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A novel organic neutral radical system: topological effects in oxophenalenoxyls

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Abstract

An idea of molecular topology for spin alignment in π-electron networks, which has been widely accepted in high-spin chemistry, can be expanded to monoradical π-systems. In this paper, we describe the importance of the topology of π-electron network for elucidating spin structures in the monoradical systems. An oxophenalenoxyl is a phenalenyl-based neutral monoradical and has many topological isomers depending on the positions of introduced two oxygen atoms. We have focused on a series of α, α-type of oxophenalenoxyls, 3-, 4-, 6- and 9-oxophenalenoxyl systems with two oxygen substituents at α-positions on the phenalenyl skeleton. Our experimental studies have demonstrated that the spin-delocalized nature of the oxophenalenoxyl systems extremely depends on the topological symmetry of the introduced two oxygen atoms. The π-spin density distributions have been calculated by density functional theory, supporting the topology-dependent spin diversity nature inherent in a series of oxophenalenoxyl systems.

Keywords: Oxophenalenoxyl; Monoradicals; Spin topology; Spin density distribution; Molecular spin diversity; Density functional calculation

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1. Introduction

Syntheses of novel stable organic radicals are important for the development of spin chemistry underlying molecule-based magnetic materials [1,2]. The appropriate understandings of their π-spin structures play crucial roles not only in the elucidation of magnetic properties of the single molecules or molecular assemblies in the solid state but also in molecular designing of novel organic radicals. It is known that the spin alignment in organic open-shell systems with high-spin multiplicities is frequently governed by the molecular topology of their π-electron networks [2]. For example, in alternant-conjugated non-Kekulé molecules such as *m*-xylylene, the high-spin preference for unpaired electrons in diradical or high-spin molecular systems is well interpreted in terms of the dynamic spin polarization mechanism due to the topological symmetry. In principle, such an idea of the molecular spin topology is copious and can be generalized by expanding the idea to monoradical systems. In this paper, we describe monoradical systems showing a remarkably topology-dependent spin diversity nature appearing in a series of oxophenalenoxyl systems [3,4] as well as two kinds of naphthoxyls in terms of the π-spin density distributions calculated by density functional theory.

2. Experimental and theoretical

Hyperfine splittings due to protons of oxophenalenoxyl radicals were obtained by solution ESR/ENDOR spectroscopy. ESR and ENDOR spectra were measured with Bruker 300E/350 ESR and ENDOR spectrometers. The π-spin density distributions of a series of oxophenalenoxyl systems were calculated by using Gaussian-98

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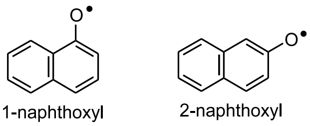
with the UBLYP/6-31G(d,p)//UBLYP/6-31G(d,p) method.

3. Results and discussion

Naphthoxyl radicals are simple and good models for grasping characteristics of spin structures in monoradical systems showing the topology-dependent spin diversity nature. There are two kinds of isomers, 1- and 2-naphthoxyls, and in these two topological isomers they differ from others only in the topology of their π-electron network. The generation and detection of 1- and 2-naphthoxyls have been reported in spite of their instability, showing that 1-naphthoxyl is more stable than 2-naphthoxyl presumably because of greater resonance stabilization [1b,5]. The π-spin density distributions calculated by density functional theory are shown in Fig. 1. It is worth noting that the spin-delocalized nature of 1-naphthoxyl is enhanced compared with 2-naphthoxyl. Such a difference in the spin-delocalized nature is derived only from the difference of topology of π-electron network, where the topology-dependent π-spin structures show up in the naphthoxyl monoradicals.



