Synthesis of Antiaromatic Compounds Utilizing Hyperconjugation and Anionic Charges
超共役と負電荷を利用した反芳香族化合物の合成

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1. Introduction

The concepts of aromaticity and antiaromaticity are significantly important to rationalize various chemical phenomena that are not found in a linear polyene. According to Hückel's rule, (anti)aromatic compounds consist of a planar sp^2-hybridized carbon-based framework with a cyclic π-conjugation. Because the Hückel's rule is the most widely used criteria for aromaticity, many chemists believe that (anti)aromatic rings should be solely composed of sp^2-hybridized atoms. Indeed, introducing an sp^3-hybridized atom into a π-conjugated system generates non-aromatic system due to a disrupted cyclic conjugation. In other words, the proposal of the synthesis of (anti)aromatic compounds involving sp^3-hybridized atom provide us new alternatives of a design guideline for aromatic systems. Then, the author focused on hyperconjugation between a σ* orbital of an sp^3-hybridized atom and a π orbital of an sp^2-hybridized atom.

Generally, hyperconjugation does not occur efficiently because an energy gap between σ*(C–R) and π orbital is too large, and that is why a cyclopentadiene is nonaromatic (Figure 1, left). In contrast, because an energy level of a σ* orbital involving main-group element is low, some heterocyclic compounds such as a phosphole oxide[1] is considered to have weak antiaromaticity originating from a delocalization of 4π-electron system via the σ*(P–O) orbital due to a small energy gap between π and σ* orbitals. From these backgrounds, the author focused on an anionic compound to create a novel hyperconjugative antiaromatic system, because the negative charges play crucial roles to raise the energy levels of the filled π-orbitals for effective hyperconjugation between the anionic π-system and σ*(heteroatom–R) orbital. Motivated by this idea, a dibenzo-annulated silepin was selected as a precursor of the target molecule due to a high electron acceptability derived from an extended π-skeleton to readily yield dianionic spieces. In this doctral thesis research, synthesis of a dibenzosilepinyl dianion and its antiaromaticity are demonstrated.
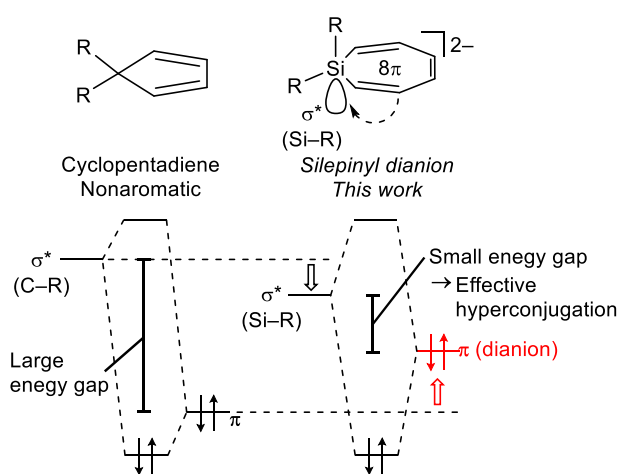

Figure 1. Hyperconjugative antiaromaticity.

2. Synthesis of a dibenzosilepinyl dianion[2]

Treatment of dibenzosilepin **1** with lithium in THF afforded dilithium dibenzosilepinide **2** quantitatively (Scheme 1). Recrystallization from a THF solution deposited black-purple crystals of **2** suitable for X-ray diffraction analysis. The ^{1}H NMR spectrum of **2** in THF-d_8 shows signals assignable to the dibenzosilepinide core at a high-field region (δ 5.63, 5.34, 4.99, 4.22, and 2.88) in comparison to the signals of **1** (δ 7.45-7.27). The ^{29}Si{^{1}H} NMR signal of **2** was detected at δ −31.0, which is upfield-shifted relative to that of **1** (δ −13.9). In the ^{13}C{^{1}H} NMR spectrum of **2**, characteristic upfield-shifted signals, for instance, δ 78.4 (C_{vinyl}) and 103.8 (C_α), were observed. These upfield shifts imply that the anionic charges are delocalized over the dibenzosilepinide scaffold by negative hyperconjugation as well as classical π-conjugation.
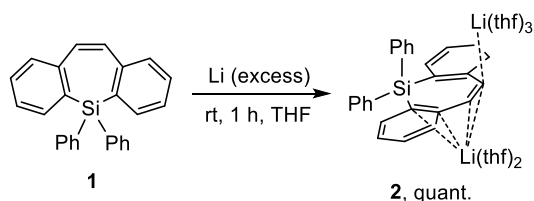
Scheme 1. Synthesis of **2**

