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Topological Symmetry Control in Spin Density Distribution: Spin Chemistry of Phenalenyl-Based Neutral Monoradical Systems

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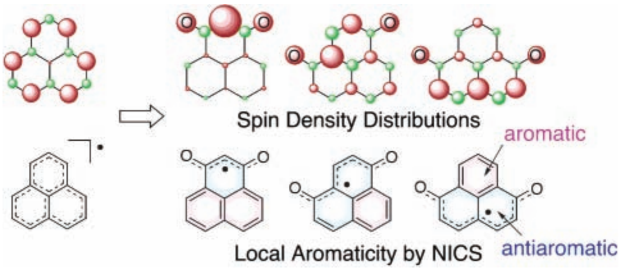
ABSTRACT



Topological symmetry-based extensions of a π-conjugation network in an odd alternant phenalenyl radical have enabled us to control the spin density distribution systematically. ESR/ENDOR and NICS studies on the topological isomers of oxophenalenoxyl have revealed that the unpaired electron tends to localize in the antiaromatic ring systems.

One of the highlighted advances in the field of organic magnetism and molecule-based magnetic materials[1] has been the use of topological symmetry requirement for high-spin preference in neutral open-shell π-conjugated hydrocarbons. The use of the topological symmetry enables an unlimited number of electron spins to align parallel to each other in the ground state,[2] which is termed the unlimitedness of topological degeneracy. On the other hand, the orbital degeneracy due to the group theoretical high symmetry is finite, e.g., the utmost quartet ($S = 3/2$) state demonstrated even in a ground-state C_{60}^{3-}.[3] The *meta*- or 1,3,5-connectivity-based topological degeneracy of SOMOs (π-NBMOs) has been a primary guiding principle for molecular design of organic high-spin systems.[4,5]

We have recently demonstrated that 3- and 6-oxophenalenoxyl systems (**1**[6a] and **2**,[6b−e] respectively), persistent neutral

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(1) For a recent overview of molecule-based magnetic materials, see, e.g.: (a) Itoh, K., Kinoshita, M., Eds. *Molecular Magnetism*; Kodansha, and Gordon and Breach Science Publishers: Tokyo, 2000; pp 1−347. (b) Lahti, P. M., Ed. *Magnetic Properties of Organic Materials*; Marcel Dekker: New York, 1999; pp 1−728.

(2) (a) Itoh, K. *Chem. Phys. Lett.* **1967**, *1*, 235−238. (b) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076−5078. (c) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372−376. (d) Itoh, K. *Bussei* **1971**, *12*, 635−646.

(3) Shohoji, M. C. B. L.; Franco, M. L. T. M. B.; Lazana, M. C. R. L. R.; Nakazawa, S.; Sato, K.; Shiomi, D.; Takui, T. *J. Am. Chem. Soc.* **2000**, *122*, 2962−2963.

(4) (a) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201−220. (b) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88−94. (c) Kollmar, C.; Kahn, O. *Acc. Chem. Res.* **1993**, *26*, 259−265. (d) Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109−116. (e) Rajca, A. *Chem. Rev.* **1994**, *94*, 871−893.

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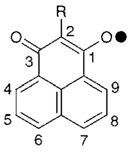
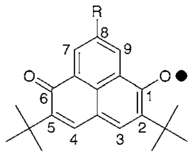
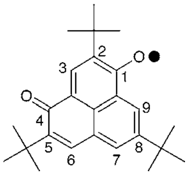
“monoradicals” based on an odd alternant phenalenyl system,[7] exhibit a unique π-electronic delocalization nature caused by the two oxygen atoms introduced into the phenalenyl skeleton as a heteroatomic π-extension.[6] The salient feature in spin density distribution underlines a new topological symmetry control due to the connectivities of the two oxygen atoms on the phenalenyl skeleton. We here focus on the synthesis of a 4-oxophenalenoxyl derivative **3** and characterizations of the electronic spin structures of three topological isomers, 3-, 6- and 4-oxophenalenoxyl, in terms of the spin density distributions, the resonance structures, and the nucleus-independent chemical shifts (NICS),[8] showing the appearance of the spin topological symmetry control in spin density distribution.[9]



