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Stable free imino and nitronyl nitroxyl radicals of the acetylene series: synthesis, electronic absorption spectra and magnetic resonance parameters

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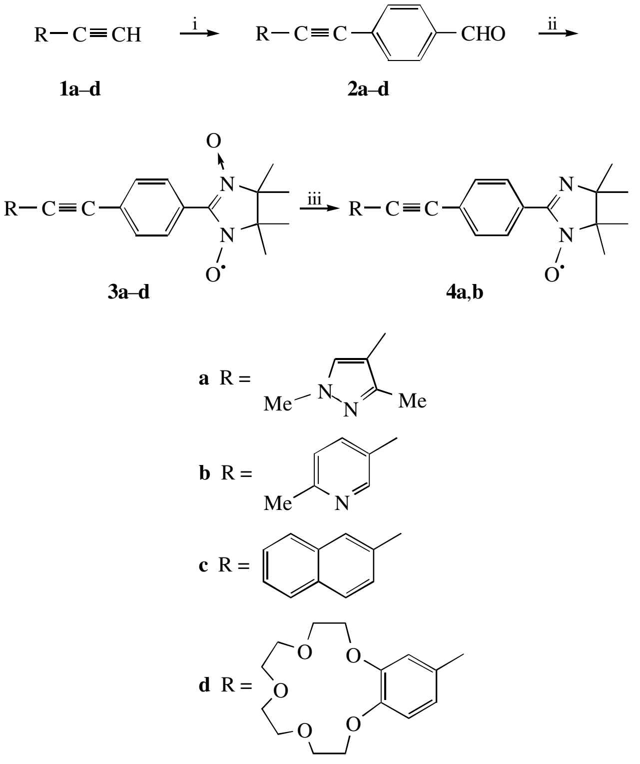
Methods for the synthesis of aryl(hetaryl)ethynylphenyl-2-imidazoline nitroxides have been developed; the *g*-tensor and HFI components for imidazoline-1-oxyl were found to depend (in contrast to imidazoline-3-oxide-1-oxy derivatives) on the properties of substituent at the 2-position.

The practical solution of the problem of creating new classes of optical and magnetic materials (molecular ferromagnetics, liquid crystals and photosensitive switches) is hampered by rigid electron and steric requirements on a substrate.[1,2] In this context, radicals with triple bonds, in which the coordination centre (a functional group at an aromatic ring or a heteroatom in a heterocycle) and the paramagnetic unit are bound by a rigid phenylacetylene bridge included in the entire molecular conjugation system, are rather promising.

The appropriate use of magnetically active compounds considerably depends on the accuracy and completeness of the optical and magnetic parameters of spin-labelled compounds. As far as we know, systematic studies of 2-imidazoline nitroxides by 2 mm band EPR spectroscopy were not conducted. The magnetic parameters of only one derivative of imidazoline-1-oxyl and one imidazoline-3-oxide-1-oxyl were measured.[3] In this study, we examined previously unknown acetylene derivatives of nitroxide radicals from the 2-imidazoline series using electronic absorption spectroscopy and 2 mm band EPR spectroscopy. We found for the first time that the substituent at the 2-position of an imidazoline unit poorly influences the magnetic-resonance parameters of imidazoline-3-oxide-1-oxyl. At the same time, components of the *g*-tensor and HFI constants of imidazoline-1-oxyl derivatives essentially depend on the nature of the substituent at the 2-position. The structure of spin-labelled acetylenes includes either heterocyclic (-electron-rich pyrazole and -electron-deficient pyridine) or -carbocyclic residues, including a benzocrown ether, and derivatives of 4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl [nitronylnitroxyl (NN) radicals] and 4,4,5,5-tetramethylimidazoline-1-oxyl [iminonitroxyl (IN) radicals] as stable radical components. NN and IN radicals were produced according to Scheme 1.



Scheme 1 *Reagents and conditions*: i, *p*-bromobenzaldehyde, Pd(OAc)$_2$, CuI, PPh$_3$, NEt$_3$, C$_6$H$_6$, 40–80 °C;[4] ii, 2,3-dimethyl-2,3-bis(hydroxylamino)-butane, MeOH, 25 °C, then NaIO$_4$, CH$_2$Cl$_2$, water, 15 °C;[5,6] iii, NaNO$_2$, AcOH, CHCl$_3$, 60 °C.[5]

The synthesis of new nitronylnitroxyls **3a**–**d** was performed by condensation of aldehydes with 2,3-dimethyl-2,3-bis(hydroxylamino)butane and subsequent oxidation of cyclic adducts by sodium periodate. Iminonitroxyls **4a**,**b** were produced by reducing NN radicals **3a**,**b** with sodium nitrite in the presence of glacial acetic acid.[†] Initial acetylene compounds **2** were obtained *via* cross-coupling of corresponding ethynyl derivatives **1** with *p*-bromobenzaldehyde in the presence of Pd(PPh$_3$)$_2$(OAc)$_2$, CuI and NEt$_3$.