The Si–Ph bond lengths of **2** are slightly elongated in comparison to those of **1** (1.8999(14) and 1.8976(14) for **2** vs. 1.8709(19) and 1.8748(19) Å for **2**), while the endocyclic Si–C bonds are shortened upon reduction (1.8470(14) and 1.8424(14) Å for **2** and 1.8680(18) and 1.8682(19) Å for **1**). These structural changes provide evidence for negative hyperconjugation between the π-electrons of the alpha carbon atoms (C_α) and the σ*(Si–Ph) orbitals. Thus, dilithium dibenzosilepinide **2** has a 16π-electron system involving negative hyperconjugation.
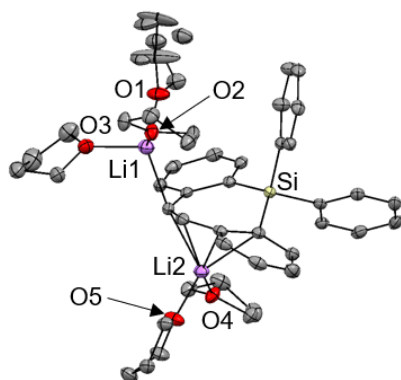

Figure 2. Crystal structure of **2**.

To gain more insight into the electronic properties of **2**, DFT calculations were conducted. NICS calculation is a useful method to evaluate aromaticity and antiaromaticity of a molecule by a calculated chemical shift of a dummy atom at the center of a ring skeleton. Negative NICS values indicate aromaticity, while positive indicate antiaromaticity. NICS calculations were conducted for **1** and the lithium-free structure of **2** (denoted as **2′**) (Table 1). Since dibenzosilepin cores are non-planar, NICS(+1) and NICS(−1) were defined. All NICS values for the dibenzosilepin skeleton of **2′** are positively higher than those of **1**, suggesting **2′** has antiaromatic character.

In stark contrast, lithium reduction of the tin analog of **1** (dibenzostannepin) resulted in the reductive cleavage of one or two Sn-Ph bonds to give mono- or dilithiostannepin, respectively.[3] The monolithiated species was fully characterized by a diffraction study to reveal its nonaromatic character.

Table 1. NICS(X)$_{iso}$ values for **1**, **2′**, and **7′**.

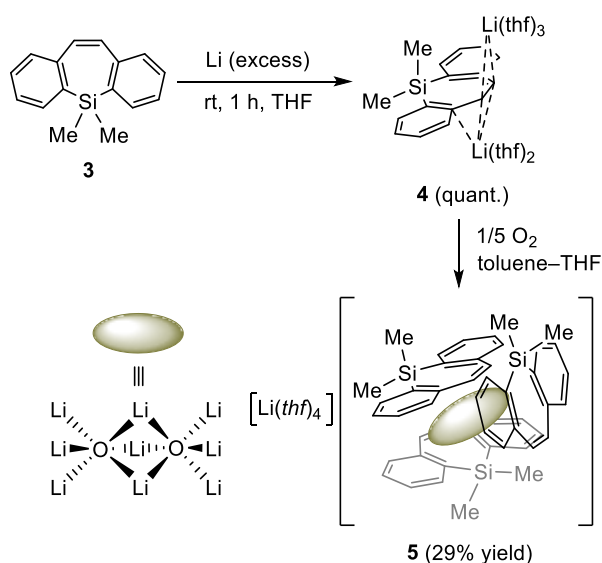|		six-membered rings	seven-membered rings
1	NICS(+1)	−10.6/−10.6	−1.2
	NICS(0)	−7.7/−7.7	2.5
	NICS(−1)	−10.7/−10.8	−1.2
2′	NICS(+1)	7.0/8.0	2.1
	NICS(0)	13.6/12.8	5.1
	NICS(−1)	8.2/7.5	4.2
7′	NICS(+1)	−0.5[a]/−2.9[b]	−3.4
	NICS(0)	2.8[a]/−0.3[b]	−3.4
	NICS(−1)	−2.8[a]/−6.2[b]	−6.3

[a] The outer six-membered rings. [b] The inner six-membered rings (see Scheme 3).

3. Trimerization of dibenzosilepinyl dianions[4]

If a compound has lithium cations, ^{7}Li NMR spectroscopy is usable for experimental evaluation of (anti)aromaticity, because ^{7}Li NMR chemical shifts are affected by ring currents, as do ^{1}H NMR chemical shifts. For example, ^{7}Li NMR signals of lithium salts of anionic aromatic compounds such as metallole dianions[5] appear at characteristic high-field ($\delta(^7Li)$ = −4.4 to −5.8), whereas those of general organolithium compounds (butyllithium, phenyllithium, etc) and free-lithium cations resonate at around 0 ppm. In contrast, the signal of dilithium salts of benzene dianion ($\delta(^7Li)$ = 10.2)[6] shifted to low-field, reflecting their antiaromaticity. In this section, the antiaromaticity of dibenzosilepinyl dianions is experimentally revealed by ^{7}Li NMR spectroscopy.

