Corannulene-Based Radicals

DOI: 10.1002/ange.200704752

Curved Aromaticity of a Corannulene-Based Neutral Radical: Crystal Structure and 3D Unbalanced Delocalization of Spin**

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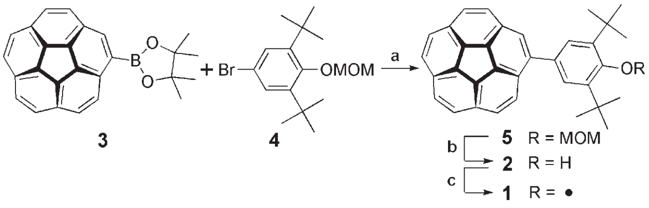
Bowl-shaped polycyclic aromatic hydrocarbons such as corannulene, which shares a fullerene substructure itself with a non-alternant π conjugation, have been studied extensively in recent years.[1] Such studies have emphasized the description of their aromaticity and electron interactions on curved surfaces or between a curved surface and a metal ion from both the experimental and theoretical perspectives. In contrast to the closed-shell systems studied so far, neutral open-shell molecules with curved π conjugation have been studied only in degassed solution owing to their low stability in air.[2,3] Spin delocalization on a curved π-conjugated system is intrinsically three-dimensional, and thus elucidation of the crystal/electronic-spin structures and intra- and intermolecular exchange interactions in the crystalline state is a current issue for studying the 3D interelectronic exchange and dipolar interactions in curved π systems such as fullerenes.[4]

In this study, we have synthesized a corannulene-based neutral radical with a phenoxyl moiety (**1**) and determined for the first time the crystal structure of a neutral radical derivative with curved π conjugation. The high stability and extensively spin-delocalized nature of the corannulene moiety **1** have enabled us to investigate curved aromaticity and intermolecular interactions of this class of curved neutral radical systems with a non-alternant π conjugation,[5] thus emphasizing the occurrence of unbalanced delocalization of spin within the corannulene moiety.

A synthetic route for **1** is depicted in Scheme 1. The radical precursor **2** was obtained as colorless plates by Suzuki coupling of a pinacol boronate derivative **3**[6] with methoxymethyl-protected (MOM-protected) bromophenol **4** and subsequent deprotection. Treatment of **2** with an excess of PbO_2 and recrystallization gave **1** as black plates. The radical **1** in the crystal is stable in air at −30 °C for a few weeks, and is extremely stable also in degassed solution.



Scheme 1. Synthesis of neutral radical **1**: a) $[Pd(PPh_3)_4]$, K_2CO_3, DMF, 110 °C, 39 %; b) 2 M HCl, AcOH, room temperature, 95 %; c) PbO_2, CH_2Cl_2, room temperature, 99 %.

We have succeeded in the crystal structure analysis of radical **1** (Figure 1 a).[7] The structural features of **1** were revealed by comparison with the molecular structure of the phenol **2**.[8] While the bowl depth and POAV (π-orbital axis vector) angles[9,10] of **1** are similar to those of **2**, significant changes in bond lengths of the phenoxyl moiety and C7−C8 and C8−C17 of the corannulene moiety were observed (Figure 1 b, Table 1). Particularly, the O−C1 bond of **1** (1.250(2) Å) is closer to the C=O bond length of *p*-benzoquinone (1.222 Å)[11a] and *p*-terphenoquinone (1.231 Å),[11b] indicating that the C−O bond of **1** has a substantial double-bond character. IR measurements of **1** and **2**[12] also demonstrated the double-bond character of the O−C1 bond of **1**. In

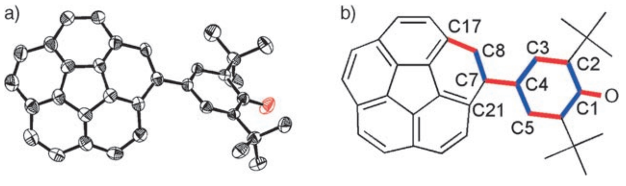


Figure 1. a) Molecular structure of **1**; hydrogen atoms are omitted for clarity. b) Major changes of bond lengths in **1** from **2**. Red and blue bonds represent shorter and longer bonds, respectively, in **1** as compared with corresponding bonds in **2**.

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[**] This work was supported by PRESTO-JST, Grant-in-Aid for Scientific Research (No. 18655058) from the Ministry of Education, Culture, Sports, Science and Technology (Japan), and the Global COE Program "Global Education and Research Center for Bio-Environmental Chemistry" of Osaka University.

Supporting information for this article, including detailed synthetic procedures for **1** and **2**, is available on the WWW under http://www.angewandte.org or from the author.