One of the origins of the topological effects in the naphthoxyl monoradicals is most likely in that the naphthoxyls are the fused ring systems that constitute their own topological symmetry, since well-known phenoxyl radicals obviously do not show any topological effects on their π-spin structures. Thus, there has been the consecutive interest in spin structures of open-shell fused ring systems with more extended π-conjugation systems. In this context, we have focused on a phenalenyl system which is an odd alternant hydrocarbon π-radical with a non-bonding molecular orbital (NBMO) [6]. Oxophenalenoxyls, which have been designed by introducing two oxygen atoms into the phenalenyl skeleton, also belong to the odd alternant system and have many topological isomers. These isomers can be classified into two types of categories, α, α-type and α, β-type, depending on the positions of introduced two oxygen atoms, as shown in Fig. 2. In these isomers, the α, α-type of oxophenalenoxyls are interesting synthetic target molecules as the novel spin sources due to the expectation of the characteristic delocalization mode of an unpaired electron between the two oxygen atoms. This feature leads to a remarkable difference from the electronic structures of α, β-type of oxophenalenoxyls and well-known aroxyl radicals [1a]. Thus, we have focused on α, α-type of oxophenalenoxyls, 3-, 4-, 6- and 9-oxophenalenoxyls.

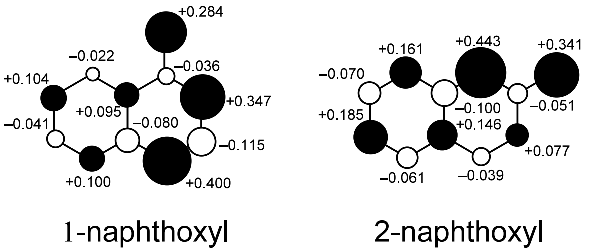


Fig. 1. The π-spin density distributions of 1- and 2-naphthoxyls calculated by using Gaussian-98 with the UBLYP/6-31G(d,p)// UBLYP/6-31G(d,p). Vacant and filled circles denote negative and positive π-spin density, respectively.

We have already reported the generation of 3-oxophenalenoxyl derivatives **1a** and **1b** [3a], and the successful synthesis of 6-oxophenalenoxyl derivatives **2a** and **2b** [3b] and other derivatives [3c,3d] which are isolable in an air atmosphere by the resonance stabilization and the kinetic stabilization due to bulky *tert*-butyl groups substituted with appropriate positions. Moreover, we have recently succeeded in the synthesis and isolation of a 4-oxophenalenoxyl derivative **3** [4]. The experimental studies for these topological isomers have demonstrated that the π-spin-delocalized nature in the oxophenalenoxyls is extensively influenced by the positions of introduced oxygen atoms.

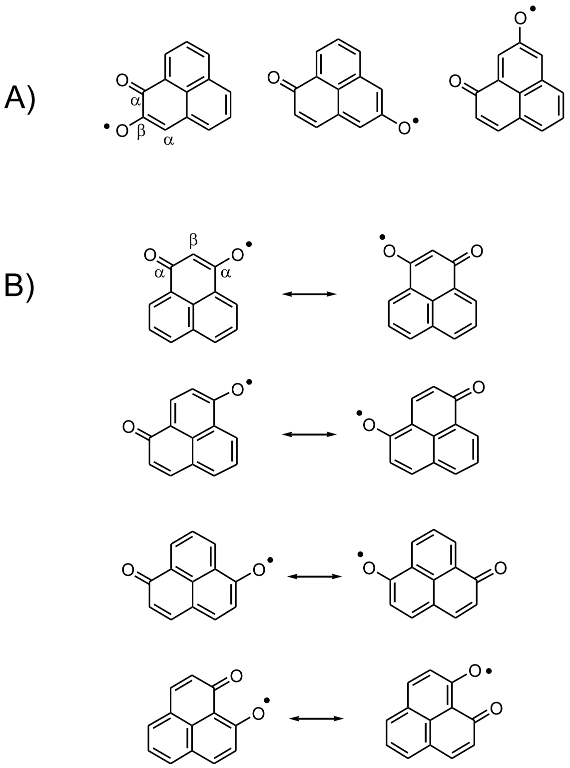
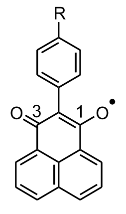
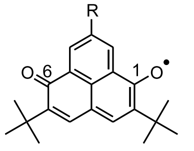


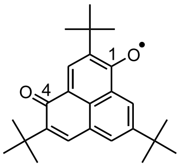
Fig. 2. The possible topological isomers of the oxophenalenoxyl systems. (A) α, β-Type and (B) α, α-type.



