Controlled Synthesis of Cyclopenta-Fused B2N2-Pyrene and Diazaborepin: Structures and Optical Properties

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Abstract
Cyclopenta-fused B2N2-pyrene (B2N2CP) and diazaborepin (NBNM) have been accomplished from a same bi-indoles pre-cursor in three steps. Borylative cyclization of bi-indoles precursor with 2.0 equivalents BCl₃ afforded NBNM as the major product, whereas increasing the BCl₃ to 3.0 equivalents delivered B2N2CP as the major product. Both B2N2CP and NBNM are highly emissive in solution. B2N2CP emit in deep blue region, while NBNM emit in the region of blue to green. Moreover, we found that fluoride anion addition to the solution of B2N2CP and NBNM led to great change of their absorption and emission spectra.

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Controlled Synthesis of Cyclopenta-Fused B2N2-Pyrene and Di-azaborepin: Structures and Optical Properties

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Keywords
Cyclopenta-fused PAHs | Pyrene | Borepin | Photophysical properties | BN-aromatics |

Comprehensive Summary

Text: The text is applied here to display the beauty of your excellent contribution with the help of comprehensive graphic abstract above.

Background and Originality Content

Boron-doped polycyclic aromatic hydrocarbons (PAHs) are of high importance in the organic synthesis and functional materials.[1] Due to the vacant p-orbital, the trivalent boryl group is usually unstable.[2] Kinetic protection on the boron center with bulky groups is one way to provide sufficient stability for these boron aromatics. Alternatively, boron can be stabilized by adjacent X-donor (X = N, S, O . . .). In particular, substitution of a CC unit with an isostructural and isoelectronic BN unit (BN/CC isosterism) in PAHs is
proved highly useful to tune the photophysical properties of PAHs.\(^3\) There are many BN-doped PAHs have been synthesized. Taking pyrene for example,\(^4\) Dewar \textit{et al.} reported the first example of BN-pyrene (P-I, Figure 1) with two BN unit on the peripheral position in 1960s.\(^5\) Attempt to synthesize P-I’s orientational isosteres P-II failed (P-II, Figure 1). Later on, Dewar \textit{et al.} synthesized the mono-BN-doped pyrene (P-III, Figure 1).\(^6\) In the year of 2007, Piers’ group reported the synthesis and photophysical studies of pyrene with an internalized BN unit (P-IV, Figure 1), utilizing the PtCl\(_2\)-catalyzed cyclization as the key step.\(^7\) Wang \textit{et al.} prepared the fifth BN-pyrene (P-V, Figure 1) in the year of 2015, showing that P-V could be used as emitter for electroluminescence devices.\(^8\)

Figure 1 Top: Selected examples of BN-doped pyrene (P-I to P-V); Middle: Selected examples of (non)-fused borepins (B-I to B-VI); Bottom: Cyclopenta-fused B\(_2\)N\(_2\)-pyrene and diazaborepin studied in this work.

On the other hand, borepin featuring a unique \(\pi\)-conjugated heptagonal core have attracted a lot attention.\(^9\) Borepin is isoelectronic with tropylium cation. The mono-benzoborepin (B-II) was synthesized in 1967, demonstrating the aromatic character of the B-seven membered ring for the first time.\(^10\) Minimally substituted borepin (B-I) was reported by Ashe \textit{et al.}, in particular, an X-ray crystal structure of a B-Cl borepin derivative clear gave evidence of a \(\pi\)-delocalized structure.\(^11\) Later on, research group of Piers\(^12\) and Tovar\(^13\) independently developed a series of bis-aryl fused borepins, such as dibenzo- (B-III) and dithieno-fused borepins (B-IV). Quadruply (B-V)\(^14\) and triply (B-VI)\(^15\) annulated borepins were also investigated recently. Bulky substituents such as mesityl (Mes) or mesityl (Mes) are required to protect the boron in the above cases.\(^10-15\) N-heterocyclic carbene and structural constraint strategy were also applied recently to shield the empty \(p\) orbital of boron center of borepin from nucleophilic attack.\(^16\) Beside the blooming research on the borepins, investigation of diazaborepin derivatives have been rarely explored.\(^9, 17\)

In parallel with our efforts to develop the family of cyclopenta-fused BN-aromatics,\(^18\) herein, we reported the preparation and photophysical studies of cyclopenta-fused B\(_2\)N\(_2\)-pyrene and diazaborepin by a straightforward way (Figure 1, bottom). An important feature of the synthetic strategy is that the synthesis of the two types of BN-aromatics shared a same precursor. The photophysical studies showed that boron in both the B\(_2\)N\(_2\)-pyrene and diazaborepin maintained some degree of Lewis acidity, their absorption and emission spectra will strongly change by accommodate a lone pair of electrons from fluoride ion.