[†] The structure of all new compounds were proved by elemental analyses and spectroscopic data. Examples of detailed procedures of synthesis of NN radicals **3b** and IN radicals **4b** were given below.

2-[4-(6-Methylpyridinyl-3-ethynyl)phenyl]-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl **3b**:

(1). 1.60 g (0.011 mol) of 2,3-dimethyl-2,3-bis(hydroxylamino)butane in 50 ml of methanol was added at –30 °C to the suspension of 2.21 g (0.01 mol) of aldehyde **2b** in 40 ml of methanol. Thereafter, the reaction mixture was mixed up at room temperature for five days and diluted by 40 ml of diethyl ether. The precipitate was filtered, washed out by 20 ml of ether and recrystallised from ethyl acetate. The yield of 1,3-hydroxy-2-[4-(6-methylpyridinyl-3-ethynyl)phenyl]-4,4,5,5-tetramethylimidazoline (adduct) was 2.84 g (80.9%). Mp 163–165 °C. ^{1}H NMR ([^{2}H$_6$]DMSO) δ: 1.04 (s, 6H, Me), 1.09 (s, 6H, Me), 2.51 [s, coincides with a solvent signal, Me (Py)], 7.37 [d, 1H, -H (Py)], 4.54 [s, 1H, CH (Im)], 7.50–7.58 (m, 4H, Ph), 7.81 (s, 2H, OH), 7.86 (d, 1H, -H), 8.65 (d, 1H, -H). IR (KBr, ν/cm^{-1}): 2220 (C≡C), 3500 (O–H). Found (%): C, 71.22; H, 7.45; N, 11.46. Calc. for C$_{21}$H$_{25}$N$_3$O$_2$ (%): C, 71.77; H, 7.17; N, 11.96.

(2). The solution of 0.39 g (0.018 mol) of NaIO$_4$ in 15 ml of water cooled to 10 °C was added by mixing to the suspension of 0.43 g (0.012 mol) of adduct in 15 ml of chloroform. The mixture was stirred for 8 h. The chloroform layer was separated and the water layer was extracted by chloroform (2×15 ml). Organic extracts were dried by CaCl$_2$ and concentrated *in vacuo* to intimate mass. The residue was chromatographed on silica gel (eluent chloroform). The dark blue oil resulting from eluate distillation was rubbed up with hexane. The forming dark blue crystals were filtered, washed with hexane and recrystallised from a 3:1 hexane–benzene mixture. Yield of **3b** was 0.3 g (70.4%). Mp 165–166 °C. IR (KBr, ν/cm^{-1}): 2215 (C≡C). Found (%): C, 72.68; H, 6.29; N, 12.43. Calc. for C$_{21}$H$_{22}$N$_3$O$_2$ (%): C, 72.39; H, 6.36; N, 12.06.

2-[4-(6-Methylpyridinyl-3-ethynyl)phenyl]-4,4,5,5-tetramethylimidazoline-1-oxyl **4b**: 0.60 g (0.0017 mol) of **3b**, 0.5 g of NaNO$_2$ and 0.1 ml of glacial acetic acid in 30 ml of chloroform were mixed up upon boiling for 30 min. The reaction mixture was filtered through silica gel. The solvent was distilled *in vacuo*. The residue was recrystallised thrice with activated coal from hexane. Yield of **4b** was 0.41 g (71.6%). Mp 155–155.5 °C. IR (KBr, ν/cm^{-1}): 2228 (C≡C). Found (%): C, 75.74; H, 6.62; N, 12.44. Calc. for C$_{21}$H$_{22}$N$_3$O$_2$ (%): C, 75.88; H, 6.67; N, 12.64.

Table 1 Visible spectra of NN and IN radicals.

