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Synthesis of nitronyl- and imino-nitroxide-triradicals interconnected by phenyl ethynyl spacer

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Abstract

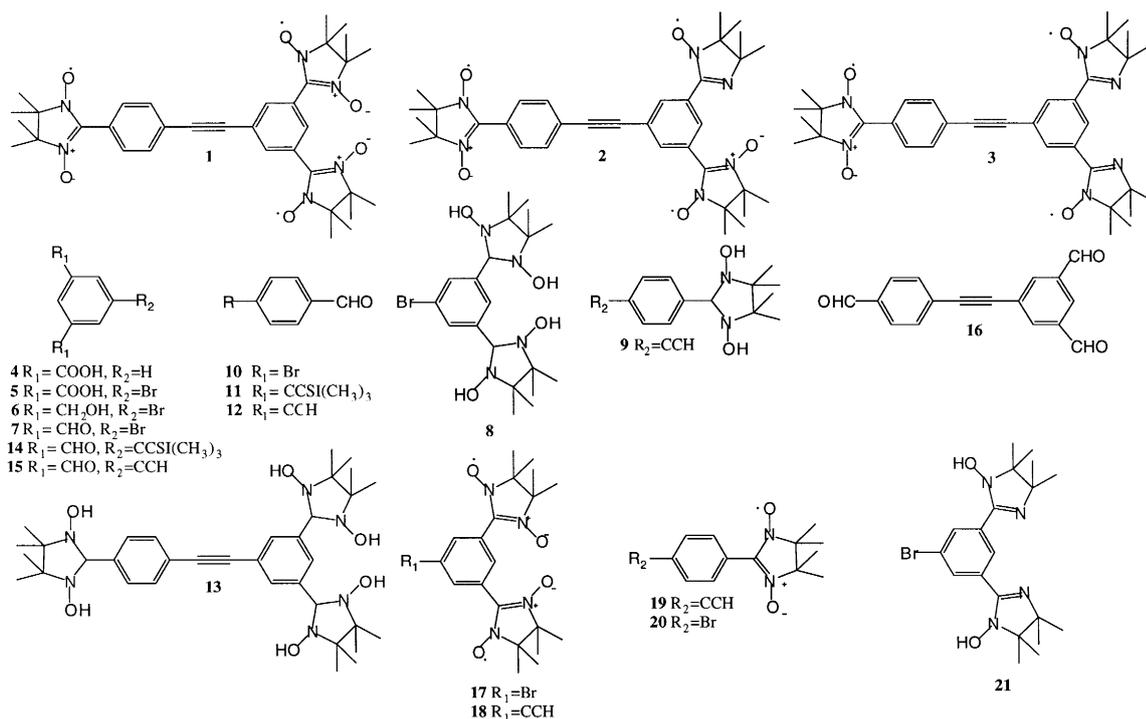
The design and synthesis, as well as solid state and ESR characterisation of three new triradicals based on phenyl ethynyl backbone bearing nitronyl-nitroxide and imino-nitroxide groups, are reported. The synthesis of these compounds was based on palladium-coupling reactions between alkynyl and bromo derivatives. An ESR study showed magnetic interactions between the radicals through the phenyl ethynyl-coupling unit in solution. © 2000 Published by Elsevier Science Ltd. All rights reserved.

In the area of molecular magnetism, purely organic materials based on radicals are still under active investigation.¹ High spin organic molecules may be obtained through interconnection of paramagnetic centres using an active magnetic coupling unit (MCU). In order to achieve ferromagnetic coupling, the positioning of unpaired electrons relatively to the MCU and the nature of the latter must fulfil electronic as well as topological rules.² The assessment of the nature and the strength of the magnetic interactions through the MCU units requires model systems based on oligoradicals which may be of interest for understanding more complex polyradicals.³

