Forced proximity of nitroxide groups in pincer compounds with a xanthene spacer

Naoki Koizumi, Takayuki Ishida *

Department of Engineering Science, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan

A B S T R A C T

We designed bisnitroxide compounds where the radical sites are located close to each other in a molecule. Two new pincer-type bisnitroxide compounds have been synthesized, involving xanthene-4,5-diyl as a spacer and *tert*-butyl phenyl nitroxides as arms. From the X-ray crystal structure analysis, the shortest intramolecular interatomic N···O and O···O distances respectively are 5.074(6) and 5.258(6) Å for the *m,m′*-derivative and 3.624(3) and 3.771(3) Å for the *p,p′*-derivative. The N···O distance in the latter satisfies the empirical criterion for possible dimerization/degradation reaction accompanied by dia-/paramagnetic transition. However, the magnetic study clarified paramagnetic behavior in all the temperature range. According to a singlet-triplet model, antiferromagnetic couplings were characterized with $2J/k_B = -7.71(2)$ and $-8.83(4)$ K for the *m,m′* and *p,p′*-derivatives, respectively. The present result suggests that a more flexible spacer is required for realization of possible dia-/paramagnetic transition.

© 2017 Elsevier Ltd. All rights reserved.

Introduction

Various solid-state magnetic and chromic switches are attracting much interest for future applications to memory, display, computing, and other devices.[1–9] There have been several π-radicals such as dithiadiazolyls and dithiazolyls exhibiting changes of the spin state, crystal structures, and physical properties in the solid state.[2] Phenalenyls[3,4] and triazinyls[5] showing π-dimerization have also well been studied with respect to transport behavior as well as magnetic properties. Triphenylimidazolyls display dramatic photochromism in solution.[6] We have reported spin transition behavior in BPBN derivatives (Scheme 1a),[7] where BPBN stands for biphenyl-3,5-diyl bis(*tert*-butyl nitroxide). The special feature resides in the reversible formation and cleavage of intermolecular σ-bonds between two nitroxide groups. The head-to-tail assembly of the nitroxide groups is explained in terms of a dipolar character: >NO· ←→ >N⁺·O⁻ (Scheme 2).[8] Another instance of such dimerization was found among dialkyl nitroxide family, and 2-azaadamantan-2-oxyl has been reported to show a similar chromism and magnetism.[9] On the other hand, the >N-O·····O-N< contact like a peroxide bond is very rare.[10]

Such solid-state dimerization/degradation reactions are regulated through the compensation of enthalpic and entropic gains. When intermolecular interaction is disregarded, a dimerized form is favorable for the enthalpy term while a paramagnetic form for the entropy term. Preorganization generally reduces the entropy loss during dimerization (Scheme 1b), and this technique has competently been applied to a series of triphenylimidazolyls.[6] In this study, we designed pincer-type bisnitroxide compounds where the radical sites would be located close to each other in a molecule. The distance between two nitroxides is important, and we assumed that various molecular spacers could control the distance. Suitable distances and molecular spacers can be predicted from computer chemistry,[11] and a xanthene-4,5-diyl group has been introduced as a first choice for a spacer function.

Results and discussion

Synthesis and crystal structures

New bisnitroxide compounds **4m** and **4p** have been synthesized according to Scheme 3. The Suzuki coupling reaction of **1**[12] with **2m** or **2p**[13] is a key step. Resultant bishydroxylamines **3m** and **3p** were oxidized with Ag_2O to give bisnitroxides **4m** and **4p**, respectively. The products were characterized by means of spectroscopic and elemental analyses.

