Synthesis of a Hyperconjugative Antiaromatic Compound and Weakened Antiaromaticity in Its Dimeric Structure

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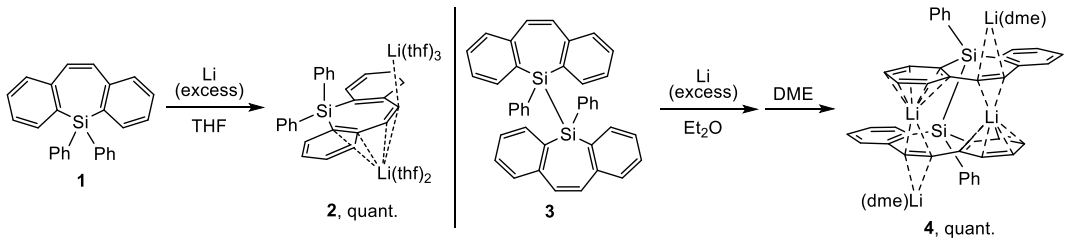
In contrast to well-established chemistry of conventional antiaromatic compounds with 4nπ electron systems, studies of hyperconjugative antiaromatic compounds, in which an sp^3 hybridized atom is doped into a cyclic π conjugated system, are very limited.[1] Herein, we report a novel anionic hyperconjugative antiaromatic compound that shows weakened antiaromatic character in a dimeric structure.

Reaction of diphenyldibenzosilepin **1** and excess lithium in THF yielded dilithium diphenyldibenzosilepinide **2**. The ^{1}H and ^{29}Si{^{1}H} NMR signals of the dibenzosilepin skeleton of **2** in THF-d_8 were found in a characteristic high-field region (δ(^{1}H): 5.63–2.88 ppm), suggesting the anionic charges are delocalized over the dibenzosilepin scaffold. The Si–Ph and the endocyclic Si–C bonds of **2** are slightly elongated and shortened compared to those of **1**, respectively. These structural changes suggest the anionic charges are delocalized through the σ* orbitals of the Si–Ph bonds. The NICS(0) values were calculated to be 13.6 and 12.8 ppm for the annulated benzene rings and 5.1 ppm for the silepin ring, which indicates the antiaromatic character of **2** originating from the 16π-electron system.

Treatment of a Et_2O solution of bis(phenyldibenzosilepin) **3** with excess lithium afforded lithium salt of bissilepinyl tetraanion **4**. The NICS(0) values of **4** were calculated to be nearly zero (2.8 and −0.3 ppm for the annulated benzene rings and −3.3 ppm for the silepin ring), which is in sharp contrast to the positive NICS(0) values in **2**. Importantly, the ^{1}H NMR signals of the dibenzosilepin skeleton of **4** in THF-d_8 were low-field shifted compared to those of **2** (Δδ = +0.12–0.90 ppm), suggesting the antiaromatic character of the dibenzosilepin skeltons is weakened in **4**. This phenomenon seems to be closely related to three-dimensional aromaticity.[2]



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