Here, we report the design and synthesis, as well as structural determination and ESR characterisation of three new triradicals **1**, **2** and **3**, based on phenyl ethynyl backbone bearing nitronyl-nitroxide and imino-nitroxide groups. The homotrimeric **1** is based on three nitronyl-nitroxide units, whereas the other two hetero systems **2** and **3** are based on a combination of nitronyl-nitroxide and imino-nitroxide moieties. The phenyl ethynyl spacer has been previously used as a connector between two identical radicals.⁴

For the synthesis of compounds **1** and **2**, three different strategies based on palladium-catalysed coupling reactions⁵ between alkynyl and bromo derivatives were investigated (Scheme 1). The first strategy was based on the Pd-coupling of compounds **8** and **9** both bearing the *N,N'*-dihydroxyimidazoline moiety.

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Scheme 1.

Compound **8** was obtained in four steps starting from the commercially available isophthalic acid **4**. Bromination of **4** by bromine in sulfuric acid in the presence of silver sulfate afforded the compound **5** in 86% yield.⁶ The reduction of the latter by $\text{BH}_3 \cdot \text{THF}$ gave the diol **6** in 93% isolated yield.⁶ Oxidation of **6** using pyridinium chlorochromate at room temperature afforded the dialdehyde **7** in 82% yield.⁷ Condensation of **7** in methanol with a slight excess (2.3 equivalents) of *N,N'*-dihydroxy-2,3-diamino-2,3-dimethylbutane, prepared in two steps following the published procedure,⁸ gave the compound **8** in high yield. It is worth noting that the high yield of 90–95% for the compound **8** could only be obtained upon slow bubbling of argon into the reaction mixture at room temperature and over a period of 3 days in order to avoid the precipitation of the monocondensed product. On the other hand, compound **9** was obtained by reacting at room temperature *N,N'*-dihydroxy-2,3-diamino-2,3-dimethylbutane with compound **12** in MeOH (91% yield). The latter was obtained upon deprotection of **11** (94% yield) using K_2CO_3 in MeOH at 25°C. Compound **11** was prepared by a Pd-coupling reaction between trimethylsilylacetylene (TMSA) with the commercially available 4-bromobenzaldehyde **10** in 93% yield. Dealing with the palladium catalyst used for the coupling reaction, in the case of the synthesis of diimino-nitroxide derivatives, it has been previously observed⁴ that when $\text{PdCl}_2(\text{PPh}_3)_2$ was prepared in situ by reacting PdCl_2 , PPh_3 in Et_3N in the presence of $\text{Cu}(\text{OAc})_2$, the dehydration of *N,N'*-dihydroxyimidazolines into *N*-hydroxyimidazolines systematically occurred. Interestingly, we found that for the coupling reaction of **8** with **9** (48 h, 80°C), when commercially available $\text{PdCl}_2(\text{PPh}_3)_2$ complex was used in the presence of CuI in Et_3N , the side dehydration reaction could be considerably reduced. However, the reaction afforded a mixture mainly containing the desired compound **13** and the mono dehydrated derivative. Unfortunately, due to low solubility, they could not be separated. The oxidation by MnO_2 at room temperature of the mixture in suspension in CH_2Cl_2 gave a mixture of radicals which afforded both compounds **1** and **2** after chromatography (SiO_2 , CH_2Cl_2 :AcOEt:MeOH, 80:19:1) in 11 and 15% overall yields, respectively.

In order to increase the yield of compound **1**, another strategy based on the preparation of the

trialdehyde **16** by the Pd-coupling reaction prior to the introduction of the *N,N'*-dihydroxyimidazoline functionality was exploited. The coupling of aldehydes **10** and **15** leading to the trialdehyde **16** was achieved in 74% yield in the presence of 10% Pd(PPh₃)₄ in a 1:10 mixture of diisopropylamine:benzene. Before this, compound **14** was obtained in 94% yield, by Pd-coupling reaction between TMSA and **7** in diisopropylamine:THF, 1:5, mixture and in the presence of PdCl₂(PPh₃)₂ and CuI. Deprotection of **14** by K₂CO₃ in MeOH afforded the compound **15** in 99% yield. Using the same conditions as described above for the preparation of **8**, upon condensation of compound **16** with 3.3 equivalents of *N,N'*-dihydroxy-2,3-diamino-2,3-dimethylbutane in MeOH, the precursor compound **13** could be obtained in 90% yield. The oxidation at room temperature of the pure compound **13** by MnO₂ in CH₂Cl₂ afforded the desired compound **1** in 74% yield.

