Curved π Diradical

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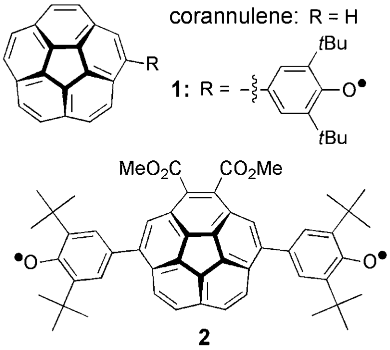
Three-Dimensional Intramolecular Exchange Interaction in a Curved and Nonalternant π-Conjugated System: Corannulene with Two Phenoxyl Radicals**

Akira Ueda, Shinsuke Nishida, Kozo Fukui, Tomoaki Ise, Daisuke Shiomi, Kazunobu Sato, Takeji Takui, Kazuhiro Nakasuji, and Yasushi Morita**

In recent years, curved π-conjugated molecules such as fullerenes and carbon nanotubes have attracted much attention not only in chemistry but also in materials science.[1] Their intra/intermolecular interactions within/between three-dimensional (3D) curved π-electron networks play intrinsically vital roles in their unique properties and functionalities. Among them, intramolecular magnetic interaction between electronic spins on a curved π surface was extensively studied for ionic species of C_{60} such as $C_{60}{}^{2-}$ and $C_{60}{}^{3-}$.[2] Their electronic structures are greatly influenced by not only the dynamic spin polarization of electrons but also the negative charges on the spherical π-conjugated system and the countercation.

Thus, we have focused on neutral diradical systems, which are known to be the most useful probes for studying intramolecular magnetic interactions in organic molecules.[3] While many neutral diradical derivatives relevant to planar π-conjugated systems have so far been investigated, studies on curved π-conjugated neutral diradicals are limited to a single C_{60}-based system in which [60]fullerene is linked to two nitroxide radicals.[4] However, their intramolecular exchange interaction J through the C_{60} skeleton was very weak ($|Jk_B^{-1}| < 0.1$ K)[4b] because of the small spin delocalization onto the C_{60} π network from the nitroxide radicals with spin-localized nature on the NO moieties. Therefore, in order to evaluate an intramolecular exchange interaction in a curved π-conjugated system in a quantitative manner, synthesis and isolation of a stable neutral diradical derivative with extensively spin-delocalized nature on its curved π-conjugated system have been the focus of current attention in molecular magnetism and open-shell chemistry.[2,5]

Recently, we studied corannulene[6]-based stable neutral monoradical systems,[7] such as a phenoxyl radical derivative **1**[7d] with highly spin-delocalized nature on the intrinsically 3D bowl-shaped and nonalternant π-conjugated network. These studies inspired us to propose a 3D intramolecular exchange interaction in this class of curved π radicals: in terms of geometry, they are intermediate between a planar π radical such as a phenalenyl system[8] and a tetrahedral σ radical. We have now, for the first time, synthesized and isolated a corannulene-based neutral diradical, namely, **2**, which has two phenoxyl radical moieties, as air-stable crystals. Due to its highly spin-delocalized nature, **2** shows strong intramolecular exchange interaction ($Jk_B^{-1} = -405 \pm 2$ K) through the 3D corannulene π-electron network. Bond-length analyses and DFT calculations showed that **2** has contributions from diradical canonical forms **α**–**γ** and closed Kekulé structure **δ** (Scheme 1). Furthermore, in the crystalline state the presence of three crystallographically independent diradical molecules with different curvature enabled us to study the relationship between the curvature of the corannulene π skeleton and the



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[*] A. Ueda, Prof. Dr. K. Nakasuji, Prof. Dr. Y. Morita
Department of Chemistry
Graduate School of Science, Osaka University
Toyonaka, Osaka 560-0043 (Japan)
Fax: (+81) 6-6850-5395
E-mail: morita@chem.sci.osaka-u.ac.jp
Homepage: http://www.chem.sci.osaka-u.ac.jp/lab/nakasuji/morita/index_eng.html
Dr. S. Nishida, Dr. T. Ise, Prof. Dr. D. Shiomi, Prof. Dr. K. Sato, Prof. Dr. T. Takui
Departments of Chemistry and Materials Science
Graduate School of Science, Osaka City University
Sumiyoshi-ku, Osaka 558-8585 (Japan)
Fax: (+81) 6-6605-2522
E-mail: takui@sci.osaka-cu.ac.jp
Homepage: http://www.sci.osaka-cu.ac.jp/chem/phy2/indexe.html
Dr. K. Fukui, Prof. Dr. Y. Morita
PRESTO (Japan) Science and Technology Agency (JST) (Japan)

