in **figure 5**, and show a major signal [**7**+ H]$^+$ at m/z 348.2096, [**8**+2H]$^+$ at m/z 333.2252 which could be attributed to the protonated hydroxylamine. [13-15] The fragmentation mechanism of nitronyl nitroxide (**7, 2, 4**) and imino nitroxide (**8, 9, 3, 5**) is illustrated in **Figure 6** for compounds **7** and **8** respectively according to previous report.[12]

Particularly, in the case of radicals bearing bromine (**2** and **3**) a significant abundance of $[MH_2\text{-}O]^+$ ions is observed resulting probably from a direct loss of O. Theoretical and measured isotopic patterns are also an additional identification tool to accurate mass determination of bromine compounds (**Figure S2**, supporting information).

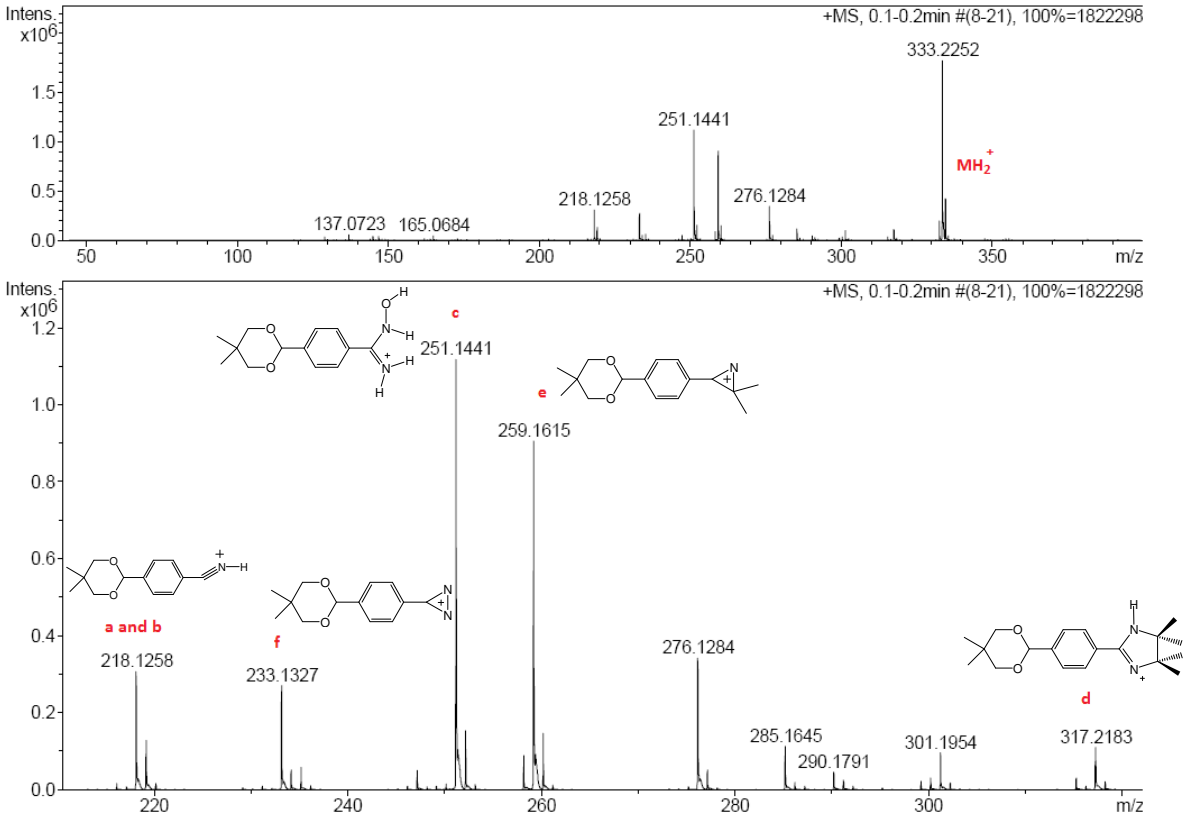


Figure 5: ESI-MS spectrum of imino nitroxide **8**.