A third strategy, already employed for the synthesis of pyridine containing nitronyl-nitroxide groups,⁹ consisting in coupling preformed nitronyl-nitroxide derivatives such as **17**, **19** or **18** and **20** was also attempted. However, using Pd(PPh₃)₄ as the catalyst in an amine:benzene, 1:10, mixture, the coupling of either **17** with **19** or **18** with **20** failed. Attempts by varying the nature of the amine (triethylamine, pyrrolidine, diisopropylamine) were unsuccessful.

Dealing with the synthesis of the heterotriradical **3** bearing two imino-nitroxide and one nitronyl-nitroxide groups, following the first synthetic strategy presented above, it could be obtained in 22% yield upon coupling precursors **9** and **21** followed by oxidation by MnO₂. Compound **21** was obtained in 85% yield by catalytic dehydration of **8** using 15% SeO₂ in methanol.¹⁰

All triradicals **1**, **2** and **3** were characterised by IR, UV–visible spectroscopy, FAB spectrometry and elemental analysis. Furthermore, they were also characterised in the solid state by X-ray diffraction on single-crystal obtained upon slow evaporation of the desired compound in CH₂Cl₂/hexane mixture.¹¹ All three compounds were isostructural (monoclinic, P2₁/*n* space group). For compounds **1** and **3**, the solid state structure of the molecular units are presented in Fig. 1.

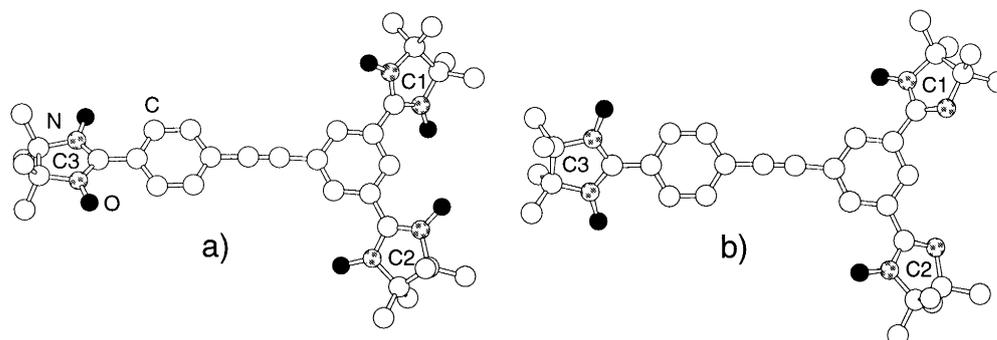


Fig. 1. Structure of the molecular units of: (a) compound **1**; and (b) compound **3** (H atoms have been omitted for the sake of clarity)

The conjugated ethynyl diaryl skeleton is close to planarity with a tilt angle of 11–12°, and the cyclic radical units C1, C2 and C3 (see Fig. 1) are tilted from the plane of ethynyl diaryl with torsion angles of 46° (C1), 26° (C2) and 18° (C3) for compound **1** and 37° (C1), 22° (C2) and 15° (C3) for compound **3**. In the crystal, the molecular units are arranged as head-to-tail dimers with a distance of 3.6 Å between the aromatic planes.