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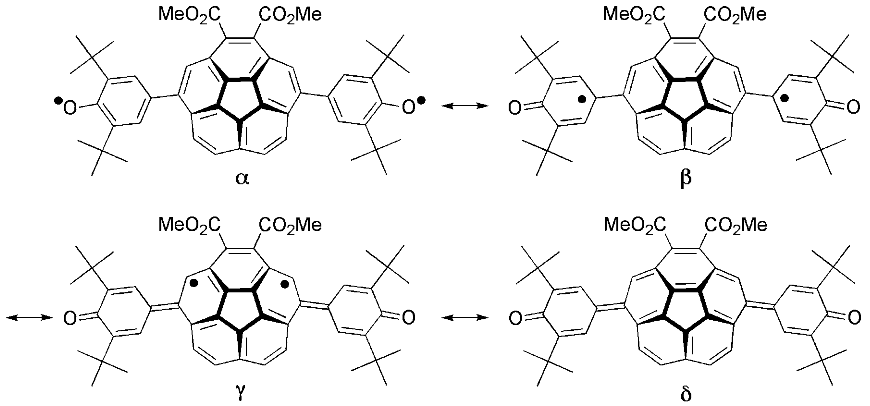
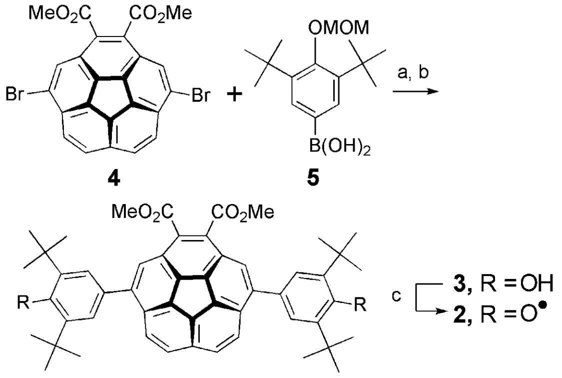


Scheme 1. Canonical resonance structures of **2**.

magnitude of the intramolecular exchange interaction or diradical character.

A synthetic route for **2** is depicted in Scheme 2. The diradical precursor, bis-phenol derivative **3**, was obtained as yellow blocks[9] by Suzuki coupling reaction of dibromo derivative **4**[10] with boronic acid **5**, followed by deprotection of the methoxymethyl (MOM) groups. Oxidation of **3** with an excess of PbO_2 and subsequent recrystallization gave single crystals of **2** suitable for X-ray crystal structure analysis. In the crystalline state, most of **2** survives in air at −30 °C for a few weeks. Diradical **2** is also stable in degassed solution.

The crystal structure of **2** is illustrated in Figure 1. This is the first X-ray structure analysis of neutral diradical derivatives with a curved π-conjugated system. The unit cell contains three crystallographically independent molecules **2A**, **2B**, and **2C** (Figure 1c).[11] They stack in a convex–concave fashion.[12] Judging from their bowl depths[13] and π-orbital axis vector (POAV) angles[14,15] of the corannulene skeleton (**2A**: 0.84 Å, 7.8°; **2B**: 0.80 Å, 7.7°; **2C**: 0.85 Å, 8.1°; **3**: 0.88 Å, 8.3°), the curvature decreases in the order $\mathbf{3} > \mathbf{2C} > \mathbf{2A} > \mathbf{2B}$. As shown in Figure 1b,[11] the O1−C1 and O2−C7 bond lengths of **2** (1.282 Å) are shorter than those of **3** (1.385 Å) and are close to the corresponding C−O bond length of **1** (1.250 Å)[7d] and the C=O bond length of *p*-terphenoquinone (1.231 Å).[16] This indicates that the O1−C1 and O2−C7 bonds of **2** have a certain degree of C−O double-bond character.[17] In addition, we found that significant changes of bond lengths arise in the two six-membered rings (C1–C6 and C7–C12) and the C4−C13 and C10−C18 bonds. On the other hand, the C23−C28, C24−C29, and C28−C29 bond lengths in the corannulene skeleton of **2** remain almost unchanged from those of **3** (Figure 1b). Thus, **2** has much larger contributions of the diradical structures with quinoidal character such as **β** and **γ**[18] than closed Kekulé structure **δ** (Scheme 1). These significant diradical contributions are strongly supported by natural orbital occupation number (NOON) analysis[19] (see below) and comparison between the observed and calculated bond lengths.[20] Furthermore, the dihedral angles between the corannulene skeleton and the phenoxyl or phenol moieties are significantly decreased (by 11–19°) in **2** from **3**.[9,11] These changes can be interpreted as a result of the shortened C4−C13 and C10−C18 bond lengths in **2** and their increased double-bond character. These bond-length and dihedral-angle analyses experimentally illustrate that two electronic spins of **2** are delocalized onto the corannulene skeleton with retention of diradical character in the crystal.



