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ARTICLE TYPE

Benzo[*f*]benzo[5,6]indolo[3,2-*b*]indole: a Stable Unsubstituted $4n\pi$ -Electron Acene with an Antiaromatic 1,4-Diazapentalene Core†

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A stable unsubstituted $4n\pi$ -electron acene with an antiaromatic 1,4-diazapentalene core, was prepared via an unprecedented mild oxidation. On the other hand, its (2,3)-isomer, was too unstable to be prepared. Theoretical calculations indicate that the dilution of antiaromaticity depends not only on the number of aromatic ring fused on the antiaromatic core, but also on the fusion patterns.

Pentalenes, a class of antiaromatic hydrocarbons, have aroused tremendous interest recently¹ thanks to the development of novel synthetic methods toward it (Fig. 1, 1-3).² The parent pentalene core is not chemically stable due to its strong antiaromaticity,³ and fusing aromatic rings to pentalene core seems to improve its stability to a limited extent. For example, **1a** was obtained as a fairly stable solid but polymerized easily in solution to give an amorphous product when heated.⁴ Despite that much progress has been made in this area, for longer heteroacenes bearing the pentalene core, only those with bulky substituents (such as **2b** and **3b**) have been synthesized, probably due to the challenges encountered in synthesizing the unsubstituted ones (such as **2a** and **3a**). Azapentalenes (Fig. 1, 4-7) have been studied even less,⁵ although the replacement of the C=C double bonds with imine bonds in pentalene might affect the stability of the system⁶ and the electron-poor character of azapentalene might be interesting for the design of novel n-type organic semiconductors.⁷ One example is dibenzo-1,4-diazapentalene, also known as indolo[3,2-*b*]indole (II, Fig. 1, **5**), which was reported but not fully characterized,⁸ and its stability remains unclear. Longer linear acenes bearing the 1,4-diazapentalene core have not yet been reported, and little is known about their stability, especially the evolution of their antiaromaticity and stability when more aromatic rings are fused to the antiaromatic core. Intuitively, larger antiaromatic systems are more stable than smaller ones, since the antiaromatic character is spread over the perimeter and

diluted.⁹ Thus, benzo[*f*]benzo[5,6]indolo[3,2-*b*]indole (Fig. 1, **6**, BBII) and its (2,3)-isomer **7** (Fig. 1, *iso*-BBII) should be more stable than compound **5**. We herein report our synthetic efforts towards these heteroacenes and the investigation on their structure-stability relationship.

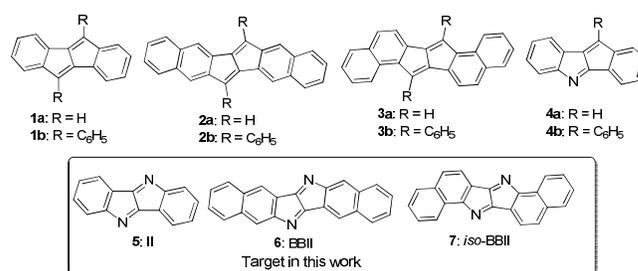


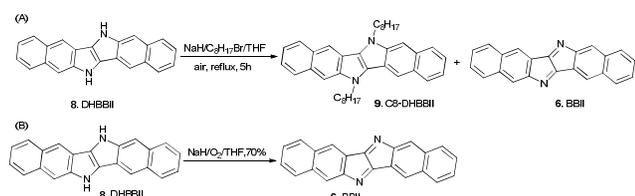
Fig. 1 Structures of acenes containing antiaromatic pentalene core and its aza-derivatives.

An unprecedented synthesis route towards BBII was discovered in a serendipitous way, while we attempted to alkylate dihydrobenzo[*f*]benzo[5,6]indolo[3,2-*b*]indole (**8**, DHBBII).¹⁰ Specifically, when DHBBII was treated with NaH/C₈H₁₇Br in THF solution, a small amount of reddish solid was obtained together with the target compound **9** (C8-DHBBII) when the system was not fully deoxygenated. The reddish solid was only slightly soluble in CHCl₃ or THF and its structure was confirmed to be BBII by NMR and HRMS analysis (Scheme 1, EqA). We reasoned that it might be formed via the oxidation of the dianion of DHBBII by O₂.^{5c} The yield of BBII was then improved to 70% using pure O₂ as the oxidant (Scheme 1, EqB).¹¹ Interestingly, although 1,4-diazapentalene is not stable due to its antiaromatic character,⁶ BBII turns out to be an air-stable compound and can exist both in solid and solution states under ambient conditions. Thermogravimetric analysis (TGA) showed the decomposition of BBII up to 250 °C, indicating its good thermo-stability (Fig. S1, ESI†). Compared with its parent pentalene derivatives such as **2a** (which has not been synthesized yet), the stability of BBII is promising, given that it has no bulky groups on the antiaromatic core to increase its stability.