Results and Discussion

The synthesis of B\(_2\)N\(_2\)-pyrene (B\(_2\)N\(_2\)CP) and diazaborepin (NBNM) are shown in Scheme 1. The synthesis is commenced with 7-bromo-1H-indole (1), which was obtained via Bartoli indole synthesis (Scheme S1). Miyaura boylation of 1 delivered crude indole-7-boronic acid pinacol ester. Upon complete conversion of the 1 into the boronate intermediate, another equivalent of 1 was added, followed by addition of Pd(PPh\(_3\))\(_4\) and NaOH. The one-pot Miyaura-Suzuki coupling reaction gave bi-indoles (2) in 50% yield. Then, attempt to synthesize B\(_2\)N\(_2\)-pyrene bia borylation of 3 failed, presumably due to the formation of BNB-type by product\(^19\), or due to the positively charged nitrogen in the intermediate deactivated the adjacent ring.\(^5\) We decided to protect one of the nitrogens in bi-indoles (2). Compound 3 reacted with di-tert-butyl decarbonate (1.3 equivalent) afforded the mono-Boc-protected product 3 in good yield. It is worthy noting that the compound’s solubility is much better than the non-protected bi-indoles (2). To our delight, two-fold nitrogen-directed borylative cyclization occurred smoothly using excess of boron trichloride (BCl\(_3\)) as the borylative reagent at 110°C in toluene. The resulted B-Cl intermediate reacted with mesityl Grignard reagent, giving the desired B\(_2\)N\(_2\)-pyrene (B\(_2\)N\(_2\)CP) in good yield, along with a small amount of diazaborepin (NBNM). It should be noted that the protecting group (Boc) was deprotected at the same time by BCl\(_3\). The diazaborepin (NBNM) was synthesized in the similar manner using the mono-Boc-protected product 3, simply reducing the loading of BCl\(_3\) to 2.0 equivalents (Scheme 1, bottom). It should be noted that the attempt to synthesize NBNM by borylative cyclization of non-protected bi-indole 2 was failed as well. It worth noting that there is a small amount of urea by-product (NCN) was obtained in the above reaction system. Possible mechanism of formation of NCN was illustrated in the supporting information (Scheme S6).
Scheme 1 Synthesis of B$_2$N$_2$-pyrene (B$_2$N$_2$CP) and diazaborepin (NBNM)

The obtained B$_2$N$_2$-pyrene (B$_2$N$_2$CP) and diazaborepin (NBNM) are stable toward air and can be purified by column chromatography. Compounds B$_2$N$_2$CP and NBNM could be soluble in various of organic solvents. Both B$_2$N$_2$CP and NBNM were fully characterized by diverse techniques including $^1$H, $^{13}$C, and high-resolution mass spectroscopy. Diazaborepin NBNM was unequivocally confirmed by X-ray crystal analysis (Figure 2, Figure S1 and Table S1), single crystal of suitable for crystallographic determination were obtained by slow evaporation NBNM in solution of CH$_2$Cl$_2$/petro ether.[20] As shown in Figure 2, X-ray diffraction analysis of NBNM confirmed the proposed molecular skeleton that features a seven-membered diazaborepin ring fused to the indole moieties. The main borepin scaffold of NBNM exhibit a slightly twisted structure, the dihedral angle between the phenyl ring in the top indole motif and the bottom indole motif is 14.59°. The pendant B-mesityl substituent is almost perpendicular to the main diazaborepin backbone of NBNM (dihedral angle: 87.74°). Sum of bond angles around triaryl boron centers is 360°, consistent with the SP$^2$ hybridization character of boron atom, and also confirming the trigonal planar geometry of the boron atom. The inner-ring B-N, C, N-C-N and C-C-C angles are around 130°. The inner-ring B-N bonds length (1.426(3)) is sitting in between the typical B=N double bond (1.403(2)) and and sum of BN covalent radii (1.56)[22], indicating their strong double bond character. Endocyclic C-B bond length (ca. 1.58) of NBNM is comparable to the values of the reported borepins[9]. In addition, NBNM exhibit the parallel stacking pattern. The shortest π-π distances was 3.314 Å. It should be noted that dipole of NBNM oppose each other within the dimeric head-to-tail π stacking. Effort to grow the crystal of B$_2$N$_2$-pyrene (B$_2$N$_2$CP) failed. Instead, we simulated the solid-state structure of B$_2$N$_2$CP. The simulated structure of is shown in Figure 2b, the main scaffold of B$_2$N$_2$CP exhibit a highly planar geometry.