Scheme 2. Synthesis of **2**. a) $[Pd(PPh_3)_4]$, Na_2CO_3, toluene/EtOH/H_2O, 100 °C; b) 2 M HCl, AcOH, 40 °C, 73 % in two steps; c) PbO_2, CH_2Cl_2, room temperature, 100 %.

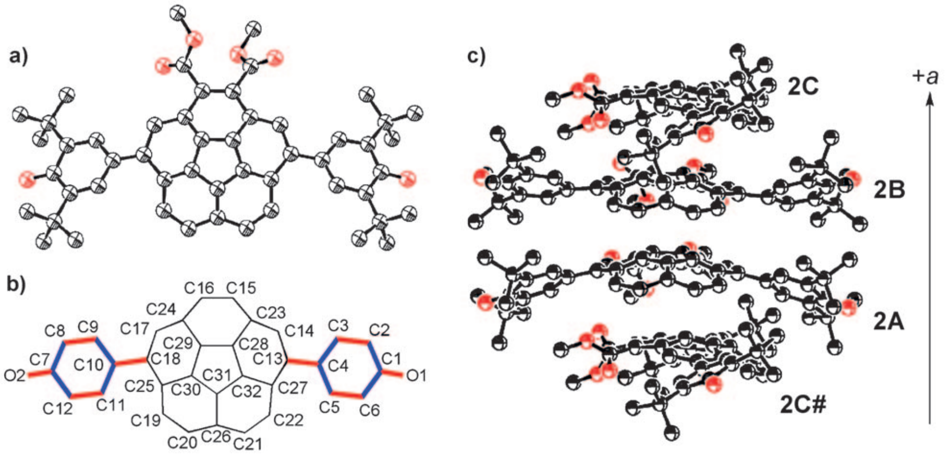


Figure 1. a) Molecular structure **2A** and c) packing structure of **2** along the *a* axis. # denotes the symmetry operation $x+1,y,z$. The thermal ellipsoids are scaled to the 50 % probability level. Hydrogen atoms are omitted for clarity. b) Major changes of bond lengths in **2** relative to **3**. Red bonds are shorter and blue bonds are longer than the corresponding bonds in **3**.

To evaluate the intramolecular magnetic interaction through the corannulene π-conjugated network, we carried out temperature-dependent magnetic susceptibility measurements on a polycrystalline sample of **2** in the range of 1.9–298 K.[21] Because of the lack of effective intermolecular magnetic contacts,[12] we concluded that the very strong intramolecular antiferromagnetic interaction ($Jk_B^{-1} = -405 \pm 2$ K) occurs through the curved and nonalternant 3D π conjugation of corannulene in the crystalline state. Thus, diradical **2** has a singlet ($S=0$) ground state and a thermally accessible excited triplet ($S=1$) state. The singlet–triplet energy gap $2Jk_B^{-1}$ is estimated to be −810 K. In addition, we experimentally determined the magnitude and relative sign of hyperfine coupling constants (hfccs) of the triplet species by solution-phase ESR and ^{1}H ENDOR/TRIPLE spectroscopy (Figure 2 a,b).[22] Glass-phase ESR measurements (Figure 2 c) gave the characteristic fine structure ($\Delta M_s = \pm 1$) and forbidden transition ($\Delta M_s = \pm 2$). The zero-field splitting parameters (D, E) and principal g values were determined by spectral simulation.[22] Estimating the spin–spin distance suggested considerable contributions of canonical resonance structures **β** and **γ** (Scheme 1) in the triplet state. In this estimation, we carefully noted that a nonvanishing E value is consistent with significant contributions of the structures **β** and **γ**. All these experimental results demonstrate that the extensive spin delocalization onto the corannulene moiety (Figure 3, see below) results in significant electronic-spin communication via the curved and nonalternant π-surface of corannulene.[23] Furthermore, in terms of the curved π-conjugated structure, we believe that diradical **2** has its own place as an intermediate case between thus-far reported planar π-conjugated systems and completely 3D π-conjugated species such as neutral C_{60} in the triplet state, noting that spin–orbit contributions are relevant to the particular canonical resonance structures (see Figure S12 in the Supporting Information).[2d,f]