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Table 1: Bowl depths, POAV angles, selected bond lengths, and dihedral angles of **1** and **2**.

Compound	**1**	**2**
Bowl depth [Å][a]	0.91	0.92
POAV angle [°][b]	8.5	8.4
Bond lengths [Å]		
O–C1	1.250(2)	1.385(5)
C1–C2	1.468(2)	1.409(5)
C2–C3	1.362(3)	1.382(5)
C3–C4	1.414(2)	1.394(5)
C4–C7	1.471(3)	1.494(5)
C7–C8	1.409(2)	1.394(5)
C8–C17	1.414(3)	1.441(6)
Dihedral angles [°]		
C3-C4-C7-C8	35.9(2)	38.6(5)
C5-C4-C7-C21	41.5(2)	43.7(5)

[a] Bowl depths were measured from the plane containing the five-membered ring to the plane containing the peripheral aromatic carbon atoms. [b] Average of carbon atoms of the five-membered ring.

the radical **1**, the O–H stretching found in **2** (3636 cm^{-1} in the KBr, 3631 cm^{-1} in CH$_2$Cl$_2$ solution) disappeared, and a new sharp absorption appeared at 1565 cm^{-1} in the solid and at 1567 cm^{-1} in solution. These new absorptions are similar to the C=O vibration frequency of *p*-terphenoquinone (1575 cm^{-1} in the solid state).[11b,13] Table 1 also shows that the dihedral angles between the corannulene and phenoxyl moiety of **1** (C3-C4-C7-C8 35.9(2)°, C5-C4-C7-C21 41.5(2)°) are slightly decreased from those of **2** (C3-C4-C7-C8 38.6(5)°, C5-C4-C7-C21 43.7(5)°). These changes are reasonably interpreted by considering a quinoidal structural contribution in the classical canonical resonance structures of **1**.[14] All the experimental results suggest extensive spin delocalization onto the corannulene moiety from the phenoxyl moiety in the solid state.

DFT calculations of **1** based on the crystal structure also showed extensive spin delocalization onto the corannulene moiety from the phenoxyl moiety (Figure 2),[15] as revealed by comparing the sum of the absolute spin density on the corannulene moiety of **1** (0.553)[16] with those of verdazyl (0.241)[17] and iminonitroxide (0.175)[17] derivatives of corannulene. This trend of the spin delocalization depending on radical moieties is attributable to the topological nature of the substituted position in the corannulene moiety, that is, the positive sign of the spin density at the carbon atom attached to the corannulene skeleton (C4 in Figure 1 and Figure 2).[18] Notably, the highly delocalized unpaired electron on the corannulene moiety in **1** effects an unbalanced delocalization of spin, that is, the uneven spin distribution over spin-rich (rings A and B) and spin-poor regions (rings D and E) within the corannulene moiety. This differential spin distribution attributable to the topological effect of the corannulene π conjugation can also be interpreted in terms of classical canonical resonance structures.[14]

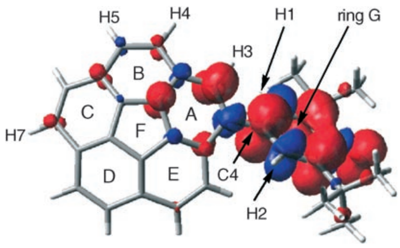

Figure 2. Spin-density distribution of **1** calculated at the UB3LYP/6-31G(d,p) level. The molecular geometry was taken from the X-ray crystal structure. The red and blue colors denote positive and negative spin densities, respectively.

This unique spin delocalization on the corannulene moiety affects the packing structure of **1** in the solid state. As shown in Figure 3, radical **1** forms a dimeric pair with an intermolecular separation of 3.791 Å between carbon atoms (C8···C8i) of the corannulene moieties (symmetry operation i: $-x$, $-y+1$, $-z+2$). Because the DFT calculations indicate that these carbon atoms have relatively large amounts of spin density (Figure 2), a sizable intermolecular exchange interaction between the corannulene moieties was expected. To evaluate this interaction and characterize the bulk magnetic properties of the crystalline state of **1**, the magnetic susceptibility χ_p of a polycrystalline sample was measured in the range from 1.9 to 300 K in a static magnetic field of 0.1 T.[19] The result showed a ground-state spin-singlet formation with an antiferromagnetic intermolecular interaction ($J/k_B = -22.5 \pm 0.2$ K) owing to the intermolecular exchange interaction of **1** in the crystal. This experimental J value is in good agreement with the calculated one ($J/k_B = -27.0$ K).[20]