1 R = H, Ph



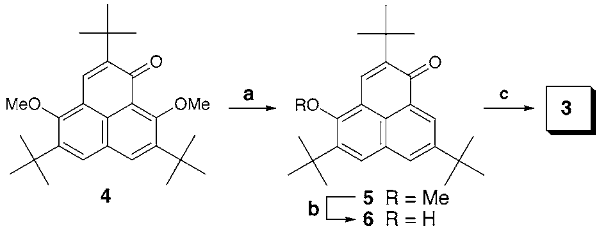
2 R = H, *t*-Bu



3

The preparation of the radical precursor **6** was efficiently achieved by a regioselective demethoxylation reaction in dimethoxyphenalenone **4**[6c] (Scheme 1); treatment of **4** with LiAlH$_4$−CuI reagent[10] in THF followed by LiI afforded **6** in good yield.[11] The chemical structure of monomethoxyphenalenone **5** was unequivocally determined in terms of the ^{1}H NMR analysis based on NOESY data, which gave reasonable assignments of all protons, including the *tert*-butyl groups. The treatment of **6** with an excess amount of active PbO$_2$ gave the radical **3** as a green solid in quantitative yield.[12] The radical **3** is stable in the absence of air, and most of the radical remains unchanged in air for a few weeks in the solid state. In a degassed toluene solution the radical **3** decomposes in a few days at room temperature, indicating a lesser stability compared with a tri-*tert*-butylated 6-oxophenalenoxyl derivative **2** (R = *t*-Bu).[6b]

Scheme 1[a]



[a] Reagents and conditions: (a) LiAlH$_4$ (3 equiv), CuI (12 equiv), THF, rt, 79%. (b) LiI (20 equiv), *N*,*N*-dimethylacetamide, 170 °C then NaCl aqueous solution, rt, 85%. (c) Active PbO$_2$, toluene, rt, quant.

A hyperfine ESR spectrum and the liquid-phase ^{1}H ENDOR/TRIPLE spectra of **3** were observed from a degassed toluene solution of the isolated radical (5×10^{-5} M) at 243 K (Figure 1). The ^{1}H ENDOR spectrum showed four pairs of sharp lines and a pair of broad lines attributed to the four protons of the phenalenyl skeleton and *tert*-butyl protons, respectively. Furthermore, the ^{1}H TRIPLE spectrum

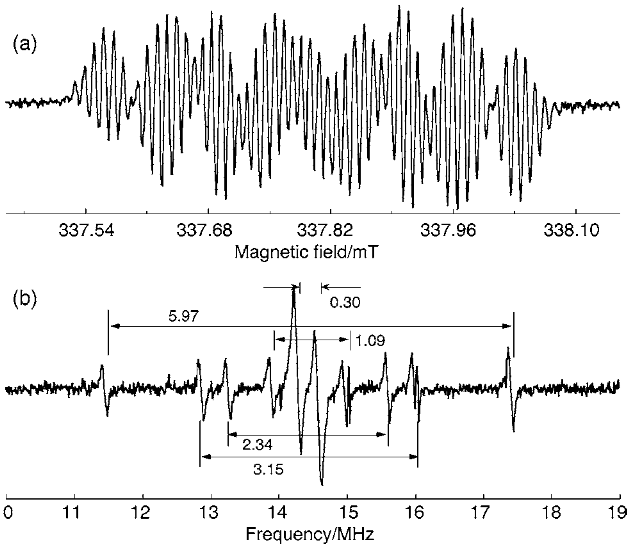


Figure 1. Observed hyperfine ESR (a) and ^{1}H ENDOR (b) spectra for **3** in a toluene solution (5×10^{-5} M) at 243 K; the microwave frequency used for the ESR measurement was 9.479762 GHz. The observesd *g*-value is 2.0052.

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(5) Applicability of this topological symmetry rule has been carefully investigated for heteroatomic and/or pluri-charged π-conjugated “high-spin” systems; see: (a) Matsushita, M.; Nakamura, T.; Momose, T.; Shida, T.; Teki, Y.; Takui, T.; Kinoshita, T.; Itoh, K. *J. Am. Chem. Soc.* **1992**, *114*, 7470−7475. (b) Nakamura, T.; Momose, T.; Shida, T.; Sato, K.; Nakazawa, S.; Kinoshita, T.; Takui, T.; Itoh, K.; Okuno, T.; Izuoka, A.; Sugawara, T. *J. Am. Chem. Soc.* **1996**, *118*, 8684−8687.

