

## Synthesis and magnetic properties of stable nitroxyl tri-radicals

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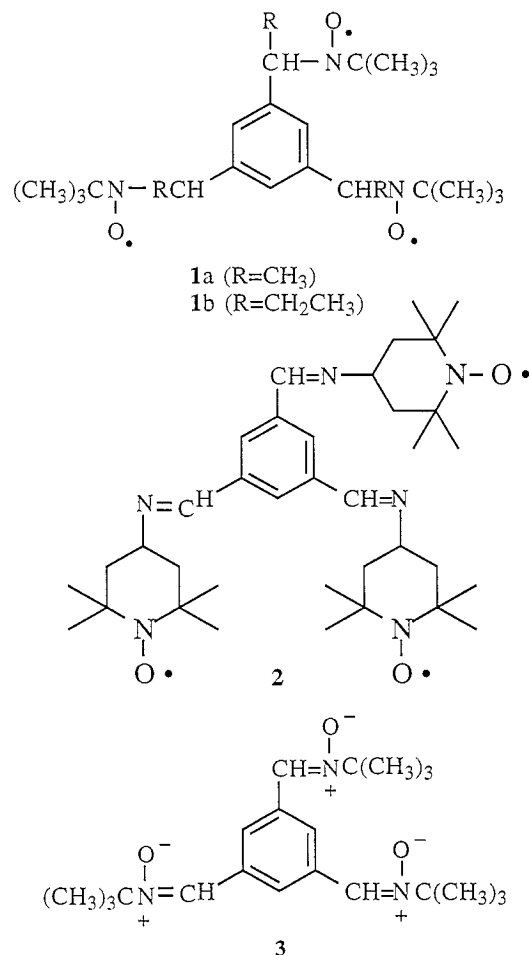
### Abstract

Several stable nitroxyl tri-radicals, such as tris- $\alpha, \alpha', \alpha''$ -(*t*-butylnitroxyl alkyl)mesitylene (**1**) and  $N, N', N''$ -mesitylenylidenetris (4-amino-2,2,6,6-tetramethylpiperidinyloxy) (**2**), were synthesized by either an addition reaction of alkyl Grignard reagents with corresponding trinitrone molecules or the condensation reaction of 4-amino-2,2,6,6-tetramethylpiperidinyloxy with 1,3,5-benzenetricarboxaldehyde (trimesic aldehyde). The  $\chi_m T$  ( $\chi_m$  = molar magnetic susceptibility) value was found to increase slightly as the temperature decreased. It reached a maximum value of 1.01 emu-mol<sup>-1</sup>K at 45 K followed by a sharp decline of the  $\chi_m T$  value, indicating the existence of intermolecular antiferromagnetic interactions ( $\theta = -1.91$  K) in this molecular system. The effective magnetic moment was found to be 2.85  $\mu_B$ .

**Keywords:** tris- $\alpha, \alpha', \alpha''$ -(*t*-butylnitroxyl alkyl)mesitylene;  $N, N', N''$ -mesitylenylidenetris (4-amino-2,2,6,6-tetramethylpiperidinyloxy); nitroxide radicals.

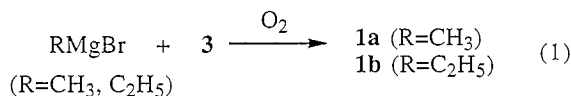
### 1. Introduction

One of recent challenges in the field of molecular based ferromagnetic materials is focused on the development of new molecular radicals [1]. For example, stable phenoxyl radicals, including galvinoxyl radicals, have been found to exhibit ferromagnetic intermolecular spin interactions at temperatures below 7 K [2]. Stability of phenoxyl radicals can be enhanced by introducing sterically hindered *t*-butyl group at adjacent positions of the radical center or by introducing oxygen-interactive cyano functions in conjugation with the phenoxy radical [3]. In our laboratory, we have prepared new radical materials and carried out electron spin resonance spectroscopic studies of some stable nitroxyl radicals [4], since stable nitroxyl radicals represent one of the most promising ferromagnetic materials [5]. They can be synthesized by known synthetic routes. It is known that relatively high symmetry and ground-state molecular orbital degeneracy in organic molecules are necessary for the stabilization of ferromagnetic couplings in the McConnell mechanism [5]. Stable radicals with  $D_{2d}$ ,  $C_3$  or a higher symmetry are, therefore, among the most desirable target molecules to be synthesized. In this report, we present a synthetic scheme and ESR spectra of three new nitroxyl tri-radicals, **1**(a-b) and **2**, using trimesic aldehyde as a starting reagent. Recently, trimesic aldehyde was utilized in the synthesis of a nitronyl nitroxide triradical (TNN) [6] which exhibited antiferromagnetic interactions between radicals in the bulk solid materials.