Radical	ν/cm^{-1} (ε/l mol^{-1} cm^{-1})					
3a	13900 sh (120)	15200 (295)	16500 (310)	17700 sh (210)	20000 (145)	21500 (135)
3b	13650 sh (60)	15150 (190)	16300 (210)	18300 sh (140)	19900 (145)	21500 (150)
3c	13680 sh (100)	15120 (318)	16300 (350)	17570 sh (230)	19120 sh (100)	
3d	13700 sh (110)	15000 (310)	16400 (330)	17700 sh (215)		21500 sh (60)
4a	18900 (340)	20300 (600)	21300 (610)	22800 sh (485)	24000 (515)	25500 sh (540)
4b	18690 (305)	20130 (540)	21420 (560)	22960 (500)	24480 sh (440)	25920 (530)

Table 2 Near-UV spectra of NN and IN radicals.

Radical	ν/cm^{-1} (ε/l mol^{-1} cm^{-1})					
3a	26100 (9800)	29300 (25600)	30500 (29900)			34850 (13300)
3b	26000 (7780)	27000 (4450)	29400 sh (18900)	31000 (29300)	32100 sh (26800)	34200 sh (19800)
3c	25760 (10200)	28720 (33800)	30000 (39700)	31680 sh (30300)	34080 (26200)	35440 (19700)
3d	26000 (12900)	29300 (38500)			33900 sh (19000)	
4a	29100 sh (6600)	30900 (27400)	32500 (28000)	34900 sh (20200)		
4b	28190 sh (1640)	31000 sh (25200)	32740 (33970)	34400 sh (29590)		

The electronic absorption spectra of NN and IN radicals have two sets of bands in the visible and near-UV regions of the spectrum (Figure 1, Tables 1 and 2).[‡] The splitting of both groups (visible and UV regions) is related to the vibrational structure of electronic transitions (characteristic frequencies of 1200–1500 cm^{-1}). The absorption bands of IN radicals are shifted towards a short-wave region to change the colour of these radicals. It should be noted that all NN radicals are blue both in the solid state and in solution, and IN radicals are red.

The radicals of the same group with different structures have similar optical absorption spectra. This fact indicates that electronic transitions involve only the groups O–N–C–N–O or O–N–C–N. In the case of NN radicals, an increase in the size of such a group leads to the general shift of bands to the red spectrum region.

A set of long-wave absorption bands (peaks at about 16500 cm^{-1} for NN radicals and 21500 cm^{-1} for IN radicals) with small molar absorption coefficients refers to n–π* transitions involving the lone electron pairs of oxygen atoms. For many imidazoline nitroxyl radicals with isolated N–O groups, a similar band[7] is observed in the region 2400–2100 cm^{-1}. The band in the UV region also has a vibrational structure (peaks at about 30500 cm^{-1} for NN radicals and 32600 cm^{-1} for IN radicals). The high intensity of this band allows it to be referred to the resolved π–π*-transition. For imidazoline radicals with isolated N–O groups, this band is also shifted to the short-wave region[7] (40500–42500 cm^{-1}). Thus, the UV and visible spectra of all radicals are determined by the presence of groups at which an unpaired electron is delocalised.

A fundamental parameter characterising the EPR signals of radicals is g-tensor which depends on the electronic structure and the environment of the radical. In this case, a conventional X-band technique (wavelength of 3 cm and frequency of 9.6 GHz) of determining g-tensors is ineffective because the anisotropy and the mean values of g-tensors for most organic radicals are responsible for the spacing between the lines of different components of about several gauss, which is comparable with the linewidth. The use of a 2 mm wave allows one to get the g-factor resolution up to 10^{-5} by increasing the Zeeman interaction by one order of magnitude. This accuracy makes it possible to determine all g-tensor components, which are individual parameters of radicals.

Figure 2 shows the EPR spectra for the two studied radicals with defined g-tensors and HFI components. The EPR spectra of other radicals have a similar shape.[§] The spectra display three lines whose positions are determined by orientations of the magnetic field along each of the principal axes of the g-tensor. The positions of the centres of three components allow one to determine the principal values of a g-tensor (g_{xx}, g_{yy}, g_{zz}). The hyperfine interaction with one or two nitrogen nuclei leads to additional splitting of components. In most cases, it is possible to detect the splitting of a Z-component into five lines upon the interaction with two equivalent nitrogen nuclei (Figure 2, NN radical **3a**). If two nitrogen nuclei are non-equivalent (IN radicals), the Z-component splits into seven components (Figure 2, IN radical **4a**) owing to the overlapping of two pairs of the lines. Table 3 shows the magnetic resonance parameters of radicals **3a**–**d**, **4a**,**b**, which were obtained by analysing the line positions in 2 mm band EPR spectra.