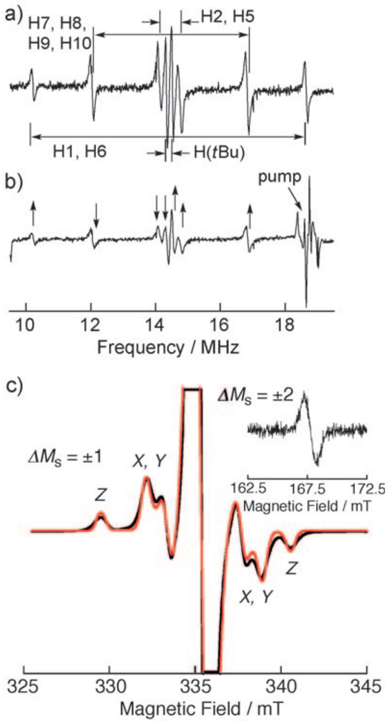


Figure 2. a) ^{1}H ENDOR (290 K) and b) TRIPLE (290 K, pump frequency 18.674 MHz) spectra of **2** in a degassed toluene solution (1.3×10^{-3} M). The vertical arrows in (b) denote increase or decrease in intensity when the outermost ENDOR line at 18.674 MHz is pumped. The intensity of the pumped line decreased. c) Fine-structure ESR spectra of **2** ($\Delta M_s = \pm 1$: microwave frequency 9.40792 GHz, $\Delta M_s = \pm 2$ (inset): microwave frequency 9.40799 GHz) in a degassed frozen toluene glass (1.3×10^{-3} M) at 158 K. The black and red lines indicate observed and simulated spectra, respectively.

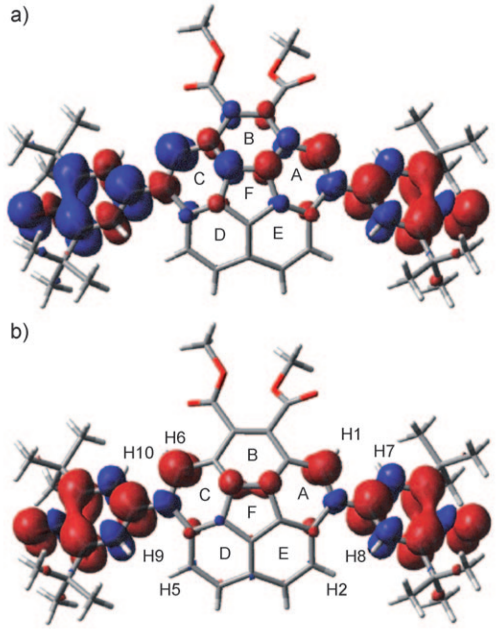


Figure 3. Calculated spin-density distributions of a) BS singlet state and b) triplet state for **2A** at the UB3LYP/6-31G(d,p) level. Red: positive, blue: negative spin densities.

Calculated spin-density distributions obtained by DFT methods[24] indicate an extensive spin-delocalized nature of **2** in both broken-symmetry (BS) singlet and triplet states (Figure 3).[25] Especially in the BS singlet state (Figure 3 a), rings A, B, and C of corannulene have a large amount of spin density, and rings D and E a relatively small amount. Thus, the unbalanced spin-delocalized nature, that is, spin-rich (rings A–C) and spin-poor regions (rings D and E) on the curved π-conjugated system of corannulene, is generated in the diradical system **2** as well as in the monoradical system **1**.[7c,d] The origin of this unique nature is the topological effect arising from the nonalternant π conjugation of the corannulene system, which is illustrated by the canonical resonance structures.[26] Furthermore, the differences in spin-density distributions between the two spin states (see Figure S13 in the Supporting Information) affect sensitively their curved aromaticity, as suggested by the nucleus-independent chemical shift (NICS)[27] method.[28]

