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The forgotten borole: synthesis, properties and reactivity of a 1-boraindene†

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The chemistry of unsaturated boron heterocycles, including five-membered boroles, continues to attract substantial interest. Herein, we report the synthesis of 1,2,3-triphenyl-1-boraindene, a benzene-fused borole, and examine its Lewis acidic, electrophilic, and antiaromatic properties relative to non-fused and bis-benzannulated boroles (9-borafluorenes). Reactivity studies with organic azides reveal that the boraindene behaves similarly to other boroles, undergoing ring expansion to a BN-naphthalene through insertion of a nitrogen atom.

Introduction

Boroles, boron heterocycles containing 4π electrons in a five-membered BC_4 ring, exhibit fascinating electronic and optical properties as well as unique reactivities, due to their anti-aromatic character and three-coordinate boron atom.[1] Over a decade of research into boroles has deepened our understanding of the critical relationship between structure and properties, paving the way for diverse applications in synthesis, catalysis, and material science.[1]

Highly reactive by nature, boroles depend on the stabilizing influence of surrounding substituents in order to be isolable.[2] Both the presence of aryl groups and ring-fusion strategies, whereby the five-membered borole ring becomes part of a larger conjugated system, have been demonstrated to effectively enhance the kinetic or thermodynamic stability of the anti-aromatic unit.[1,3–5] Fusing two benzene rings onto the borole core, yielding 9-borafluorenes,[3] significantly enhances stability, reflected in both diminished antiaromatic character and reduced Lewis acidity. Dilution of the parent borole's anti-aromaticity through ring fusion, a strategy that has resulted in a variety of aromatic–antiaromatic hybrids,[4] surprisingly encounters an exception in cases where heteroarene units are fused to boroles. These species, first reported by the group of Yamaguchi in the form of dithiophene-fused boroles,[6] deviate from the expected trend by exhibiting even more pronounced antiaromaticity.[7] Studies on mixed heteroarene-benzene-fused

boroles further support these findings,[8] clearly implicating the heteroarene ring in enhancing the antiaromatic and Lewis acidic character of the central borole unit. In addition to electron-rich five-membered heterocycles, fusion with electron-poor pyridine also strengthens the Lewis acidity of boroles, as demonstrated by Marder and coworkers.[9]

While extensive research has explored the modification of borole properties through ring fusion, our understanding is limited almost entirely to systems where the borole unit sits between two aromatic rings. In contrast, singly fused boroles, like the boraindene scaffold, have been largely neglected in the literature. In 2014, Piers reported a perfluorinated 1-boraindene derivative, bridging the gap between non-fused and doubly fused boroles.[10,11] Its reactivity towards dihydrogen revealed some interesting differences between these different classes of borole compounds. Leveraging its slightly lower reactivity towards dihydrogen relative to that of per-fluoropentaphenylborole, the perfluorinated 1-boraindene derivative proved valuable as a mediator for the hydrogenation of olefins.[10] Kaufmann synthesized one additional derivative, 1-chloro-1-boraindene, using pyrolytic dehydrogenation.[12] However, its presence could only be indirectly confirmed through trapping experiments. Beyond these studies, the chemistry of boraindenes remains unexplored.[13]

In this work, we report the synthesis of 1,2,3-triphenyl-1-boraindene, expanding the class of benzene-fused borole derivatives alongside established families like the 9-borafluorenes. Employing a range of spectroscopic and computational techniques, we explore the properties of the boraindene and compare them to its non-fused and doubly benzene-fused borole analogues, revealing fundamental insights into the effect of single benzene ring fusion. Beyond the exploration of Lewis acid–base adduct formation, this study complements the understanding of the boraindene's reactivity by investigating its reaction with organic azides, leading to the formation of BN-naphthalenes.