1a R = H
1b R = OMe



2a R = H
2b R = *tert*-Bu



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All isomers, 3-, 4-, 6- and 9-oxophenalenoxyls, are nearly planar in the UBLYP/6-31G(d,p)-optimized structures (see Fig. 3). Thus, these oxophenalenoxyl systems allow us to discuss their π-spin structures only by the difference of the topology of π-electron network. The calculated π-spin density distributions in the four isomers, 3-, 4-, 6- and 9-oxophenalenoxyls, are depicted in Fig. 4, showing the robust π-spin polarization nature in all cases and unique tendency of the π-spin density delocalization in the oxophenalenoxyl systems; the unpaired electron is dominantly delocalized on the two oxygen atoms and on the carbon atoms located at a shorter peripheral conjugation path between the two oxygen atoms. This tendency gives rise to the remarkable difference in the spin-delocalized nature inherent in the oxophenalenoxyl systems; the spin densities in 4- and 6-oxophenalenoxyls are delocalized over the entire molecules while those of 3- and 9-oxophenalenoxyls are more localized. In solution cw-ESR spectra of the 3-oxophenalenoxyl derivatives **1a** and **1b**, the hyperfine coupling constants due to protons on the phenalenyl skeleton were not observed [3a]. These experimental results are indicative of no appreciable contributions of the unpaired electron on the phenalenyl skeleton of the 3-oxophenalenoxyl system, well agreeing with the calculated π-spin density distribution. Fig. 5 shows the experimentally determined spin densities of 6-oxophenalenoxyl derivatives **2a** and **2b** [3b] derived from the observed hyperfine coupling constants and McConnell's equation ($Q = -2.30$ mT) [7], giving satisfactory agreements between the observed π-spin densities and calculated ones in Fig. 4. It is worth noting that the DFT

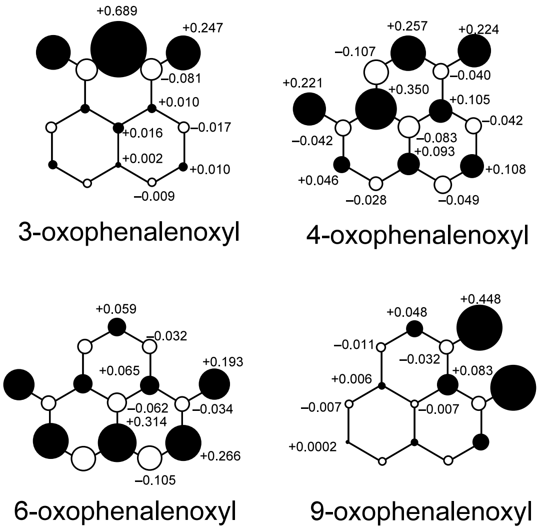

Fig. 4. The π-spin density distributions of topological isomers of the oxophenalenoxyl system. Vacant and filled circles denote negative and positive π-spin density, respectively.