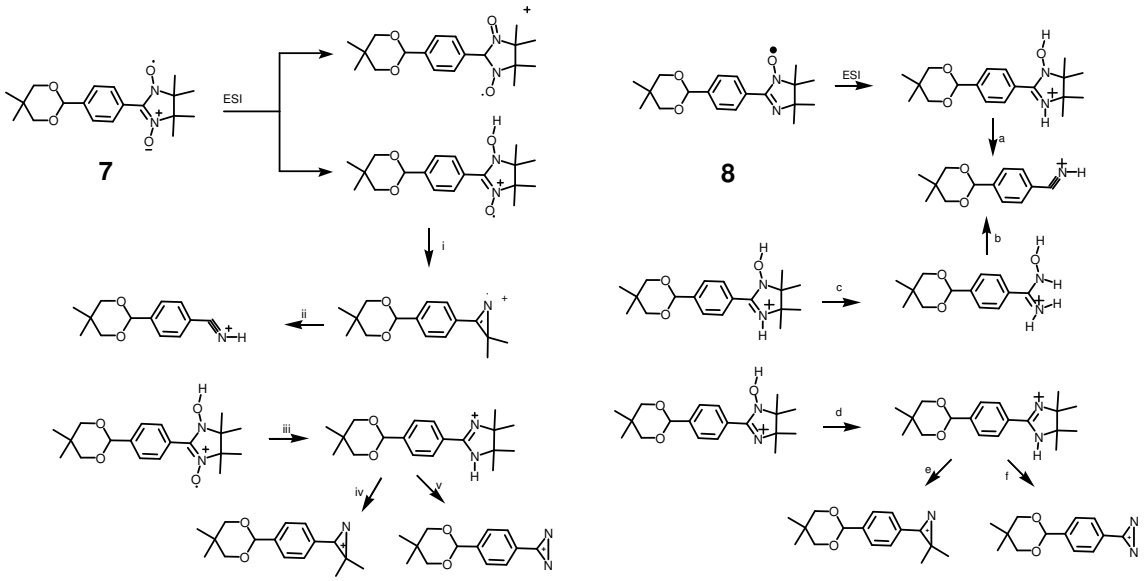


Figure 6: Proposed fragmentation mechanism of **7** and **8**

Consequently, ESI-MS is a quick-acting method to characterize radical moieties, as the fingerprint for nitroxide radicals is a $[MH]^{+\cdot}$ radical cation whereas the one of imino radicals is detected as the $[MH_2]^+$ ion.

X-ray crystallography Analysis

Single crystals suitable for X-ray studies were obtained for compounds **2**, **3**, **4'** and **8** and the structures were determined and confirmed. The crystal data and refinement parameters for compounds **2**, **3**, **4'** and **8** are summarized in **Table 3**. Selected bond lengths and angles are given in **Table 4**.

Table 3: Single-crystal X-ray diffraction data collection details and structure refinement results

Compounds	**2**	**3**	**4'**	**8**
Formula	$C_{13}H_{15}Br_2N_2O_2$	$C_{13}H_{15}Br_2N_2O_1$	$C_{14}H_{15}Br_1N_3O_2$	$C_{19}H_{27}N_2O_3$
Formula weight (g.mol-1)	391.07	375.08	337.20	331.43
Crystal System	orthorhombic	orthorhombic	monoclinic	monoclinic
Space Group	$Pca2_1$	$Pca2_1$	$P2_1/c$	$P2_1/c$
a (Å)	7.3552(5)	7.3060(4)	7.426(1)	6.177(5)
b (Å)	18.8781(8)	18.7395(9)	16.678(3)	13.704(5)
c (Å)	21.2531(15)	20.9306(11)	11.512(2)	21.888(5)
α (deg.)	90	90	90	90
β (deg.)	90	90	101.259(3)	94.245(5)
γ (deg.)	90	90	90	90
V (Å^3)	2951.0(3)	2865.6(3)	1398.2(4)	1848(2)
Z	8	8	4	4
T (K)	150	150	150	293
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
Density	1.760	1.739	1.597	1.188
μ (mm^{-1})	5.493	5.648	2.945	0.081
No. reflections used	2772	2438	2887	2354
No. refined parameters	343	334	181	217
R^a [I>=2σ (I)]	0.0334	0.0366	0.0365	0.0686
R^b [All data]	0.0791	0.0838	0.0944	0.1968
Flack parameter	-0.013(8)	-0.001(10)	-	-
S	1.010	1.020	1.047	1.06
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ (e$^-$. Å^{-3})	0.67/-079	0.80 / -0.52	0.67 / -0.69	0.31 / -0.34

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

Table 4. Selected bond lengths [Å] and angles [°].