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Results and discussion

Synthesis of the 1-boraindene

Using the well-established tin–boron exchange strategy for borole synthesis, we treated 1,1-dimethyl-2,3-diphenyl-1-stannaindene[14] with one equivalent of dibromo(phenyl)borane in toluene (Fig. 1). A color change from colorless to red signaled conversion to the boraindene product (1), as evidenced by the observed appearance of a signal at 65.3 ppm in the ^{11}B NMR spectrum.[15] Standard workup, which included sublimation, effectively removed the dimethyltin dibromide byproduct, affording 1 as a high-purity red solid in 66% yield. Single crystals of compound 1 suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated solution in benzene at room temperature. The structure shows a planar boraindene core, with the phenyl substituents twisted out of this plane: the phenyl group at boron is twisted by 32.6°. The pronounced alternation of carbon–carbon single (1.503(4) Å) and double bonds (1.375(3) and 1.415(3) Å) within the boracycle is consistent with electron localization and the antiaromatic nature of the ring.[10]

Occupying an intermediate position between monocyclic boroles and tricyclic 9-borafluorenes, we explored the influence of ring fusion on the properties of compound 1. When comparing the frontier orbital energies of boraindene 1, 9-phenyl-9-borafluorene and pentaphenylborole, a clear trend becomes evident (Fig. 2, see ESI† for computational details). Calculations show a gradual increase in the HOMO–LUMO gap across this series with the number of fused benzene rings, a consequence of both HOMO stabilization and LUMO destabilization. In accordance with this trend, the UV-vis absorption maxima show a hypsochromic shift, with the longest wavelength observed for pentaphenylborole ($\lambda = 560$ nm),[15] followed by boraindene ($\lambda = 485$ nm), and then 9-phenyl-9-borafluorene ($\lambda = 405$ nm).[16] The trend observed in the frontier orbital

Fig. 1 Synthesis and molecular structure of 1 (displacement ellipsoids at 50% probability level and hydrogen atoms removed for clarity).

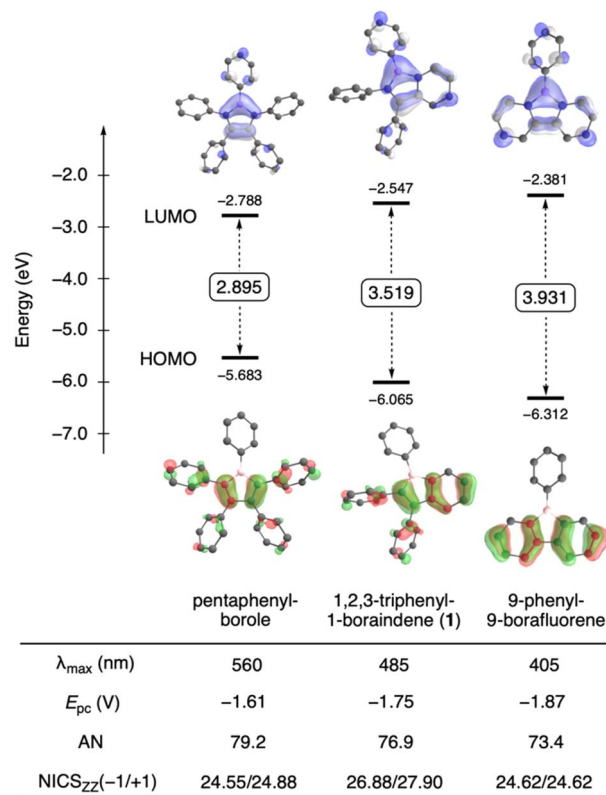|	pentaphenyl-borole	1,2,3-triphenyl-1-boraindene (1)	9-phenyl-9-borafluorene
λ_{max} (nm)	560	485	405
E_{pc} (V)	−1.61	−1.75	−1.87
AN	79.2	76.9	73.4
NICS$_{ZZ}$(−1/+1)	24.55/24.88	26.88/27.90	24.62/24.62

Fig. 2 Comparative analysis of key properties in non-fused (pentaphenylborole), singly benzene-fused (boraindene 1), and doubly benzene-fused borole (9-phenyl-9-borafluorene) systems. Details and references are provided in the main text.