Furthermore, we have found that the calculated intramolecular exchange interactions J[29] and singlet diradical characters of the three crystallographically independent diradical molecules **2A**–**2C** with different curvature provide very intriguing findings for this class of curved diradical systems. Diradicals **2A**–**2C** all show large negative J values (**2A**: −425.0 K, **2B**: −525.4 K, **2C**: −339.5 K), which means the occurrence of strong antiferromagnetic intramolecular exchange interaction. Their average value ($Jk_B^{-1} = -430.0$ K) reproduces well the experimentally obtained one ($Jk_B^{-1} = -405 \pm 2$ K). In addition, we are interested in the considerable differences between the calculated J values of **2A**–**2C**. Detailed studies on their structural differences related to such differences in J value strongly suggest that the magnitude of the J value becomes larger when the curvature of the corannulene π-conjugated system decreases.[30] It is notable that such small differences in curvature of **2A**–**2C** (0.05 Å in bowl depth) give rise to very large differences in the J values (186 K).[31] This is due to the enhancement of the π conjugation between the corannulene skeleton and the radical moiety. An NOON analysis[19] also indicates that **2A**–**2C** in the singlet ground state have much larger contributions of diradical structures [ca. 83% (**2A**: 83.7%, **2B**: 80.1%, **2C**: 84.6%)] than of the closed Kekulé structure (ca. 17%; see also Table S4 in the Supporting Information). This pronounced diradical character is probably attributable to aromatic stabilization of the corannulene π system, which prevents **2** from forming Kekulé structure **δ** with fewer 6π benzene-structure contributions than **β** and **γ** (Scheme 1).[26] Importantly, the difference in curvature also correlates with the magnitude of the diradical character of **2** as well as the intramolecular exchange interaction J. These results suggest that the singlet diradical character of **2** decreases with increasing magnitude of the antiferromagnetic intramolecular exchange interaction J. In this context, a theoretical analysis of the zero-field splitting tensor for **2** in the thermally accessible triplet state gives a clue to understanding the three-dimensional electronic-spin structure in a straightforward manner (see the Supporting Information).

In summary, corannulene-based stable neutral diradical **2** bearing two phenoxyl radical moieties has been synthesized and isolated as crystals stable in air. Thanks to the high stability and the sizable spin delocalization onto the corannulene skeleton from the radical moieties, we have experimentally revealed, for the first time, the occurrence of 3D intramolecular exchange interaction via the curved and nonalternant π-conjugated system of corannulene. Furthermore, we have successfully illustrated that the magnitude of the intramolecular exchange interaction is enhanced by decreasing the curvature of the corannulene skeleton. In addition to this geometrical effect, we have illustrated the topological effect of the nonalternant π-conjugated network, which influences the spin-delocalized nature, diradical character, and curved aromaticity of **2**. These findings demonstrate the intriguing aspects of a 3D intramolecular exchange interaction of neutral diradical systems having curved and nonalternant π-conjugated networks. Thus, we believe that our present study will contribute not only to opening up a new field of open-shell chemistry and molecular magnetism with dynamic electronic-spin behaviors arising from bowl-to-bowl inversion behavior,[7e,32] but also to developing functionalities based on 3D intra/intermolecular interactions of molecular assemblies composed of bowl-shaped π-conjugated open-and/or closed-shell molecules with unique geometrical and topological features.[6,7,33]

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[11] Molecular structure, bond lengths, and dihedral angles of **2A**–**2C** are shown in the Supporting Information.

[12] There are no intermolecular magnetic contacts between carbon atoms with a large amount of spin density. However, π–π concave–convex interactions occur between the corannulene skeletons with short distances close to the sum of the van der Waals radii of two carbon atoms (3.40 Å). For details, see the Supporting Information.

[13] Bowl depths are the average of the perpendicular distances between the plane containing the central five-membered ring composed of C28–C32 and the peripheral ten carbon atoms (C13–C22) of the corannulene skeleton.

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[15] These POAV angles are the average values of the carbon atoms in the five-membered ring (C28–C32). POAV values of all carbon atoms in the five-membered rings of **2** and **3** are given in the Supporting Information.

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[20] The experimentally obtained bond lengths were significantly closer to those calculated for the singlet diradical structure than those of the Kekulé structure. For details, see the Supporting Information.

[21] The results of magnetic susceptibility measurements and its fitting data are given in the Supporting Information.

[22] The solution-phase ESR spectrum, hfccs, zero-field splitting parameters, and *g* values are given in the Supporting Information.

[23] UV/vis measurements for **2**, **3**, and **1** demonstrate the occurrence of a sizable degree of π conjugation between the corannulene and two phenoxyl moieties. For details, see the Supporting Information.

[24] All DFT calculations were performed with Gaussian 03 (revision B.05), Gaussian, Inc., Wallingford CT, 2004; the full reference is listed in the Supporting Information.

[25] All of the spin density distributions of BS singlet and triplet states of **2A**–**2C** are given in the Supporting Information.

[26] For details of the canonical resonance structure studies on **2**, see the Supporting Information.

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[28] For details of the curved aromaticity of **2** and **3**, which is the aromaticity in six- and five-membered rings of the curved π-conjugated system, see the Supporting Information.

[29] Their J values were obtained by using calculated spin expectation values and total energies for the BS singlet ($\langle S^2\rangle_{BS}$ and E_{BS}) and triplet states ($\langle S^2\rangle_T$ and E_T). These parameters are listed in the Supporting Information. See S. Yamanaka, T. Kawakami, H. Nagao, K. Yamaguchi, *Chem. Phys. Lett.* **1994**, *231*, 25.

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