(6) (a) Hatanaka, K.; Morita, Y.; Ohba, T.; Yamaguchi, K.; Takui, T.; Kinoshita, M.; Nakasuji, K. *Tetrahedron Lett.* **1996**, *37*, 873−876. (b) Morita, Y.; Ohba, T.; Haneda, N.; Maki, S.; Kawai, J.; Hatanaka, K.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *J. Am. Chem. Soc.* **2000**, *122*, 4825−4826. (c) Morita, Y.; Maki, S.; Fukui, K.; Ohba, T.; Kawai, J.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *Org. Lett.* **2001**, *3*, 3099−3102. (d) Morita, Y.; Kawai, J.; Haneda, N.; Nishida, S.; Fukui, K.; Nakazawa, S.; Shiomi, D.; Sato, K.; Takui, T.; Kawakami, T.; Yamaguchi, K.; Nakasuji, K. *Tetrahedron Lett.* **2001**, *42*, 7991−7995. (e) Morita, Y.; Nishida, S.; Kawai, J.; Fukui, K.; Nakazawa, S.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *Org. Lett.* **2002**, *4*, 1985−1988.

(7) Recent progress in phenalenyl-based molecules: (a) Goto, K.; Kubo, T.; Yamamoto, K.; Nakasuji, K.; Sato, K.; Shiomi, D.; Takui, T.; Kubota, M.; Kobayashi, T.; Yakushi, K.; Ouyang, J. *J. Am. Chem. Soc.* **1999**, *121*, 1619−1620. (b) Itkis, M. E.; Chi, X.; Cordes, A. W.; Haddon, R. C. *Science* **2002**, *296*, 1443−1445. (c) Morita, Y.; Aoki, T.; Fukui, K.; Nakazawa, S.; Tamaki, K.; Suzuki, S.; Fuyuhiro, A.; Yamamoto, K.; Sato, K.; Shiomi, D.; Naito, A.; Takui, T.; Nakasuji, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 1793−1796.

(8) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318. (b) Gogonea, V.; Schleyer, P. v. R.; Schreiner, P. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1945−1948. (c) Allen, A. D.; Tidwell, T. T. *Chem. Rev.* **2001**, *101*, 1333−1348.

(9) Although hundreds of aryloxyl and related radicals are known, the spin topological symmetry control in the present paper is a unique property only in odd alternant π-systems. These π-systems are also the model systems suitable for the development of MO-based VB method.[6b]

(10) Ashby, E. C.; Lin, J. J.; Kovar, R. *J. Org. Chem.* **1976**, *41*, 1939−1943.

confirmed the relative signs of the hfcc values of all the protons to be the same.[13] The observed ESR spectrum was successfully simulated by use of the hfcc values obtained from the ^{1}H ENDOR spectrum.[13] The calculation of the spin density distribution and proton hfcc values in terms of density functional theory (DFT)[14a] indicated that the calculated value for the hfcc values of **3** gave a rationale for the assignments of the experimentally obtained hfcc values (Table 1).

Table 1. Observed and Calculated Proton Hfcc Values for **3**

	A_H/mT						
	3	6	7	9	2-*t*-Bu	5-*t*-Bu	8-*t*-Bu
obsd[a]	+0.214	+0.039	+0.112	+0.084	+0.011		+0.011
calcd[b]	+0.153	+0.025	+0.079	+0.049	+0.014	+0.003	+0.010
calcd[c]	+0.236	+0.047	+0.106	+0.073			

[a] Observed hfcc values were determined by ^{1}H ENDOR and simulated ESR spectra. The hfcc values of protons of 5-*tert*-butyl groups could not be determined experimentally. [b] Calculated hfcc values were determined by the DFT method.[14a] [c] Calculated hfcc values were determined by the DFT method[14a] with the help of McConnell's equation ($Q = -2.25$ mT).