energies is further supported by the experimentally determined Lewis acidity and electrophilicity. Based on the Gutmann–Beckett method,[17] evaluation by ^{31}P NMR spectroscopy using triethylphosphine oxide (Et$_3$PO) in deuterated benzene revealed an acceptor number (AN) of 76.9 for 1, indicating a slightly higher Lewis acidity than 9-phenyl-9-borafluorene (AN = 73.4).[18] This observation is consistent with the general trend of reduced Lewis acidity in boroles with increasing numbers of fused benzene rings (cf. AN = 79.2 for pentaphenylborole).[18] A similar trend is seen for the electron deficiency of the boracycle 1. Cyclic voltammetry of 1 in dichloromethane reveals a reduction potential ($E_{pc} = -1.75$ V) that lies between those of non-fused (pentaphenylborole, $E_{pc} = -1.61$ V)[19] and doubly fused (9-phenyl-9-borafluorene, $E_{pc} = -1.87$ V) derivatives.[20] Fig. 2 summarizes these comparisons of various borole structures, collectively confirming the observed trends with increasing benzene ring annulation. More specifically, as the number of fused benzene rings increases, the LUMO energy of the borole unit rises, leading to a decreased Lewis acidity and electron deficiency.

Nucleus-independent chemical shift (NICS) calculations[21] reveal a more nuanced relationship between antiaromaticity and structure within this series of three boroles (Fig. 2). NICS calculations indicate NICS$_{zz}$(−1/+1) values of 26.88/27.90 ppm at the PBE1PBE/6-311+G(d,p)/D3(BJ) level of theory for the
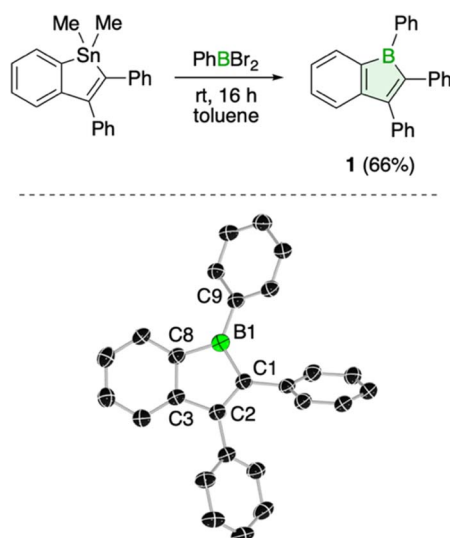
borole unit in **1**. These values surpass those of 9-phenyl-9-borafluorene (24.62/24.62 ppm), consistent with the expected decline in antiaromaticity as the degree of benzannulation increases.[6,7,22] However, pentaphenylborole (24.55/24.88 ppm) deviates from this trend, displaying a slightly lower degree of antiaromatic character than in boraindene **1**. The four phenyl groups on the carbon atoms of the borole ring likely influence its π-electron structure. Due to their twisted (propeller-like) arrangement, their ability to donate electrons through resonance will be, however, limited. Interestingly, calculations on 1-phenylborole (PhBC$_4$H$_4$), which lacks the phenyl substituents on the backbone, reveal a more pronounced antiaromatic character (NICS$_{zz}$(−1/+1) = 28.06/28.05 ppm) than pentaphenylborole and even boraindene **1**. In boraindene **1**, the two phenyl substituents around the borole ring appear to have a smaller influence on its antiaromaticity, as shown by nearly unchanged NICS values of its hydrogen analogue (NICS$_{zz}$(−1/+1) = 27.94/27.11 ppm, see ESI† for details).