	2A	2B	3A	3B	4'	8
O1-N1	1.282 (14)	1.269 (13)	1.248(7)	1.222(12)	1.273(3)	1.268(2)
O2-N2	1.282 (10)	1.279 (10)			1.277(3)	
N1-C7	1.341 (12)	1.352 (12)	1.383(8)	1.331(9)	1.356(3)	1.398(2)
N2-C7	1.366 (13)	1.347 (13)	1.327(9)	1.330(9)	1.354(3)	1.279(2)
N1-C1	1.482 (16)	1.482 (16)	1.473(8)	1.485(10)	1.508(3)	1.494(2)
N2-C2	1.492 (13)	1.508 (13)	1.327(9)	1.486(9)	1.506(3)	1.493(2)
C1-C2	1.544(11)	1.571(12)	1.572(10)	1.530(12)	1.548(3)	1.554(3)
N1-C7-N2	108.0 (9)	107.8 (9)	111.5(6)	112.8(6)	108.3(2)	113.04(16)

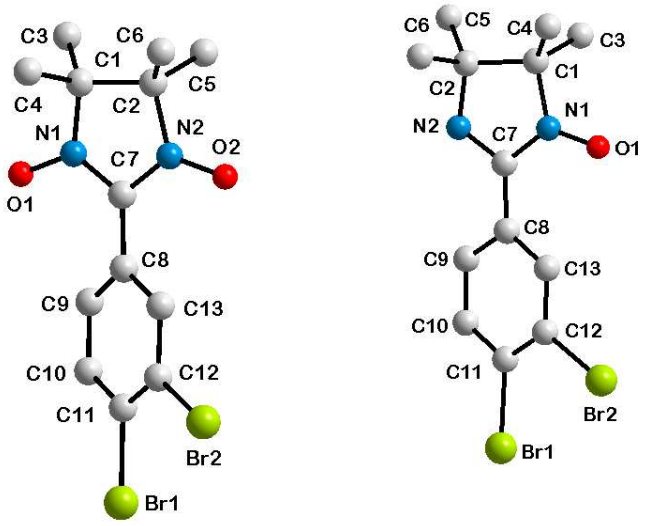


Figure 7: Representation of compound **2** (left) and compound **3** (right) from X-ray diffraction crystal structure. Hydrogen atoms are omitted for clarity.

Nitronyl nitroxide **2** and imino nitroxide **3** crystallize in the $Pca2_1$ space group of the orthorhombic crystal system with two independent molecules, labeled A and B, in the asymmetric units (**Figure 7**). Nitronyl nitroxide **4'** and **8** crystallize in the $P2_1/c$ space groups

of the monoclinic crystal system with one molecule per asymmetric unit (**Figure 8 and 9**). The bond lengths and angles are normal (**Table 4**). The main structural characteristics of **2, 3,** and **8** are unexceptional and similar to those previously described for nitronyl and imino nitroxides free radicals. Fragments 01-Nl-C7-N2-O2 of the nitronyl nitroxide and 01-Nl-C7-N2 of imino nitroxide, on which the unpaired electron is delocalized, are mostly planar and for **2, 3,** and **8** it departs greatly from planarity with adjacent phenyl ring as evidenced from the torsional angles 25.95° (**2** molecule A), 20.70° ° (**2** molecule B), 14.58° (**3** molecule A), 22.48° (**3** molecule B) and 34.78° (**8**). In contrast and surprisingly nitronyl nitroxide **4'** has a torsion angle of 1.50° which is one of the smallest ever found between the O-N-C-N and adjacent phenyl ring.[30, 31]

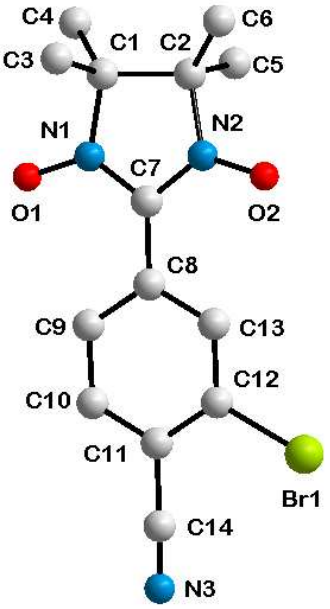


Figure 8: Representation of compound **4'** from X-ray diffraction crystal structure. Hydrogen atoms are omitted for clarity.