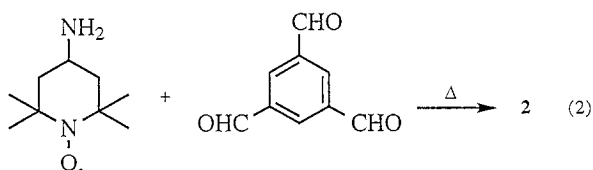


## 2. Results and Discussion

Radical **1a** and **1b** were prepared by the reaction of trinitrone **3** with the corresponding methyl lithium or methylmagnesium bromide and ethylmagnesium bromide, respectively, as a reagent in the presence of an oxygen atmosphere (equation 1) [6]. Both radicals **1a** and **1b** showed triplets of doublet peaks in e.s.r. spectra at room temperature, as shown in Fig. 1.



The hyperfine splitting constants of these radicals in interacting with nitrogen atom ( $a_N$ ) and  $\beta$ -proton ( $a_H$ ) were obtained by the analysis of their room temperature e.s.r. spectra;  $a_N = 14.7$  G and  $a_H = 3.6$  G for **1a**;  $a_N = 14.6$  G and  $a_H = 3.6$  G for **1b**. Apparently, there are no intramolecular spin-spin interactions among radical centers in **1a** and **1b**. Unfortunately, we experienced difficulties in obtaining any sizable single crystal for X-ray analyses and magnetic susceptibility measurements. Radical **2** was prepared by the condensation reaction of 4-amino-2,2,6,6-tetramethyl-piperidin-1-oxyl (4-NH<sub>2</sub>-TEMPO) with trimesic aldehyde [7] (equation 2). The e.s.r. spectrum of **2** was measured in benzene at room temperature, showing only three peak lines which correspond to hyperfine splitting constants arising from interactions of radical centers with a nitrogen atom with  $a_N = 15.4$  G and  $g = 2.0062$ .



Temperature dependent magnetic susceptibilities of a microcrystalline sample **2** was measured at 2–300 K under a magnetic field of one tesla. The plot of  $\chi_m T$  ( $\chi_m$  = molar magnetic susceptibility) vs.  $T$  was shown in Fig. 2. The  $\chi_m T$  values were observed to increase slightly in response to the decrease of temperature and reached a maximum value of 1.01 emu·mol<sup>-1</sup>K at 45 K. Below 45 K, a sharp decline of  $\chi_m T$  values was detected. The decrease of  $\chi_m T$  values below 45 K may arise from intermolecular antiferromagnetic interactions between radicals in solid. Reciprocal magnetic susceptibilities of **2** in the temperature range of 2–10 K revealed a Curie-Weiss behavior of spins with an antiferromagnetic coupling between spins of  $\theta = -1.91$ K. The effective magnetic moment ( $\mu_{\text{eff}}$ ) value of 2.85  $\mu_B$  at 50–300 K is below a theoretical value of 3.00  $\mu_B$  for  $S = 3$  of a spin 1/2 species.

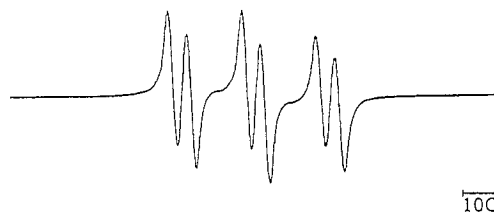


Fig. 1. ESR spectrum of the radical **1b**.

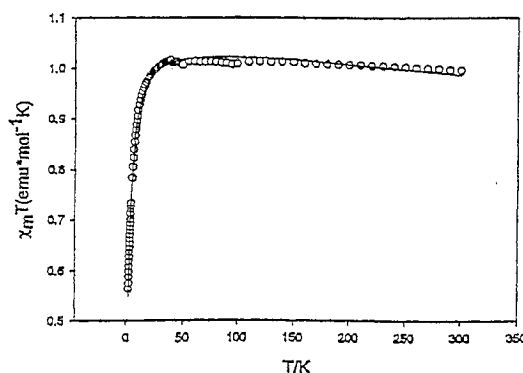


Fig. 2. The plot of  $\chi_m T$  vs.  $T$  for the radical **2**.

In conclusion, we have synthesized two stable nitroxyl triadicals (**1**) and (**2**) by either an addition reaction of alkyl Grignard reagents with the corresponding trinitrone molecules or the condensation reaction of 4-amino-2,2,6,6-tetramethylpiperidinyloxy with 1,3,5-benzenetricarboxaldehyde (trimesic aldehyde). The  $\chi_m T$  value was found to increase slightly as the temperature decreased. It reached a maximum value of 1.01 emu·mol<sup>-1</sup>K at 45 K followed by a sharp decline of the  $\chi_m T$  value, indicating the existence of intermolecular antiferromagnetic interactions ( $\theta = -1.91$  K) in this molecular system. The effective magnetic moment was found to be 2.85  $\mu_B$ .

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