Due to their pronounced Lewis acidity, boroles are particularly susceptible to adduct formation with Lewis bases, which is manifested by the reported isolation of numerous stable adducts.[1,3] In addition to Et$_3$PO, adducts of **1** with THF and the nitrogen bases 4-dimethylaminopyridine (DMAP) and pyridine (Py) were isolated and fully characterized, including structural confirmation by single-crystal X-ray crystallography (Scheme 1, see ESI† for details). The transformations are readily identified by the immediate disappearance of the red boraindene **1** solution and a shift of the ^{11}B NMR signal to lower frequencies, indicating the presence of a four-coordinate boron atom. Despite successful crystallographic characterization, the THF adduct is weakly bound and decomposes under vacuum, slowly releasing THF and reverting to the boraindene **1**.
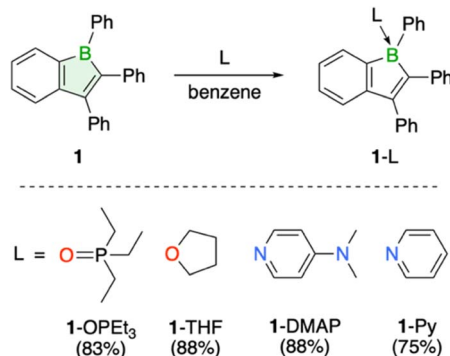
Reactivity with organic azides

Boroles, due to their antiaromatic nature, readily undergo insertion reactions to form ring-expanded products.[1d,g] A prime example is their reaction with organic azides, leading to the formation of aromatic BN heterocycles through nitrogen atom insertion.[1d,g,3,23] To explore the potential of compound **1** to undergo similar ring expansions, its reaction with mesityl and

trimethylsilyl azide was studied. Treatment of **1** with mesityl azide at room temperature led to an immediate color change from red to yellow, accompanied by the appearance of a new ^{11}B NMR signal at 38.9 ppm (Scheme 2a).

The observed ^{11}B NMR chemical shift aligns well with the range typically reported for aromatic BN heterocycles, suggesting the formation of the corresponding azaborinine ring system.[24] The product was isolated as a yellow crystalline solid in 79% yield after standard workup procedure. X-ray diffraction analysis of single crystals grown by slow evaporation of a saturated hexane solution at room temperature confirmed the planar structure of compound **2**, a BN analogue of naphthalene (see ESI† for details). Its structural features (*e.g.* B–N bond: 1.429(2) Å) are consistent with closely related derivatives.[25] Notably, the aryl groups on the heterocycle are nearly perpendicular to the ring plane, with the phenyl group on boron showing a more pronounced out-of-plane twist (68.0°) than that of **1**. Since Dewar's pioneering work in 1959 on the first BN-naphthalene derivative,[26] a variety of synthetic strategies have been developed for these compounds, enabling the generation of a wide range of substitution patterns and isomeric forms.[24d] Beyond the methods developed by Cui and Wagner, our work presents a new approach for synthesizing the specific BN-naphthalene isomer described herein.[25,27]

Treatment of **1** with trimethylsilyl azide in dichloromethane afforded the corresponding 2,1-azaboranaphthalene **3**, albeit

