



Boron Heterocycles

2,3-Dihydro-1*H*-naphtho[1,8-*cd*]borinine as a Potent Precursor for Open-Shell Singlet B-Heterocycles

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Abstract: The reaction of naphthalene-1,8-diylbis[(trimethylsilyl)methanide] and dimethyl arylboronates afforded the corresponding 2,3-dihydro-1*H*-naphtho[1,8-*cd*]borinine as single dia-

Introduction

A biradical bearing two radical centers is usually in the triplet ground state, and the open-shell character results in high reactivity, which hampers isolation. However, decreasing the open-shell character is a promising approach towards the construction of isolable biradicals in the singlet ground state.^[1-4] The quest for stable cyclic singlet biradicals has attracted great interest in molecular science and functional materials. As exemplified by sterically encumbered heavier congeners of cyclo-alkane-1,3-diyls, the introduction of a *p*-block heteroelement is a promising method for constructing functional biradicals.^[5,6]

Boron is used as a radical center for isolable congeners of singlet cyclobutane-1,3-diyl,^[7] and for constructing singlet biradicals. Figure 1 shows a molecular orbital diagram of singlet biradical 2-borapropane-1,3-diyl. The presence of boron stabilizes the $\Psi_{\rm S}$ orbital and destabilizes the $\Psi_{\rm A}$ orbital through the p orbital to produce singlet biradicals. Scheme 1 shows the isomerization of dibenzoborepine **A** upon irradiation, which



Figure 1. Schematic description for design of singlet biradicals based on 2-bora-1,3-diyl system.

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Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejic.201700372. stereomers. Single-electron oxidation of the boron-containing heterocycles provided acenaphthylene through the generation boron-containing cyclic singlet biradicals.

generates the biradical species through the dearomatization of the mesityl (Mes) substituent, as reported by Yamaguchi and coworkers.^[8] These findings prompted us to design novel cyclic singlet biradicals containing boron as the key heteroelement.^[9]



Scheme 1. Nazarov-type disrotatory cyclization of dibenzoborepine ${\bf A}$ affording singlet biradical species. $^{[8]}$

In this paper, we synthesized open-shell (OS) singlet boroncontaining cyclic compounds with an aromatic skeleton. Using both π -conjugated counterparts and heteroelements is an attractive approach for developing functional OS singlet compounds. Herein, we characterize and discuss the structure of 2,3-dihydro-1*H*-naphtho[1,8-*cd*]borinine, which could be a precursor or a formal H₂ adduct of the B-heterocyclic biradical.

Results and Discussion

Figure 2a shows the structure of the boron-containing cyclic singlet biradical **B** based on the combination of 2-bora-1,3-propanediyl and naphthalene-1,8-diyl. Density functional theory (DFT) calculations for the parent molecule [Figure 2b, wB97XD/6-31G(d)] showed that the OS singlet structure is in the ground state, and the closed-shell (CS) structure and the triplet (T) state are energetically less favorable ($\Delta E_{OS-T} = -10.2 \text{ kcal mol}^{-1}, \Delta E_{OS-CS} = -0.87 \text{ kcal mol}^{-1}$).^[10] Figure 2c shows the distribution of the spin density of the OS singlet structure, which is comparable to that of the phenalenyl radical.^[11]

In 1987, Meller and coworkers isolated a 2,3-dihydro-1*H*-naphtho[1,8-*cd*]borinine by using the carbene-analog reaction of acenaphthylene, which putatively included the borirene (boracyclopropane) intermediate (Scheme 2, $R^1 = H$).^[12] This

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Figure 2. a) Design of B-containing π -delocalized singlet biradical **B**. b) Formula of the parent molecule. c) Spin-density distribution of the parent molecule. Occupation of LUMO is 0.22e [CASSCF(2.2)/6-31G(d)].

method appeared to be quite attractive for generating B-heterocyclic singlet biradical: thus, we attempted similar reactions with 1,2-disubstituted acenaphthylenes ($R^1 = 4$ - XC_6H_4).^[13,14] Our attempts to prepare the desired 2,3-dihydro-1*H*-naphtho[1,8-*cd*]borinines by using the carbene-analog reaction were unsuccessful, and we found no evidence that the desired biradical species was obtained. However, 2,3-dihydro-1*H*-naphtho[1,8-*cd*]borinine derivatives can be synthesized by following alternative pathways, and we speculated that 2,3-dihydro-1*H*-naphtho[1,8-*cd*]borinine would be promising for Bheterocyclic singlet biradicals.



Scheme 2. The carbene-analog reaction affording 2,3-dihydro-1*H*-naphtho[1,8-*cd*]borinine.