Parameters of the EPR spectra of radicals **3a**–**d** are close to each other; this fact indicates a weak influence of peripheral groups on the orbital of an unpaired electron. The magnetic parameters of IN radicals **4a**,**b** differ considerably from each other and from the parameters of NN radicals. In this case, it is likely that substituents have a strong effect on the behaviour of the unpaired electron.

If we approximate the π-system of the symmetric group O–N–C–N–O for the NN radical by the π-system of a pentadienyl radical, the unpaired electron is located on the fourth lower orbital (the total number of electrons is seven), which has the form

$$\Psi_4 = 0.5(\varphi_1 - \varphi_2 + \varphi_4 - \varphi_5) \tag{1}$$

It can be seen that the p-orbital of the central carbon atom (φ_3) is not included in the molecular orbital of the unpaired electron. Therefore, the variation of substituents in the group coupled with the π-system *via* this carbon atom should not have any effect on both the spin density distribution and the change in the spin-Hamiltonian parameters of the radicals. The replacement of carbon atoms by heteroatoms on going from a pentadienyl radical to the group O–N–C–N–O will result in a change in the coefficients of the pairs (φ_1, φ_5) and (φ_2, φ_4). However, a zero coefficient of φ_3 will be the same due to the conservation of the plane of symmetry upon this transition.

For IN radicals **4a**,**b**, the π-system of the group N–C–N–O can be replaced, as described above, by the π-system of butadiene with five electrons, and the orbital of the unpaired electron will have the form

$$\Psi_3 = 0.6(\varphi_1 + \varphi_4) - 0.37(\varphi_2 + \varphi_3) \tag{2}$$

Table 3 The g-factors and HFI constants of radicals **3a**–**d**, **4a**,**b**.

Radical	g_{xx}	g_{yy}	g_{zz}	$A_{zz}(1)$	$A_{zz}(2)$
3a	2.0110	2.00660	2.00210	18.9	18.9
3b	2.0110	2.00660	2.00200	19.3	19.3
3c	2.0110	2.00660	2.00210	18.3	18.3
3d	2.01107	2.00665	2.00205	18.4	18.4
4a	2.00980	2.00607	2.00186	23.0	12.1
4b	2.01070	2.00590	2.00146	30.8	18.6

[‡] The optical spectra of radical solutions in benzene or toluene (‘cp’ grade) have been recorded on a ‘Specord UV-VIS’ (Karl Zeiss) spectrophotometer using quartz cuvettes with a 0.1–1 cm optical thickness. Radical concentration was varied from 10^{-4} to 10^{-3} M. The accuracy of determination of the position of absorption band maxima was ±50 cm^{-1} and that of extinction coefficients was ±5%.

[§] The EPR spectra were recorded on an 2 mm-band spectrometer (frequency being 130–150 Hz) with a superconducting solenoid produced in the CB of Donetsk Physico-Technological Institute of UAS. Radical solutions in toluene were placed in quartz capillaries with a diameter of 0.3–0.5 mm and length of about 1 cm. The field was calibrated with respect to a standard (Mn^{2+} in MgO lattice).[8] The accuracy of determination of g-tensor components was 7×10^{-5}, that of HFI constants was 0.5 G. The temperature at which the spectra were recorded amounted to 130–140 K.

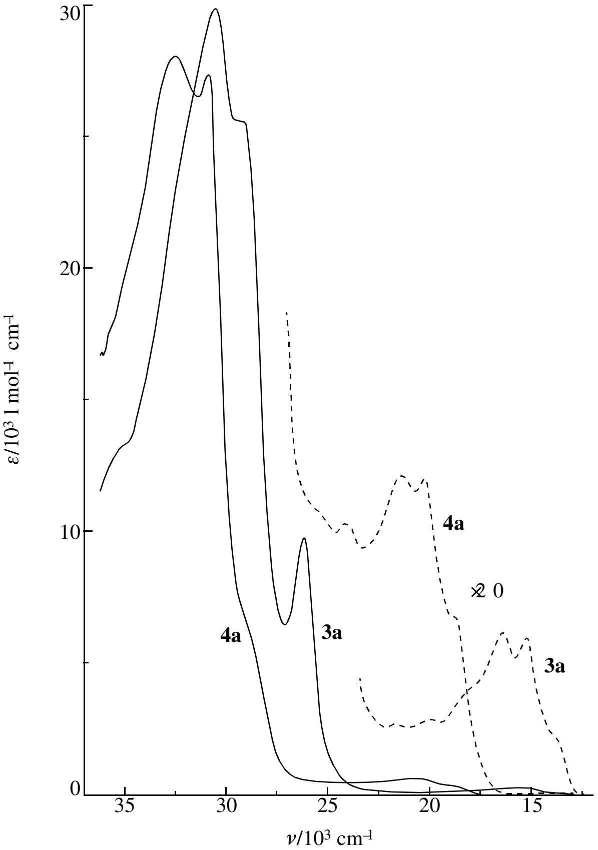


Figure 1 Electronic absorption spectra of nitroxyl radicals **3a** and **4a** in benzene.