Scheme 1 Adducts of compound **1** with triethylphosphine oxide, amines, and THF.
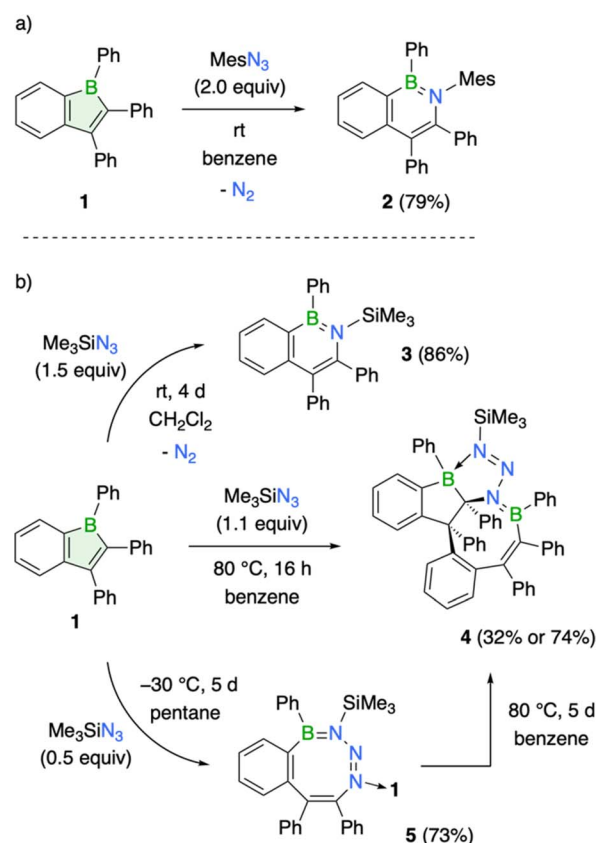
Scheme 2 Reactivity of compound **1** with organic azides: (a) mesityl azide and (b) trimethylsilyl azide.
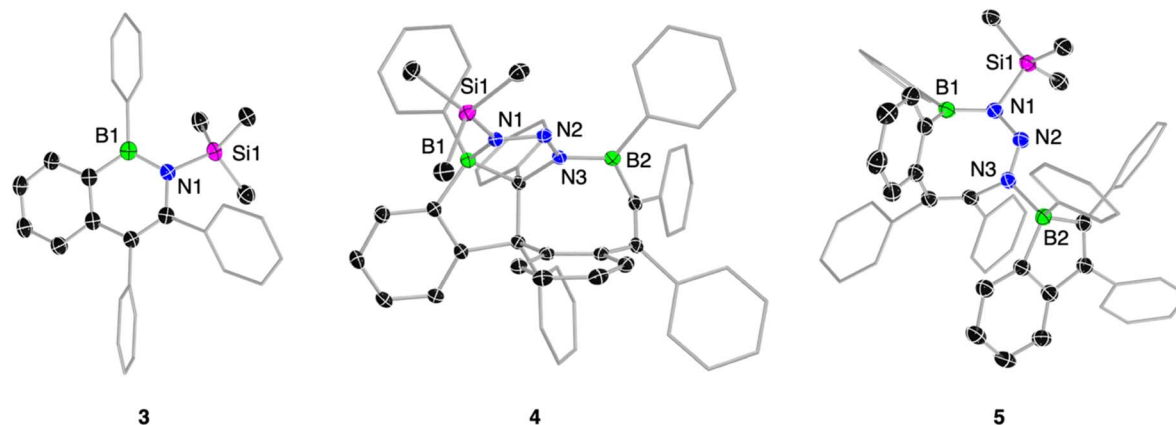
Fig. 3 Molecular structures of the products from the reaction of **1** with trimethylsilyl azide. Displacement ellipsoids are shown at the 50% probability level (ellipsoids of peripheral phenyl groups and hydrogen atoms removed for clarity).

requiring significantly longer reaction times than the reaction with mesityl azide. Stirring **1** with 1.5 equivalents of the azide at room temperature for 4 d resulted in complete conversion of **1** to **3**, yielding the BN naphthalene as an off-white solid in a yield of 86% (Scheme 2b). Multinuclear NMR spectroscopy ($\delta(^{11}B) = 44.8$ ppm) and structural analysis (B1–N1 bond: 1.439(2) Å) corroborate with the expected features of **3**. It is worth mentioning that the heterocycle in **3** is notably distorted from planarity, likely caused by repulsive steric interactions between the trimethylsilyl group and its neighboring aryl substituents (Fig. 3).