Reaction of dimethylsilepin **3** and lithium in THF afforded the dilithium salt $[(Li^+)_2(thf)_5][3^{2-}]$ (**4**) quantitatively, and recrystallization from a THF solution provided black crystals of **4** suitable for X-ray diffraction analysis (Scheme 2). To my surprise, during

recrystallization of **2** from a toluene solution with additive of THF, black crystals of a cluster $[(Li^+)(thf)_4][(3^{2-})_3(Li_9O_2^{5+})]$ (**5**), which can be understood as a complex of three dilithium dibenzosilepinide molecules and two Li_2O salts, were deposited. Since **2** reacts with excess oxygen gas to generate the corresponding neutral silepin and Li_2O, it was hypothesized that the Li_2O salts in **5** were generated by decomposition of **4** by O_2 gas during the recrystallization process. Indeed, **5** was successfully synthesized in 29% yield from the reaction of **4** and

0.2 equivalents of O_2 gas in a toluene solution with THF additive with good reproducivity.

The author obtained conclusive evidence for the antiaromatic character of the dibenzosilepinyl dianion from $^7Li\{^1H\}$ NMR studies (Figure 4). Both $^7Li\{^1H\}$ NMR spectra of **4** and **5** in THF-d_8 showed a signal at δ 0.3, indicating that both of them exist as a solvent-separated ion pair of monomeric dilithium dibenzosilepinide in THF. Importantly, the $^7Li\{^1H\}$ NMR spectrum of **5** in toluene-d_8 exhibits three distinct signals at δ 6.3, 4.4, and 0.6 with an integral ratio of 3:6:1, respectively (Figure 4). According to the integral ratio, the signals at δ 6.3 and 4.4 can be assignable to the inner three and outer six lithium cations in the Li_9O_2 cluster, respectively, and the signal at δ 0.6 to the solvent-separated lithium cation. Therefore, it was concluded that the downfield shifted $^7Li\{^1H\}$ NMR signals are caused by the paratropic ring currents of the antiaromatic dibenzosilepinyl dianions.

Scheme 2. Synthesis of dianion **4** and trimer **5**.
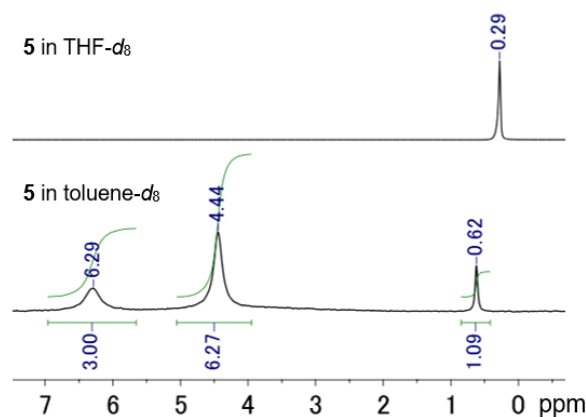
Figure 4. $^7Li\{^1H\}$ NMR signals of **5**.

4. Parallel stacking of dibenzosilepinyl dianions

It is known that some parallel stacked antiaromatic molecules gain thermodynamic stability through three-dimensional aromaticity.[7] Synthetic research of three-dimensional aromaticity is very limited, and to the best of my knowledge, such synthetic investigation for an anionic molecule has not been reported. These backgrounds prompted the author to investigate the synthesis of parallel stacked dibenzosilepinyl dianions and their through-space interactions.

Treatment of colorless Et_2O solution of **6** with excess lithium generated black purple solution. Recrystallization of the solution with the additive of DME deposited black crystals **7**. X-ray diffraction
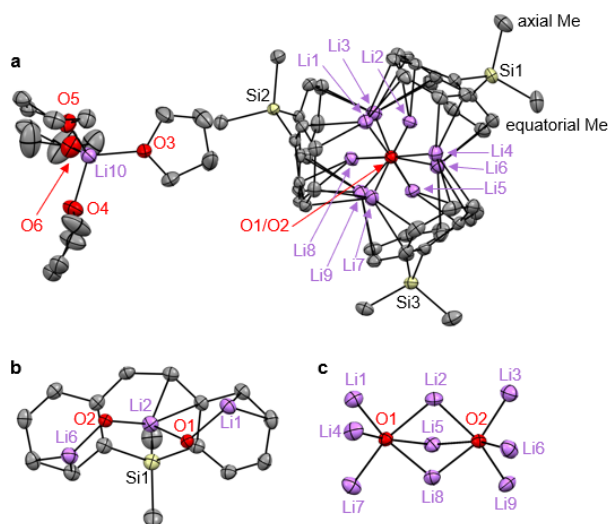