In this case, the *p*-orbital of the carbon atom (φ_3) is included in the Ψ_3 orbital, and any perturbations in the coupled -system will have an effect on the wave function of the unpaired electron. For the Ψ_3 function, the spin density at the second centre, which corresponds to the first nitrogen atom, is much smaller than the spin density at the fourth centre (the second nitrogen atom). However, this function corresponds to the butadiene -system. When changing the Coulomb integrals corresponding to the replacement of carbon atoms by heteroatoms ($_1 \approx$, $_2 \approx 2$, $_4 \approx 2$),[9] the exact solution in the framework of the Hueckel approximation or the use of the perturbation theory causes a sharp redistribution of spin density. The perturbation theory gives, for example, the values

$$\rho_1 = \rho_0 = 0.69, \rho_2 = \rho_{\mathrm{N1}} = 0.107, \rho_3 = \rho_{\mathrm{C}} = 0.18, \rho_4 = \rho_{\mathrm{N2}} = 0.023 \quad (3)$$

The spin density is larger at the first nitrogen atom, which corresponds to the large HFI constant $A_{zz}(1)$ compared to $A_{zz}(2)$ for the IN radicals (Table 3). The A_{zz} values of about 33 G are typical of imidazoline radicals with isolated N–O groups.[3,10] Lower A_{zz} values for the NN and IN radicals are related to a decreased spin density at nitrogen atoms in more extended systems.

It is well known that the deviation of g_{xx} components from the *g*-factor for a free electron can be estimated by the formula[3]

$$g_{xx} \cong \frac{\lambda \rho_{\mathrm{O}}}{E_{n\ *}} \quad (4)$$

where λ is the spin–orbital coupling constant for an oxygen atom ($\approx$ 70 cm^{-1} for a free atom), ρ_{O} is the spin density at the oxygen atom and $E_{n\ *}$ is the energy of the long-wave *n*– * transition (Table 1). Even with $\rho_{\mathrm{O}} \approx 1$ and $E_{n\ *} \approx 16500$ cm^{-1} (Table 1), $g_{xx} \approx 4.2\times10^{-3}$; this value is lower than the experimental value ($g_{xx} \approx 8.7\times10^{-3}$) for NN radicals by a factor of two. If we take into account both a decrease in the spin–orbital coupling in the molecules compared to that in isolated atoms and the ρ_{O} values really lower than unity, the difference between g_{xx} calculated by formula (4) and the experimental values increases. This disagreement can be due to the lower-energy excited states, the transition to which is forbidden by both symmetry and spin, and which are not manifested in the optical spectra. Thus, a decrease in the *g*-factor upon the transition from NN to IN radicals can be caused by both a change in the spin density ρ_{O} and an increase in the energy of transition into the state defreezing the orbital moment. Of course, the accurate determination of the electronic structure and geometry of radicals from the experimental values of magnetic parameters (*g*-factors and HFI constants) needs further quantum-chemical calculations.

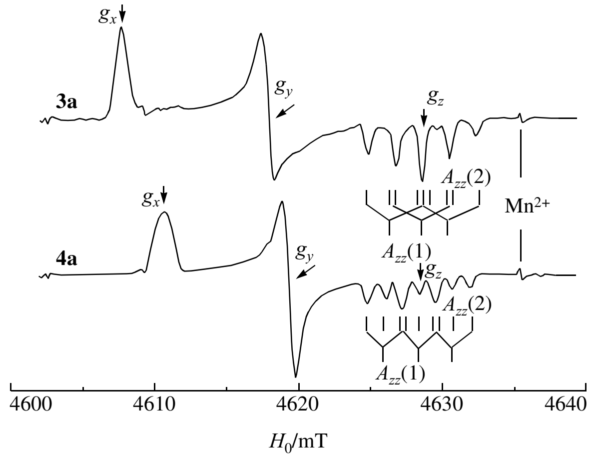


Figure 2 2 mm band EPR spectra of radicals **3a** and **4a** (5×10^{-5} M) in oxygen-free toluene at 130–140 K.

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