Figure 2 a,b): X-ray crystallographic structure of NBNM with the thermal ellipsoids drawn at 35% probability, and selected bond lengths (in angstroms). (CCDC 2351031). The H atoms have been omitted for the sake of clarity. Nitrogen, blue; Boron, red; Carbon, black. b): Calculated structure of B$_2$N$_2$-pyrene (B$_2$N$_2$CP).

To gain insight into the electronic structures and (anti)aromaticity of B$_2$N$_2$CP and NBNM, we carried out the carried out the electrostatic potential (ESP)[23], nucleus-independent chemical shift (NICS)[24], anisotropy of the induced current density (ACID)[25], and two-dimensional iso-chemical shielding surface (2D-ICSS) calculations[26] (Figure 3 and Figure S11-S12). The ESP maps of B$_2$N$_2$CP illustrate that the negative charge is evenly distributed on the bi-indoles backbone, less spread on the BN-bond. In the case of NBNM, the negative charge is evenly distributed on the bi-indoles backbone as well, while the positive charge located around the B-methyl group. In the ACID plots, clockwise ring current flows are observed over the indole units in both of B$_2$N$_2$CP and NBNM, indicating their aromatic character. In contrast, anti-clockwise ring current flows are observed over the BN-six-membered ring in B$_2$N$_2$CP and seven-membered diazaborepin ring in NBNM, indicating their anti-aromatic feature. Further analysis by 2D-ICSS also shows the weaker anti-aromaticity of the BN-six-membered ring in B$_2$N$_2$CP, and even weaker anti-aromaticity of the seven-membered diazaborepin ring in NBNM. In addition, the positive NICS values of the BN-six-membered ring (5.1) in and seven-membered diazaborepin ring (20.6) in NBNM also support their anti-aromaticity feature. In particular, the strong anti-aromaticity nature of diazaborepin core in NBNM is quite different to the other reported borepins.[9-16] The phenyl rings of B$_2$N$_2$CP exhibit NICS values (26.0) that are typical for benzene, while less negative NICS values the phenyl rings (22.4) of NBNM was observed, indicating its reduced aromatic feature. Moreover, the pyrrole rings of B$_2$N$_2$CP and NBNM exhibit a relatively less negative NICS values of -10.7 and -19.6, respectively.
The photophysical properties of B2N2CP and NBNM in dichloromethane were investigated (Figure 4 and Figure S2). Compound B2N2CP feature a strong absorption band from 300 to 340 nm, with a maximum at 314 and 326 nm. In addition, a long wavelength band partially in the region of visible region and partially in the UV region, maximums at 388 and 409 nm, was also observed for B2N2CP. By contrast, only one broad absorption band was observed for NBNM, with a maximum at 336 nm. The absorption of NBNM is completely located in the UV region, which is different from the other reported diazaborepin[17a]. Furthermore, the urea byproduct NCN features a largely blue shifted absorption spectra ($\lambda_{abs} = 296$ nm) as compared to NBNM (Figure S2).

<table>
<thead>
<tr>
<th>comp</th>
<th>$\lambda_{abs}$ nm$^a$</th>
<th>$\epsilon$(M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{em}$ ($\lambda_{ex}$) nm$^a$</th>
<th>$\Phi_{pl}$$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2N2CP</td>
<td>314, 326, 370, 388, 409</td>
<td>14363 (409)</td>
<td>418, 442, 469, 492 (326)</td>
<td>0.37</td>
</tr>
<tr>
<td>NBNM</td>
<td>336</td>
<td>9105 (336)</td>
<td>388, 411, 435, 464 (340)</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Figure 4. The normalized absorption (left) and emission spectra (right) of B2N2CP and NBNM in dichloromethane at a concentration of 10$^{-5}$ M.
Both B2N2CP and NBNM are strongly emissive in solution. The emission spectrum of B2N2CP in dichloromethane shows the present of a structured emission band centered at ca. 469 nm, with two shorter wavelength shoulders (418 and 442 nm) and one longer wavelength shoulder (492 nm). On the other hand, the diazaborepin NBNM shows a large blue shifted emission spectrum, featuring a structured emission band as well, with emission maximum at 411 nm. Unlike the emission band of B2N2CP are completely located in the region of visible region, the emission band of NBNM are located partially in the UV region of partially in the region of blue. Again, the urea byproduct NCN feature blue shifted emission spectra (λabs = 354 nm) as compared to NBNM. Moreover, the quantum efficiency of B2N2CP (Φpl = 0.37) and NBNM (Φpl = 0.38) are comparable, both of them are ten times higher than that of NCN (Φpl = 0.03). Moreover, the absorption and emission spectra of B2N2CP and NBNM are slightly dependent on the polarity of the solvents. Specifically, the fluorescence spectra of B2N2CP displayed a slightly bathochromic shift with increasing the solvent polarity from cyclohexane to methanol, while the fluorescence spectra of NBNM displayed negligible change in different solvents (Figure S3-S5).