Figure 3. Whole structure of **5** (a), selected lithium cations coordinated by a dianionic moiety in **5** (b), and the Li_9O_2 core structure in **5** (c).

analysis revealed that the two dibenzosilepin cores were almost parallel and stacked to sandwich the two lithium cations. The ^{1}H NMR signals of the dibenzosilepinyl dianion scaffolds in **7** (δ 6.01, 5.52, 5.46, 4.44, and 3.77) appeared at low-field in comparison to those of monomer **2** ($\Delta\delta$ 0.12 to 0.53 ppm for fused benzene rings, $\Delta\delta$ 0.90 ppm for vinyl protons). This phenomenon provides an experimental fact of weakened antiaromaticity in dimer **7**.
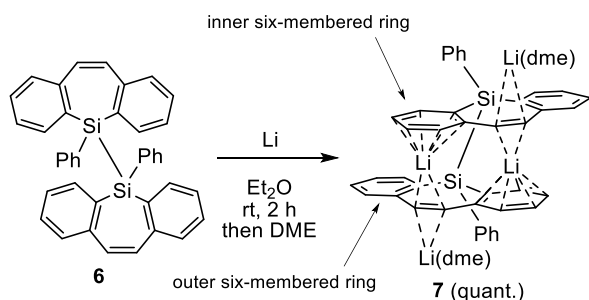
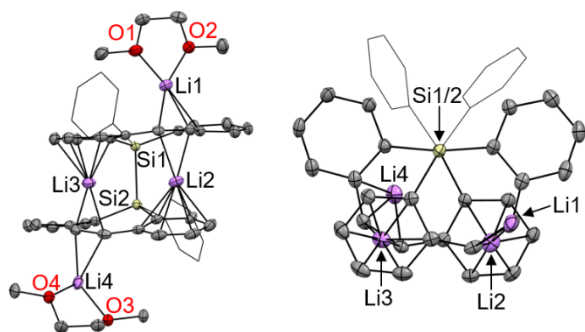**Scheme 3**. Synthesis of bissilepinyl tetraanion **7**.

Figure 4. Crystal structures of **7**.

NICS$_{iso}$ calculations were conducted on the lithium-free tetraanion of **7** (denoted as **7′**) (Table 1; the outer and inner six-membered rings are defined as illustrated in Scheme 3). All NICS values for **7′** were drastically smaller than the values of **2′**. The smaller NICS values of **7′** suggest that **7** is stabilized by three-dimensional interactions to weaken its antiaromatic character.

Through space interactions in **7** were confirmed by molecular orbitals. The frontier molecular orbitals of **2** and **7** are illustrated in Figure 5. Both the HOMO and the HOMO−1 of **7** were constructed by the HOMO of **2**. However, the HOMO and the HOMO−1 of **7** are antibonding and bonding orbitals, respectively, thus the overlaps of orbitals between the two surfaces were confirmed only in HOMO−1 of **7**. Moreover, the

energy level of HOMO−1 of **7** was lower than HOMO of **7**, suggesting that the orbital overlaps stabilize the system thermodynamically.
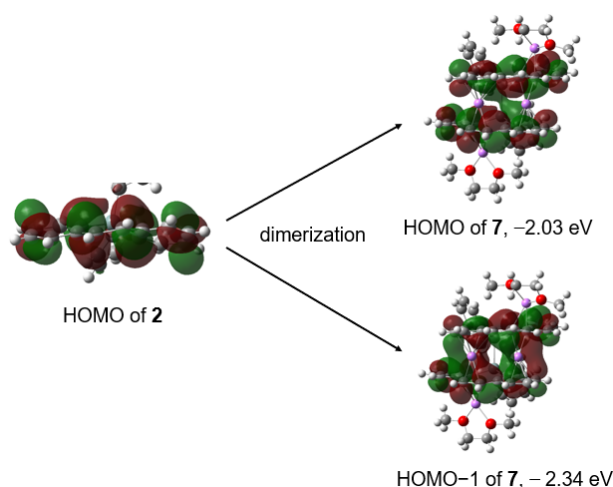

Figure 5. Frontier molecular orbitals for **2** and **7**.

4. Conclusion

In this doctoral thesis research, the author synthesized a dibenzosilepinyl dianion, which is the first example of hyperconjugative antiaromatic compound having negative charges. Antiaromaticity of a dibenzosilepinyl dianion was conclusively revealed by the low-field shifted ^{7}Li NMR signals of a trimer of dibenzosilepinyl dianions. Antiaromaticity of a dibenzosilepinyl dianion was weakened in a parallel stacked structure by through space interactions.

5. References and publications

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