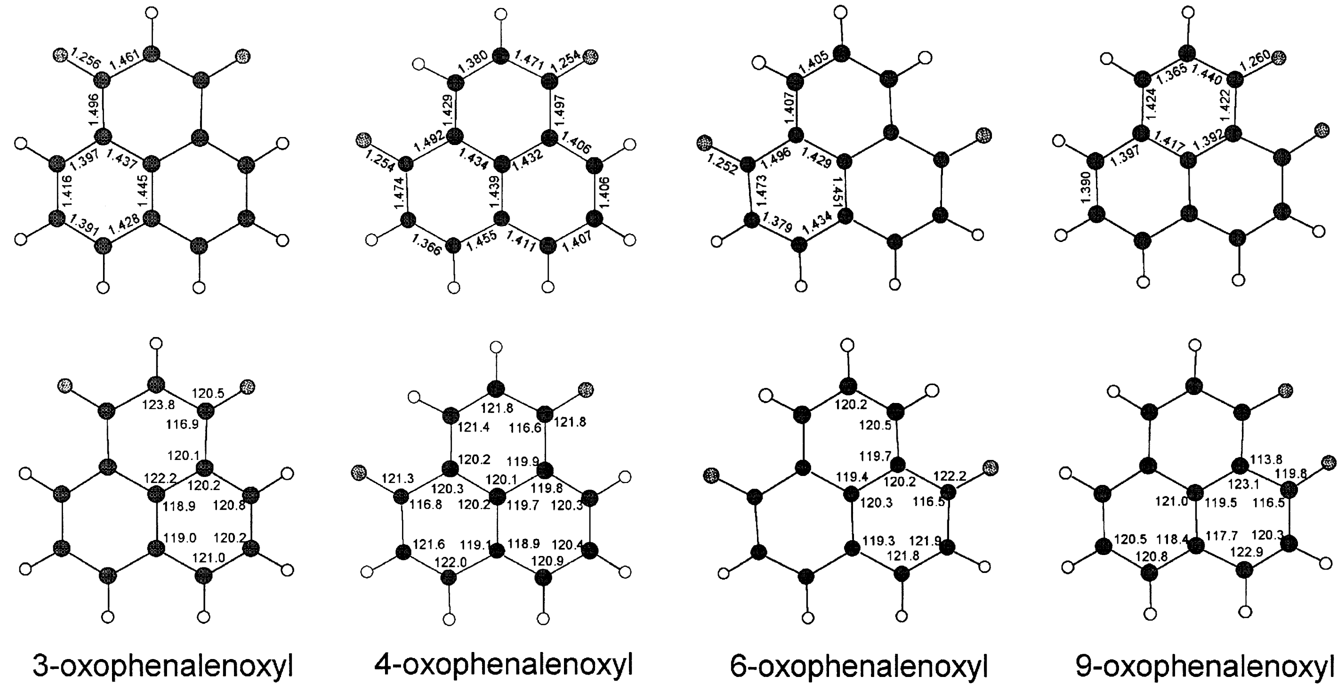

Fig. 3. Bond lengths (Å, top) and angles (°, bottom) in UBLYP/6-31G(d,p)-optimized structures of topological isomers of the oxophenalenoxyl system. All molecules are almost planar in the optimized structures.

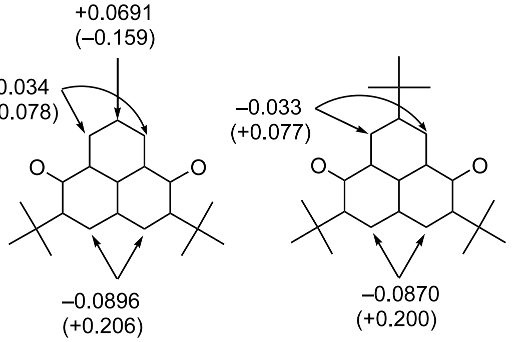

Fig. 5. The experimentally determined π-spin densities of **2a** (left) and **2b** (right). Values in parenthesis are hyperfine coupling constants (mT) observed for the adjacent protons.

calculations give a rationale for π-spin structures of the oxophenalenoxyl systems.

4. Summary

In the oxophenalenoxyl system, the topology of the π-electron network governs the intramolecular π-spin density distributions. This topology-dependent spin diversity nature inherent in the oxophenalenoxyl system shown by the experimental studies was confirmed by density functional theory in terms of spin density distributions. This work points out for the first time that the topology of π-electron network plays a vital role in the electronic structures of monoradical systems. Extended topological symmetry arguments give useful conceptual advance in spin chemistry underlying exotic materials science. We believe that this study would be helpful to design new stable radical systems and to control their spin structures, in particular novel open-shell fused ring systems such as the oxophenalenoxyl systems.

Acknowledgements

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