The calculated π-spin density distributions in three kinds of the topological isomers of oxophenalenoxyls are summarized in Figure 2a, showing a robust π-spin polarization nature in all cases. Furthermore, the spin density distribution is controlled by virtue of the spin topological symmetry inherent in the oxophenalenoxyl systems; the uniqueness is that the unpaired electron is dominantly delocalized on the two oxygen atoms and on the peripheral carbon atoms located at short distances between the two oxygen atoms. These characteristics can be well understood in terms of spin-delocalized structures, which represent dominant classical canonical resonance structures maintaining aromatic 6π-electron systems in each case (Figure 2b).[6a,b] For further evaluation of the electronic structures, we have invoked the NICS method, which is known as an interpretative tool for identifying regions of high local aromaticity and antiaromaticity (Figure 2a).[8] In the 3-oxophenalenoxyl system, the large negative (−8.6) and the positive (+7.2) NICS values obtained in the two ring systems and in the other ring system indicate a substantial degree of the local aromaticity and antiaromaticity of these ring systems, respectively. This demonstrates that an unpaired electron tends to localize in the antiaromatic ring system of 3-oxophenalenoxyl and agrees well with the results obtained from the spin density distribution and the spin-delocalized structure. This rationale is applicable to the 4- and 6-oxophenalenoxyl systems. The validity of the NICS method for open-shell organic systems of π-conjugation is exemplified for the first time from the experimental side. Interestingly, the relative order of the total energy (in units of kcal/mol) for 3- (+6.86), 4- (+2.88) and 6-oxophenalenoxyl (0) obtained by the DFT method[14b] is consistent with the length of the π-conjugation in the spin-delocalized structure; five atoms for the 3-, seven atoms for the 4-, and nine atoms for the 6-oxophenalenoxyl system (Figure 2b).

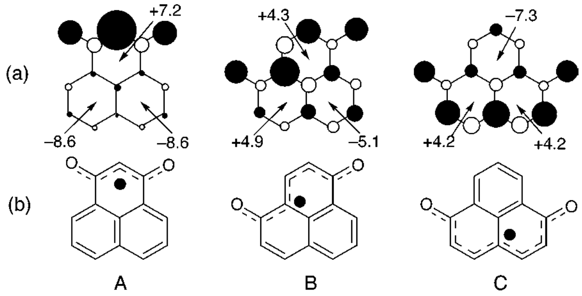

Figure 2. Spin density distribution and the NICS (ppm) (a) for 3- (A), 4- (B), and 6-oxophenalenoxyl (C) systems (unsubstituted) calculated by the DFT method.[14b] Vacant and filled circles denote negative and positive π-spin density, respectively. The spin-delocalized structure (b) represents dominant classical canonical resonance structures in each system.

In conclusion, our preparation and determination of the spin density distribution of the 4-oxophenalenoxyl **3** enabled us to characterize the electronic spin structures of the three oxophenalenoxyl topological isomers, demonstrating that the oxophenalenoxyl systems afford the first example showing spin topological symmetry control in monoradical chemistry. We emphasize the importance of organic synthetic efforts for these persistent radicals, which can lead to new conceptual advances in monoradical chemistry,[9] contributing to the molecular designs for novel organic open-shell systems and syntheses of the exotic spin-mediated crystalline materials.[15] Phenalenyl-based spin chemistry has served for the disclosure of the new spin topological symmetry control. The concept is generally applicable to homoatomic systems.

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Supporting Information Available: Experimental procedures for new compounds and ESR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Selected physical data for **6**: mp 284−285 °C; TLC R_f 0.42 (5:1 hexane/ethyl acetate); ^{1}H NMR (270 MHz, $CDCl_3/CF_3CO_2H$) δ 1.47 (s, 9), 1.49 (s, 9), 1.54 (s, 9), 7.69 (brs, 1), 7.88 (brs, 1), 8.31 (brs, 1), 8.40 (brs, 1); IR (KBr) 3600−2700, 2960, 1571 cm^{-1}; IR (CCl_2CCl_2) 3628, 2963, 1643, 1627 cm^{-1}; EI-MS, *m/z* 364 (M^+), 307 ($M^+ - C_4H_9$). Anal. Calcd for $C_{25}H_{32}O_2$: C, 82.37; H, 8.85; N, 0.00. Found: C, 82.37; H, 8.98; N, 0.00.

(12) Selected physical data for **3**: mp 162−164 °C dec.; TLC R_f 0.56 (5:1 hexane/ethyl acetate); IR (KBr) 2961, 1580 cm^{-1}. Anal. Calcd for $C_{25}H_{31}O_2{\cdot}(H_2O)_{0.2}$: C, 81.79; H, 8.62; N, 0.00. Found: C, 81.58; H, 8.56; N, 0.00.

(13) ^{1}H TRIPLE and simulated ESR spectra; see Supporting Information.

(14) (a) Gaussian 94 with UBLYP/6-31G**//UBLYP/6-31G* method. (b) Gaussian 94 with UBLYP/6-31G**//UBLYP/6-31G** method.

(15) X-ray crystallographic analyses and measurements of magnetic susceptibility for **2** and **3** are of great interest and are underway.