Synthesis and magnetic properties of stable nitroxyl tri radicals

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Abstract

Several stable nitroxyl tri-radicals, such as tris-α, α', α''-(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\(^{-1}\)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-α, α', α''-(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 phenoxyl 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 \( D_{2d} \) or \( C_3 \) 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 nitroxy triradicals, 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.

\[
\text{RMgBr} + 3 \rightarrow \text{1a (R=CH}_3\text{)} \quad \text{1b (R=C}_2\text{H}_5\text{)} \quad (1)
\]

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-piperidinyloxy 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 \(g = 2.0062\).

\[
\begin{align*}
\text{NH}_2 \quad \text{O} \\
\text{N} \quad \text{CH}_2
\end{align*}
\]

\[
\begin{align*}
\text{OHC} & \quad \text{CHO} \\
\text{CHO} & \quad \text{CHO} \\
\Delta & \rightarrow 2 \quad (2)
\end{align*}
\]

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 \(\chi_mT\) \((\chi_m = \text{molar magnetic susceptibility})\) vs. \(T\) was shown in Fig. 2. The \(\chi_mT\) values were observed to increase slightly in response to the decrease of temperature and reached a maximum value of 1.01 emu-mol\(^{-1}\)K at 45 K. Below 45 K, a sharp decline of the \(\chi_mT\) value was detected. The decrease of \(\chi_mT\) 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.

References