To construct the 2,3-dihydro-1H-naphtho[1,8-cd]borinine precursors, we used the reaction of naphthalene-1,8-diyldimethanide with electrophilic boron reagents. We expected the 1,3-positions in **B** (Figure 2) to be stabilized by delocalization of the unpaired electrons, but the synthesis of 1,3-diaryl-2,3dihydro-1H-naphtho[1,8-cd]borinine by the reaction of naphthalene-1,8-diylbis(arylmethanide)^[15] and electrophilic boron reagents failed. Therefore, we used naphthalene-1,8-diylbis[(trimethylsilyl)methanide] (1)^[16] as a reagent for constructing the alternative 2,3-dihydro-1H-naphtho[1,8-cd]borinine derivatives. The dilithiated species 2 was prepared from 1 and butyllithium in hexane/TMEDA, and to our delight, the reaction of 2 and a dimethyl arylboronate $[ArB(OMe)_2; Ar = Mes, Ph]$ afforded the corresponding 1,3-bis(trimethylsilyl)-2,3-dihydro-1H-naphtho-[1,8-cd]borinines (3) as air-stable crystalline compounds (Scheme 3). The diastereoselective formation was indicated by a single resonance peak in the ¹¹B NMR spectrum [**3a**: $\delta_{\rm B}$ = 77.5, 3b: 72.2]. The skeletal CH protons were assigned by the resonances at $\delta_{\rm H}$ = 3.68 (**3a**) and 3.66 (**3b**) in the ¹H NMR spectra. The reaction of **2** with dichloro(mesityl)borane (MesBCl₂) did not give 3.



Scheme 3. Preparation of 2,3-dihydro-1H-naphtho[1,8-cd]borinines 3.

The structure of **3a** was unambiguously determined by X-ray crystallography, and Figure 3 displays the molecular structure. Two trimethylsilyl groups form only the trans-isomeric form, which is consistent with the NMR spectra. Due to the condensed boron-containing six-membered ring, the naphthalene skeleton deviates slightly from the planar form [C1-C17--C9-C2 dihedral angle of 26.7(1)°]. The benzene ring of the Mes substituent has a dihedral angle of 62.09° with respect to the C1-B-C2 plane, which indicates the reduction of steric repulsion and the resonance between the benzene ring and the vacant p orbital of the boron atom. DFT calculations for 3a showed similar metric parameters and hyperconjugation between the vacant p orbital and C-Si sigma orbitals (Figure 4). The DFT structure of **3b** bearing the less bulky phenyl group also showed a non-coplanar conformation between the C-B-C plane and the aromatic ring (dihedral angle: 33.55°, see the Supporting Information).



Figure 3. Molecular structure of **3a** (30 % probability level). Hydrogen atoms except for H1 and H2 are omitted for clarity. Bond lengths [Å] and angles [°]: B–C19 1.592(3), B–C1 1.561(3), B–C2 1.552(3), C1–Si1 1.928(2), C2–Si2 1.932(2), C1–C17 1.517(3), C2–C9 1.506(3), C17–C18 1.434(3), C9–C18 1.426(3), C1–B–C2 116.4(2), C1–B–C19 123.4(2), C2–B–C19 120.2(2), B–C1–Si1 110.8(1), B–C1–C17 115.9(2), Si1–C1–C17 107.2(1), B–C2–Si2 108.7(1), B–C2–C9 116.6(2), Si2–C2–C9 106.9(1), Si1–C1-···C2–Si2 171.63(9).

Next we generated the corresponding heterocyclic biradicals from **3**. Removal of the skeletal CH proton with strong bases was prevented by the steric congestion, and oxidation of the







Figure 4. LUMO of the optimized structure for ${\bf 3a}$ at the M06-2X/6-31G(d) level.

dianionic intermediate leading to the desired biradical was not achieved. Thus, we examined one-electron processes that would remove dihydrogen from **3**. Although chloranils gave complex mixtures, we found that heating of **3** with DDQ afforded acenaphthylene together with recovery of the starting materials (Scheme 4).



Scheme 4. Oxidation of **3** to afford acenaphthylene.

The formation of acenaphthylene in the reaction of 3 and DDQ indicated the generation of a biradical intermediate. Scheme 4 shows a possible reaction mechanism based on the procedure for the preparation of azomethine ylides by oneelectron oxidation of bis[(trimethylsilyl)methyl]amine.[17] Removal of an electron from 3 affords the corresponding cation radical and DDQ⁻⁻, and the silvl cation is removed to generate the neutral radical 4. The Si-C bond weakened by hyperconjugation facilitates the selective desilvlation step. In these steps, DDQ may react with the silvl groups to facilitate their removal. Subsequent oxidation-desilylation processes would generate 5, which may give acenaphthylene through thermolysis.^[18] In contrast to **3b**, the steric hindrance around the boron in **3a** may promote the desilylation reaction, which may allow the substantial interaction between the silyl groups and DDQ. Attempts to trap 5 by dimethyl acetylenedicarboxylate (DMAD), N-

phenylmaleimide (PMI), and cyclohexene were unsuccessful, probably due to the facile intramolecular processes in **5**.

Conclusions

In conclusion, we synthesized and characterized 1,3-bis(trimethylsilyl)-2,3-dihydro-1*H*-naphtho[1,8-*cd*]borinines (**3**). Oxidation of **3** with DDQ upon heating afforded acenaphthylene, which indicates the generation of the desired B-heterocyclic singlet biradical species (**5**). Because of the instability of **5**, the harsh oxidation step to remove the silyl groups should be replaced. Another approach is introducing suitable substituents into the naphthalene moiety. Further efforts to capture the B-heterocyclic singlet biradicals and confirm the reaction mechanism affording **5** are ongoing.

CCDC 1542485 (for **3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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