As the solution ESR spectra show (Fig. 1a and b), both *g* values were determined to be 2.0061, typical of nitroxides, in toluene at room temperature. The hyperfine splitting constants could not be determined because of severe line broadening probably owing to
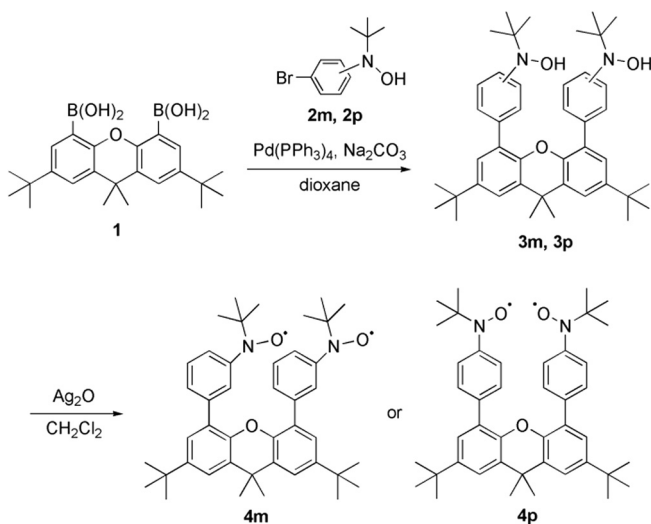
* Corresponding author.
  E-mail address: takayuki.ishida@uec.ac.jp (T. Ishida).
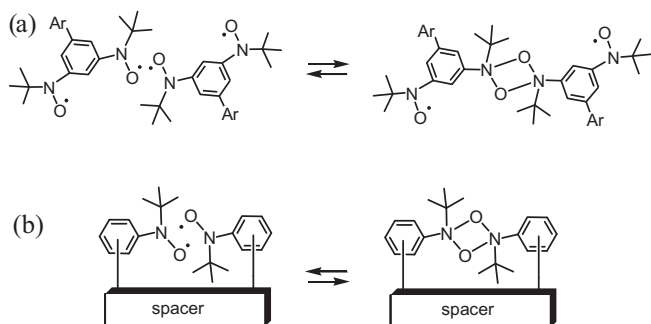
Scheme 1. (a) Inter- and (b) intramolecular dimierization/degradation reactions of nitroxides.
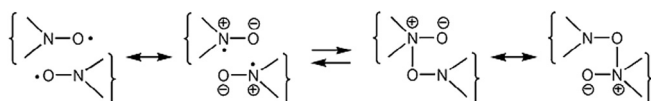
Scheme 2. Canonical structures of paramagnetic and diamagnetic forms consisting of two nitroxide groups.

Scheme 3. Synthetic route to **4m** and **4p**.

dipolar and exchange interactions within a molecule. The peak-to-peak line widths were 25 and 23 G for **4m** and **4p**, respectively.

The frozen-solution ESR spectra displayed zero-field splitting (ZFS) structures (Fig. 1c and d) and also clarified that the biradical species entirely survived down to 100 K. The ZFS parameters were determined from simulation as: $|D|/hc = 0.014 \text{ cm}^{-1}$ and $|E|/hc = 0.0014 \text{ cm}^{-1}$ for **4m**; $|D|/hc = 0.015 \text{ cm}^{-1}$ and $|E|/hc = 0.0011 \text{ cm}^{-1}$ for **4p** at 100 K in frozen toluene solutions. A forbidden signal with $\Delta m_S = \pm 2$ appeared in a half-field region for **4p** (Fig. 1d, inset).

The comparable D values were obtained from **4m** and **4p**, implying that the two nitroxide spin centers are separated by $r = 5.7$–5.5 Å in a molecule, as estimated with the point-dipole approximation. However, from a closer look at Fig. 1d, we can find minor ESR signals outside of the major one, indicating the presence of conformational isomers having shorter distance between the two nitroxide groups. The outerest signal pair afforded $|D|/hc = 0.024 \text{ cm}^{-1}$ and accordingly $r = 4.8$ Å. This analysis is compatible with the results of the X-ray crystallographic analysis (see below); the separation of the spins in **4p** comes shorter than that of **4m**.