Tricoordinate organoborane (Lewis acid) can react with fluoride ion (Lewis base) to form the tetracoordinate organoborane, many optical F- sensors were developed based on this mechanism. To verify the response of B2N2CP towards fluoride anion, we investigated this response by UV-vis spectra titration experiments (Figure 5a). A gradually decreases in intensity of the original two major absorption bands of B2N2CP at 300-340 nm and 350-425 nm was observed upon addition of TBAF solution in THF, while two new broad bands located at ca. 296 nm and 358 nm appeared. Titration of B2N2CP with fluoride anion was also monitored by fluorescence spectroscopy (Figure 5b). As illustrated in Figure 5b, its original emission band around 469 nm was diminished and generated a short-wavelength band around 422 nm. The binding constant of B2N2CP towards fluoride anion (log $K_a$ [?] 5.4 ± 0.3) was obtained in THF. In the case of NBNM, upon addition of TBAF, its original absorption band around 336 nm decreased along with generating a new band around at 363 nm(Figure 5c). Moreover, the fluoride addition to NBNM enhanced its emission band without generating a new band, only slightly blueshift of the original emission band (Figure 5d). The binding constant of NBNM towards fluoride anion (log $K_a$ [?] 6.1 ± 0.3) was obtained in THF.

Figure 5 Spectral changes in the UV/vis absorption (left) and fluorescence (right) upon addition of TBAF in THF. The excitation wavelength are as follows: B2N2CP, $\lambda_{ex} = 326$ nm; NBNM, $\lambda_{ex} = 340$ nm.

The fluoride addition experiments of B2N2CP and NBNM demonstrated that the sp2- hybridized boron atoms in both B2N2CP and NBNM can be captured by the added fluoride anion led to formation of sp3-hybridized boron atoms. In order to have insight on the mechanism of the fluoride sensing, we investigated the reversibility of the fluoride addition by UV-vis and fluorescence spectroscopy (Figures S7-S8). We found that the absorption and emission bands of B2N2CP and NBNM can be resumed by treatment B2N2CP-F and NBNM-F with BF3·OEt2, which is considered as a stronger fluoride scavenger. These results illustrate that the conformation of B2N2CP and NBNM are stable and without decomposition upon addition of fluoride anion. These results also highlight the potential utilization of the present boron-aromatics in the field of fluorescent sensor for the fluoride anion detection.

The electrochemical properties of B2N2CP and NBNM were also briefly investigated by cyclic voltammetry (Figure S9). Both of B2N2CP and NBNM exhibit irreversible oxidation and reduction process. B2N2CP and NBNM present comparable oxidation onset potentials of versus Fc/Fc+ (B2N2CP, 0.68 V; NBNM, 0.67 V). On the contrary, B2N2CP (-2.09 V) present much lower reduction onset than NBNM (-2.19 V).

Conclusions

In summary, we have developed an efficient three-step synthetic route of underdeveloped B2N2-pyrenes (B2N2CP) and diazaborepin (NBNM), both of which shared a same bi-indoles precursor. The compound NBNM was characterized by single crystal X-ray structures, elucidating the solid-state structure of heptagonal core. Furthermore, the (anti)aromaticity of the B2N2CP and NBNM were quantified by
theoretical studies. The BN-six-membered ring in B2N2CP show antiaromaticity, whereas the NBN-seven-membered ring in NBNM feature much stronger antiaromaticity. Photophysical studies showed that both B2N2CP and NBNM are highly fluorescent in solution. Moreover, fluoride anion addition to the solution of B2N2CP and NBNM led to great change of their absorption and emission spectra, which demonstrate their utilization as fluoride sensor. And the fluoride anion sensing process is fully reversible. Rapid construction and rich photophysical properties of B2N2CP and NBNM may offer new option to prepare boron-containing light-emitting material for optoelectronics.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.202400xxx.

Acknowledgement

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References


20. CCDC 2351031 contains the supplementary crystallographic data for NBNM. These data are provided free of charge by the Cambridge Crystallographic Data Centre.


22. The atomic radius of boron is 0.85 Å and the atomic radius of nitrogen is 0.71 Å; thus, sum of BN covalent radii is 1.56 Å.


26. The 2D-ICSS maps was generated using a Multiwfn software. Lu, T.; Chen, F. Multiwfn: a multifunctional wavefunction analyzer. J. Comput. Chem. 2012, 33, 580-592. Notes: The value in the color bar represents -NICS(1)zz, which is opposite the NICS(1)zz. The positive value in 2D-ICSS represents the shielding effect, while the negative value represents a deshielding effect.


The Authors

Left to Right: Authors Names You will be invited to submit the most recent photos of all the authors upon acceptance of the manuscript.

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