Compound 8 crystallizes in the $P2_1/c$ space group of the monoclinic crystal system with one molecule per asymmetric unit (**Figure 9**).

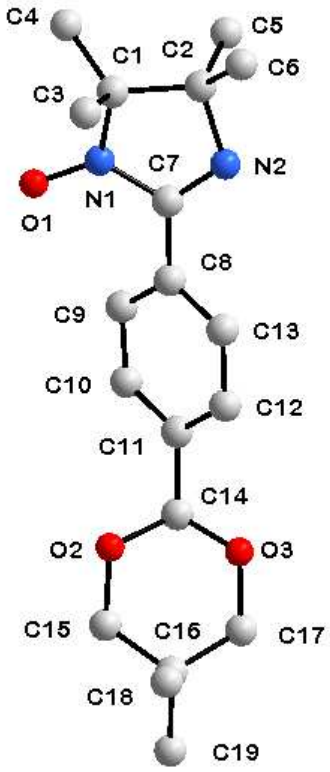


Figure 9: Representation of compound **8** from X-ray diffraction crystal structure. Hydrogen atoms are omitted for clarity.

Conclusion

Nitronyl and imino nitroxyde free radicals molecules 2-(3,4-dicyanophenyl)-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (**4**), 2-(3,4-dicyanophenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl (**5**) and 2-(4-benzaldehyde)-4, 4, 5, 5-tetramethylimidazoline-1-oxyl (**9**) have been synthesised. Their EPR spectrum which can be reproduced by spectral simulation coincide with those reported for previous nitroxides with a_N and g are in a good consistent with literature values. Depending on the nature of the radical, two ionization behaviors have been underscored; imino radicals were detected as the $[MH_2]^+$ cation ion and nitroxide radicals were detected as the $[MH]^{+\cdot}$ radical cation. This differentiation could be an efficient and rapid method for preliminary characterization of the radical moieties. These molecules are key precursors for the synthesis of paramagnetic phthalocyanine and porphyrin

macrocycles to be used as open-shell organic building blocks of molecule based magnetic materials. This work is underway and will be published afterwards.

Experimental

Mass Spectrometry: The mass analyzer was a Bruker Daltonics MicrOTOF mass spectrometer equipped with orthogonal electrospray ionization (ESI) source. The instrument was operated in positive or negative ion mode a capillary voltage of 39 V and a capillary temperature of 275 °C. Nitrogen was used as both the nebulizing gas (80 l h^{-1}) and as the drying gas (400 l h^{-1}). The solvent was a 3:2 v/v mixture of THF: acetonitrile with radical concentration $1x10^{-5}$M. All solvents (HPLC grade) were commercially available and were used without further purification.

EPR spectrometry: EPR assays were performed at room temperature in oxygen media. The EPR solution spectrum was recorded with Bruker Elexsys e500 X-band (9.4 GHz) spectrometer and Jeol JES FA 300 X-band (9.6 GHz) spectrometer, with 100 kHz magnetic field modulation. The following conditions were used: 0.64 mW microwave power, 1 G modulation amplitude, 335 sec sweep time, 20 msec time constant. Modulation amplitude was kept below of the estimated peak-to-peak width for all spectra

Single-crystal X-ray diffraction: The data have been collected using a Xcalibur diffractometer and the related analysis software.[32] The structure was solved using the SIR97 program[33] and refined by full-matrix least-square methods on F^2 using the SHELXL-97 program package[34] using the WingX platform.[35] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms belonging to carbon atoms were placed geometrically in their idealized positions and refined using a riding model. Crystallographic data are presented in **Table 3**. Selected bonds lengths and bond angles are collected in **Table 4**. Crystal data of radical **2**, **3** and **4'** were collected at low temperature in a tentative to improve the refinement of crystal structure.