The molecular structures of **4m** and **4p** were finally confirmed by means of X-ray crystal structure analysis (Fig. 2). Selected crystallographic parameters are listed in Table 1. The nitroxide N–O bond lengths in 1.288(2)–1.296(3) Å (Table 2) were typical of aryl *tert*-butyl nitroxides.[14] Intramolecular interatomic N···O, O···O, and N···N distances are also listed in Table 2.

As for **4m**, two arms are configured to be "*syn*"; namely, two *tert*-butyl nitroxide groups are almost located parallel with respect to the biphenyl axis (Fig. 2a). The dihedral angle between least-squares ring planes of A and B of **4m** is very small (17.60(6)°), and the single bonds between rings A and C and rings B and D are twisted in the same clockwise or a "conrotatory" manner (Table 3). However, the radical···radical distance was considerably distant (>5 Å) (Table 2). It seems reasonable from thinking of the C3···C13 distance of 4.659(5) Å. In a xanthene bridge, the dihedral angle between ring C and D is sufficiently small (6.56(6)°), indicating that the xanthene skeleton plays the role of a rigid planar spacer.

In the conformation of **4p** (Fig. 2b), rings A and B are twisted in a conrotatory manner (Table 3), just like **4m**. The dihedral angle between rings A and B is 5.74(9)°, which is smaller than that of **4m**. Owing to the rigid structure of the *p*-substitution, the N1···N2 distance (4.297(3) Å) in **4p** is shorter than that of **4m** (Table 2). The C4···C14 distance is 4.530(3) Å, and the shorter N1···N2 distance suggests the attractive interaction between the arms. The nitroxide N–O groups are arranged in a head-to-tail or "disrotatory" manner with respect to the conformation around the N1-C1 and N2-C11 bonds, probably because of the steric repulsion between the *tert*-butyl groups and dipolar attractive interaction between the N–O groups. The radical···radical distance was accordingly relatively short, as indicated with 3.624(3) Å for N1···O2 and 3.771(3) Å for O1···O2. These distances are longer than those of the sum of the van der Waals radii (N/O: 3.07 Å, O/O: 3.04 Å)[15] but have an importance in the research of BPBN and related compounds. The dimerizable N···O distances are usually ca. 3.7 Å (Scheme 1), as exemplified with 3.686(3) Å for BPBN and 3.696(4) Å for a difluoro derivative of BPBN,[7] and the present value is very close to these values. Namely, the N···O distance in **4p** satisfies the empirical criterion for possible dimerization/degradation reaction, thanks to the molecular design. The N···O distances usually become as short as ca. 2.4 Å after dimerization.[7] The crystallographic study results of **4m** and **4p** measured at 100 K indicate that they did not undergo dimerization down to 100 K. There still seems to be a chance to dimerize on further cooling only for **4p**, so that we move to magnetic study to answer this issue.

Magnetic measurements

The magnetic study results are shown in Fig. 3. Paramagnetic behavior was observed in the whole temperature range applied here, and the $\chi_m T$ values decreased on cooling for both compounds. The Cuire-Weiss analysis based on the equation, $\chi_m = C/(T-\theta)$, gave the optimized parameters as $C = 0.77 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -2.5$ K for **4m** and $C = 0.72 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -3.2$ K for **4p**. The theoretical C value of a biradical species is $0.75 \text{ cm}^3 \text{ K mol}^{-1}$, and the experimental values confirm the presence of two doublet spins in a molecule. The negative θ values mean the presence of dominant antiferromagnetic interaction.

A meaningful exchange coupling should be assigned to intramolecular interaction, as suggested from the X-ray crystallographic analysis. According to the Bleaney-Bowers equation based on a single-triplet model (Eq. (1)),[16] we obtained $2J/k_B = -7.71(2)$ K and $g = 2.026(8)$ for **4m** and $2J/k_B = -8.83(4) \text{ cm}^3 \text{ K mol}^{-1}$ and $g = 1.9500(8)$ for **4p**.[17] The calculation curves superposed in Fig. 3 well reproduced the experimental data. The $\chi_m T$ value of