Switching the solvent to benzene led to the formation of a side product (**4**), isolable in 32% yield following the completion of the reaction at elevated temperatures (Scheme 2b). Compound **4** is characterized by two different ^{11}B NMR signals (51.1 and 9.7 ppm), suggesting the presence of boron atoms in both three- and four-coordinate environments. Single-crystal X-ray diffraction definitively established its molecular structure. Compound **4** is a 1 : 2 azide-to-borole addition product featuring a polycyclic skeleton with a central eight-membered BNC_6 ring (B2–N3 1.442(2) Å) adopting a tub conformation. Two carbon atoms from the BN heterocycle are embedded within a fused boraindane unit. Notably, a nitrogen atom of the diazenyl moiety tethered to the incorporated nitrogen atom coordinates with this boraindane, forming a five-membered BCN_3 ring (B1–N1 bond 1.599(2) Å). The structure exhibits a polycyclic architecture reminiscent of those observed from the reaction of a thiophene-benzo-fused borole with organic azides.[8b] High-resolution mass spectrometry (HRMS) analysis provided further corroboration for the polycyclic structure, as evidenced by the molecular ion peak at $m/z = 799.3720$.

The slow conversion rate of **1** to BN-naphthalene **3** enabled the isolation of a kinetic product with an eight-membered BN_3C_4 ring system, resembling a structure reported by Martin and coworkers.[23c] Since a second equivalent of borole coordinates to the eight-membered ring, employing half an equivalent of the azide in pentane solution and allowing the reaction mixture to crystallize at −30 °C efficiently afforded product **5** in 73% yield (Scheme 2b). ^{11}B NMR spectroscopy reveals two distinct boron environments at 49.2 and 4.7 ppm, with the lower-frequency signal corresponding to the boron atom of the coordinated boraindene unit. In the solid-state structure, the eight-membered ring adopts a twist-tub conformation similar to that described by Martin.[23c] The endocyclic (1.453(3) Å) and exocyclic (1.632(3) Å) boron–nitrogen bond lengths align well with the data presented for the earlier example (Fig. 3). Although complete NMR characterization of **5** was achieved, we observed the appearance of new resonances over time, suggesting gradual and selective conversion to the polycyclic product **4**. To promote its generation, we heated compound **5** to 80 °C. After 5 d at this temperature, the kinetically favored product **5** is fully consumed, and the thermodynamic product **4** could be isolated as a white solid in 74% yield (Scheme 2b).

Overall, the reactivity profile of boraindene **1** aligns with that of both doubly fused (9-borafluorenes) and non-fused borole derivatives.[1,3] All three react with organic azides *via* formal nitrene insertion, leading to the formation of corresponding BN heterocycles: 9,10-azaboraphenanthrenes for 9-borafluorenes,[1g,3,18] 2,1-azaboranaphthalenes for boraindenes, and 1,2-azaborinines for boroles.[1d,g,23] The observed reactivity divergence of boraindene **1**, forming an eight-membered BN_3C_4 ring[23c] and a polycyclic product,[8b] mirrors findings with other borole derivatives, suggesting similar reaction mechanisms for these transformations.

Conclusions

In summary, we have prepared an aryl-substituted boraindene derivative *via* tin–boron exchange. It exhibits Lewis acidity and electrophilicity properties intermediate between those of monocyclic and double-benzannulated derivatives (9-borafluorene), thereby strengthening the established trend that these properties weaken with increasing numbers of fused benzene rings. NICS calculations reveal a remarkably strong antiaromatic character in 1,2,3-triphenyl-1-boraindene, surpassing even that of the isolable non-fused borole derivative 1,2,3,4,5-pentaphenylborole. Our study further reveals that its reactivity with organic azides mirrors the diverse reaction

pathways observed for other borole derivatives, leading to ring-expansion reactions that produce BN-aromatic hydrocarbons, eight-membered rings, and polycyclic products. Notably, bor-aindene ring expansion using organic azides provides a novel approach to the synthesis of the 2,1-azaboranaphthalene scaffold, one of several possible BN-naphthalene structures.

Data availability

The data that support the findings of this study are available in the ESI† of this article.

Author contributions

H. B. conceived and designed the research program, N. W. designed studies and performed the research, with support from S. F. L. W. performed the DFT calculations. M. M., S. N., and M. H. conducted the crystallographic studies. I. K. performed the electrochemical studies and wrote the manuscript with contributions from all authors.

Conflicts of interest

There are no conflicts to declare.

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