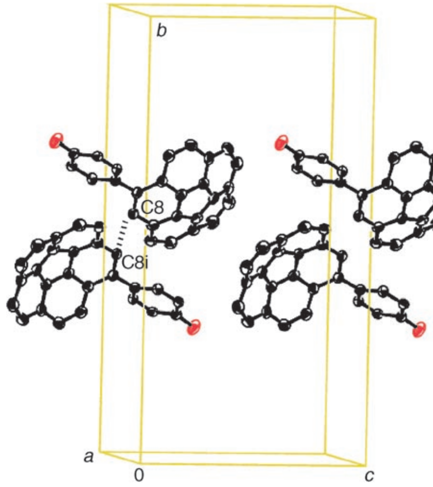

Figure 3. Crystal structure of **1**. The dashed line represents the intermolecular short contact (3.791 Å). Hydrogen atoms and the *tert*-butyl groups are omitted for clarity. The thermal ellipsoids are shown at the 50% probability level.

To elucidate the electronic-spin structure of **1** in solution, we carried out liquid-phase ESR and ^{1}H ENDOR/TRIPLE measurements. An ESR spectrum of **1** in a degassed toluene solution (4.4×10^{-4} M) shows five broad hyperfine splittings ($g = 2.0046$).[21] Hyperfine coupling constants (hfccs) and their relative signs of the protons were determined by ^{1}H ENDOR/TRIPLE spectroscopy (Figure 4).[21] These hfccs were suc-

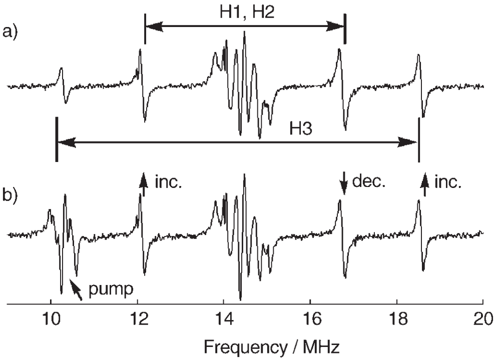

Figure 4. a) ^{1}H ENDOR and b) ^{1}H TRIPLE spectra (pump frequency 10.27 MHz) at 240 K of **1** in a degassed toluene solution (4.4×10^{-4} M).

cessfully assigned with the help of the results of the DFT calculations based on the crystal structure (see above; Table 2), and a spectral simulation well reproduced the observed spectrum.[21] Therefore, in solution, radical **1** maintains the unbalanced delocalization of spin.

Table 2: Observed and calculated hyperfine coupling constants (hfccs, in mT) of **1**.

	H1, H2	H3	H4	H5 or H7	H(tBu)
Obsd[a]	+0.165	−0.295	±0.043	±0.025	±0.007
Calcd[b]	+0.217[c]	−0.306	−0.046	+0.032 or −0.045	+0.005[d]

[a] Values and relative signs of hfccs were determined from ^{1}H ENDOR/TRIPLE spectra. [b] Values were calculated at the UB3LYP/6-31G(d,p) level based on the X-ray crystal structure. [c] Average of H1 and H2. [d] Average of all *tert*-butyl protons.

For further evaluation of the electronic structures, we have invoked the nucleus-independent chemical shift (NICS) method for both **1** and **2** using their crystal structures (Figure 5).[22] This method is known as a facile and efficient probe for evaluating aromaticity even for open-shell systems.[23] Negative NICS values indicate the presence of induced diatropic ring currents and “aromaticity”, whereas positive values denote paratropic ring currents and “antiaromaticity”. In phenol **2**, negative NICS(0) values were obtained in all six-membered rings (Figure 5a). In sharp contrast, in radical **1**, more-positive values were obtained in all ring systems on the corannulene moiety, especially for rings A and B (Figure 5b), which is in agreement with the positions having a large amount of spin density (Figure 2). Furthermore, the positive NICS(0) value (+1.3) in ring G indicates a local antiaromaticity of this (phenyl) ring system. These findings demonstrate that the local aromaticity of the ring system having a sizable spin density decreases significantly in the curved π conjugation of corannulene, which is consistent with the case of a planar odd-alternant π-radical system.[23c]

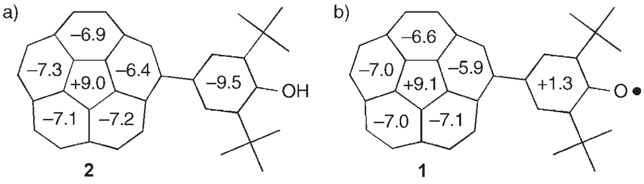

Figure 5. NICS(0) values (ppm) of a) **2** and b) **1** calculated at the UB3LYP/6-31G(d,p)//UB3LYP/6-31G level using the crystal structures as initial structures.