Synthesis : Starting materials were purchased from Aldrich, Fluka, and Alfa and used without further purification unless otherwise stated. 3,4-dibromobenzaldehyde[36] 2,3-

bis(hydroxyamino)-2,3-dimethylbutane[37] and 4-(4,4-Dimethyl-2,6-dioxan-1-yl)benzaldehyde[26, 27] were synthesize as previously described.

2-(R)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine: General procedure for **1** and **6.** Condensation of aldehyde (1.3 mmol) and 2,3-bis(hydroxyamino)-2,3-dimethylbutane (2 mmol; 1,5 equiv) in MeOH was complete after a night at reflux. Solution was dried with Na_2SO_4 and solvent was evaporated to provide crude 2-(3,4-dibromophenyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (**1**), 2-[4-(4,4-dimethyl-2,6-dioxan-1-yl)benzene]-4,4,5,5-tetramethylimidazoline (**6**) respectively. The crude compounds were used for the following steps without further purification.

Nitronyl Nitroxides 2 and 7: In a typical experiment, **2-(R)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine** (2,5 mmol) was dissolved in a mixture of dichloromethane (40 mL) and a saturated solution of $NaHCO_3$ (20 mL). The solution was cooled in an icebath and a solution of $NaIO_4$ (3,75 mmol, 1.5 equiv) in water (40 mL) was added dropwise. The color was converted to intense blue. The organic phase was dried with Na_2SO_4 and concentrated. The residue obtained was chromatographed (SiO_2, hexane/ethylacetate (2:1)) giving 2-(3,4-dibromo)-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (**2**) (yield: 83%) and 2-[4-(4,4-dimethyl-2,6-dioxan-1-yl)benzene]-4,4,5,5- tetramethylimidazoline-3-oxide-1-oxyl (**7**) as dark-blue crystals (Yield: 60%.)

Imino Nitroxides 3, 5 and 8: Imino radicals were obtained in low yield as by-products in the syntheses of the corresponding nitronyl nitroxides or quantitatively from nitronyl nitroxides by a reported procedure.[19]

2-(4-benzaldehyde])-4,4,5,5-tetramethylimidazoline-3-Oxide-1-oxyl (**9**)**:** A solution of 2-[4-(4,4-dimethyl-2,6-dioxan-1-yl)benzene]-4,4,5,5-tetramethylimidazoline-3-Oxide 1-oxyl (**7**) (0.03 g, 0.09mmol) in DCM (10 mL) was treated with TFA/water (1 mL, 1:1) to give a biphasic mixture. After stirring at room temperature for 30 min, DCM was added. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine solution, dried over Na_2SO_4 and evaporated. The residue obtained was chromatographed (SiO_2, ethyl acetate) to give a yellow solid (0.02 g, 0.085 mmol). Yield 95% .

2-(3,4-cyano)-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (4)

Dry, deoxygenated 0.3 mL DMF was added to **2** (80 mg, 0.205 mmol), $Zn(CN)_2$ (57 mg, 4936 mmol, 2.4 equiv) and $Pd(PPh3)_4$ (118 mg; 0.10 mmol, 0.5 equiv) under Argon. The mixture was heated at 85 ^oC with stirring for 5 h, then cooled to room temperature, diluted with 8% aqueous NH_3 (40 mL) and extracted with CH_2Cl_2. The organic phase was washed with 6% aqueous NH_3 (20 mL), brine (20 mL) and dried over Na_2SO_4. After evaporation of DCM the crude product was purified by column chromatography through silica gel using hexane/ethyl acetate (5/1) as eluent, giving 10 mg of 2-(3,4-dicyanophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl 3-Oxid(**4**) as dark-blue solid (yield: 17%)

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Supplementary data

Checkcif files of compounds **2**, **3**, **4'** and **8** (Cambridge database number CCDC-996671-996674), are available free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk). EPR and mass spectrometry spectra of all the radical compounds are available. Supplementary data associated with this article can be found in the online version, at doi.....

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