Complete oxidation of all three compounds was confirmed by SQUID measurements at 0.5 T, which gave values of 1.15–1.18 emu.K.mol⁻¹ at 298 K, close to the theoretical value of 1.125 emu.K.mol⁻¹. ESR spectra of compounds **1**, **2** and **3** were recorded at room temperature in diluted CH₂Cl₂:acetone, 1:1, solution (10⁻⁴ M). For both **1** and **2** the expected hyperfine patterns were observed, with 13 lines and 12 lines, respectively, indicating magnetic interactions through the MCU within the strong exchange

coupling limit $J \gg a$ (with J =exchange coupling constant and a =hyperfine coupling constant). However, for **3**, the presence of both weak and strong exchange processes was observed. The evolution of the magnetic susceptibility χ has been determined on the 4–120 K temperature range by ESR studies on dilute frozen solutions containing the triradicals **1** and **3**. The χT versus T plots obtained revealed the presence of ferromagnetic interactions in both cases, with weak coupling through the phenyl ethynyl coupler (7 K for **1**, 0.7 K for **3**), and larger magnetic exchange between two radicals through the *m*-phenylene part (23 K for **1**, 6.5 K for **3**).

In conclusion, three new triradicals based on phenyl ethynyl backbone bearing nitronyl-nitroxide and imino-nitroxide groups were prepared and structurally characterised in the solid state. ESR studies revealed the presence of magnetic interactions between the radical moieties in dilute solution, demonstrating the ferromagnetic coupling efficiency of this phenyl ethynyl spacer. Magneto-structural correlations as well as detailed ESR study of the intramolecular coupling processes in frozen solutions will be reported elsewhere.

Acknowledgements

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11. Selected data for **1**: UV-vis (CH_2Cl_2) λ_{max} , nm (ϵ , $\text{M}^{-1}\cdot\text{cm}^{-1}$), 592 (1130); IR, cm^{-1} (KBr) 1363 ($\nu_{\text{N-O}}$); anal. calcd for $\text{C}_{35}\text{H}_{43}\text{N}_6\text{O}_6\cdot\text{CH}_2\text{Cl}_2$: C, 59.34; H, 6.22; N, 11.53; found: C, 59.11; H, 6.20; N, 11.28; FAB⁺ m/z 645 [M+H]⁺; compound **2**: UV-vis 595 (700), 450 (712); IR: 1365 ($\nu_{\text{N-O}}$), 1549 ($\nu_{\text{C=N}}$); anal. calcd for $\text{C}_{35}\text{H}_{43}\text{N}_6\text{O}_5\cdot\text{CH}_2\text{Cl}_2$: C, 60.67; H, 6.36; N, 11.79; found: C, 60.55; H, 6.39; N, 11.65; FAB⁺ m/z 629 [M+H]⁺; compound **3**: UV-vis 602 (560), 445 (1380), IR 1363 ($\nu_{\text{N-O}}$), 1544 ($\nu_{\text{C=N}}$); anal. calcd for $\text{C}_{35}\text{H}_{43}\text{N}_6\text{O}_4\cdot\text{CH}_2\text{Cl}_2$: C, 62.06; H, 6.51; N, 12.06; O, 9.18; found: C, 62.14; H, 6.52; N, 11.99; O, 9.30; FAB⁺ m/z 613 [M+H]⁺; X-ray data for **1**: $\text{C}_{35}\text{H}_{43}\text{N}_6\text{O}_6\cdot\text{CH}_2\text{Cl}_2$, monoclinic, $P2_1/n$, $a=12.254(1)$, $b=18.293(2)$, $c=16.892(2)$, $\beta=93.877(7)$, $Z=4$, $R=0.061$, $R_w=0.083$; **3**: $\text{C}_{35}\text{H}_{43}\text{N}_6\text{O}_4\cdot\text{CH}_2\text{Cl}_2$, monoclinic, $P2_1/n$, $a=12.414(2)$, $b=18.2021(9)$, $c=16.643(1)$, $\beta=93.712(8)$, $Z=4$, $R=0.084$, $R_w=0.094$. Atomic coordinates, bond lengths, angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.