In conclusion, the stable corannulene-based neutral radical **1** with a phenoxyl moiety was synthesized, and its electronic-spin structure was elucidated experimentally on the basis of the crystal structure analysis with the help of resonance-structure studies, DFT calculations, and magnetic and ESR/ENDOR measurements. We have revealed, for the first time, the three-dimensional spin delocalization on a corannulene-based neutral radical. This study was inspired by the high stability and highly spin-delocalized nature in the corannulene moiety,[24] as well as the unique geometric relationship between the planar π radical[25] and tetrahedral σ radical, whereby we have focused on studying the inter- and intramolecular exchange interactions through the corannulene π surface.[26] Thus, such bowl-shaped neutral radicals with non-alternant π conjugation are useful for exploring new aspects of spin chemistry for applications in molecule-based functional materials. They also serve as a basis for both experimental and theoretical investigation of three-dimensional intra- and intermolecular exchange interactions within/between curved π-conjugated systems as well as the dynamic behavior of electronic spin and molecular structure as a function of bowl-to-bowl inversion.[27]

Experimental Section

Crystal data for **1**: $C_{34}H_{29}O$: $M_r = 453.60$, monoclinic, space group $P2_1/a$ (no. 14), $a = 8.457(8)$, $b = 23.85(2)$, $c = 12.140(12)$ Å, $\beta = 94.727(3)°$, $V = 2440(4)$ Å^3, $\rho_{calcd} = 1.234\ \mathrm{g\,cm^{-3}}$, $Z = 4$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.723\ \mathrm{cm^{-1}}$, $2\theta_{max} = 55.4°$, 18575 reflections, 5476 of which were unique ($R_{int} = 0.074$). $R_1 = 0.0785$, $wR_2 = 0.1035$, GOF = 1.058. Data were collected on a Rigaku Mercury CCD diffractometer ($\mathrm{Mo_{K\alpha}}$ radiation, $\lambda = 0.71073$ Å) at −73 °C. The structure was solved by direct methods and refined with full-matrix least-squares techniques (CrystalStructure 3.7.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC, The Woodlands, USA, **2000–2005**).

Crystal data for **2**: $C_{34}H_{30}O$: $M_r = 454.61$, monoclinic, space group $P2_1/a$ (no. 14), $a = 8.487(3)$, $b = 24.152(8)$, $c = 12.161(4)$ Å, $\beta = 95.244(11)°$, $V = 2482.1(14)$ Å^3, $\rho_{calcd} = 1.216\ \mathrm{g\,cm^{-3}}$, $Z = 4$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.712\ \mathrm{cm^{-1}}$, $2\theta_{max} = 55.0°$, 23496 reflections, 5661 of which were unique ($R_{int} = 0.047$). $R_1 = 0.0935$, $wR_2 = 0.1764$, GOF = 1.00. Data were collected on a Rigaku RAXIS-RAPID Imaging Plate ($\mathrm{Mo_{K\alpha}}$ radiation, $\lambda = 0.71073$ Å) at −73 °C. The structure was solved by direct methods and refined with full-matrix least-squares techniques (CrystalStructure 3.8., **2000–2006**).

CCDC-663934 for **1** and 663935 for **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Received: October 14, 2007
Published online: February 5, 2008

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Keywords: aromaticity · density functional calculations · EPR spectroscopy · radicals · X-ray diffraction

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[7] To our knowledge, this is not only the first crystal structure of a neutral radical with curved π conjugation, but also the first example of a crystal structure of a phenoxyl radical except for galvinoxyl.

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[14] For details of resonance structures, see the Supporting Information.

[15] All DFT calculations were performed with the Gaussian03 program (revision B.05) Gaussian, Inc., Wallingford CT, **2004**; the full reference is listed in the Supporting Information.

[16] Details of the calculated hfccs and spin densities of **1** are found in the Supporting Information.

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[18] Verdazyl and iminonitroxide derivatives have negative spin densities on this position.

[19] For details of the magnetic measurements, see the Supporting Information.

[20] Calculations were performed at the UB3LYP/6-31G(d,p) level using the crystal structure of **1**; for details, see the Supporting Information.

[21] For details of the ESR/^{1}H ENDOR spectra, see the Supporting Information.

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[26] Syntheses of corannulene derivatives with two phenoxyl moieties are underway.

[27] Bowl-to-bowl inversions of corannulene derivatives with closed-shell systems have been studied extensively; see reference [1a] and references therein.

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