The oxidation of a stable aromatic linear heteroacene (DHBBII) to a stable antiaromatic linear heteroacene (BBII) gave us the opportunity to investigate their different electronic and electrochemical properties. Since DHBBII was barely soluble, *N*-alkylated DHBBII (C8-DHBBII) was used as the alternative for

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^b University of Chinese Academy of Sciences, Beijing 100049, P. R. China †Electronic Supplementary Information (ESI) available: Synthesis of II, and BBII, single crystal X-ray structure of II, NMR spectra, photophysical and electrochemical data and theoretic details. See DOI: 10.1039/b000000x/



Scheme 1. A serendipitous conversion (A) and the improved efficient conversion (B) from DHBII to BBII.

comparison. The UV-vis spectra (Fig. 2a) show that the band absorption edge is 512 nm for C8-DHBII and 590 nm for BBII. The obvious red shift is consistent with the Hückel rule, which predicts that antiaromatic systems should have a smaller band gap than aromatic systems with similar structures.^{9c, 12} The cyclic voltammetry of C8-DHBII exhibits a pair of reversible oxidation waves with $^{ox}E_{1/2}$ at 0.43 V and 1.03 V respectively in chloroform. BBII, on the other hand, shows a pair of reduction waves with $^{red}E_{1/2}$ at -0.59 V and -1.08 V respectively (Fig. 2b). Unfortunately, because of its poor solubility, the redox current of BBII is quite small and overlapped with the background current of the solvent (especially for the second peak, Fig. S3, ESI[†]), which makes it look irreversible. The irreversibility could also be due to the high reactivity of the radical anion generated in the reduction process, since this possibility could not be ruled out at our experimental conditions. Nevertheless, the cyclic voltammetry demonstrates that BBII is a good electron-acceptor, while C8-DHBII is a good electron-donor. Compared with its parent pentalene analogues, BBII displays better electron affinity. For example, the first $^{red}E_{1/2}$ of **2b** is at -1.52 V,^{2c} much lower than that of BBII. This is due to the replacement of the C=C double bonds in pentalene by the electron-deficient imine bonds. The oxidation of DHBII into BBII represents a striking example that an aromatic electron-donor could be converted to an antiaromatic electron-acceptor under mild conditions.¹³

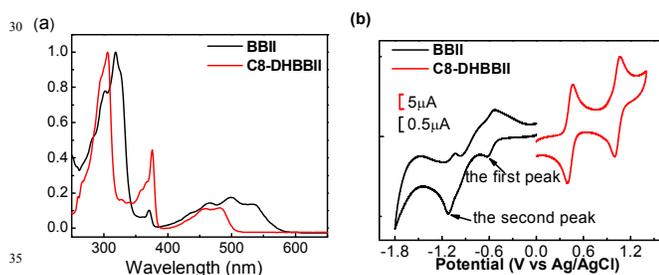
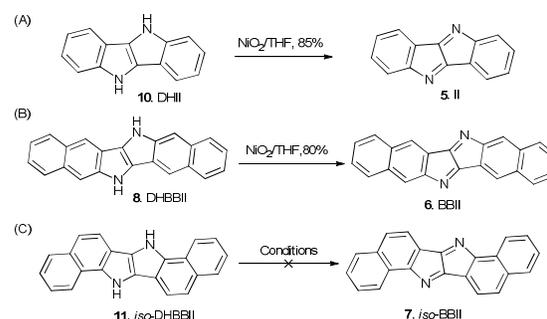


Fig. 2. (a) Normalized UV-vis spectra of C8-DHBII and BBII in THF. (b) Cyclic voltammetry of BBII (in THF) and C8-DHBII (in Chloroform), electrolyte: NBu₄ClO₄, 0.1 M, scan rate: 0.1 V/s.

The good stability and promising electron-accepting property of BBII aroused our interest to further study the synthesis of other acenes containing a 1,4-diazapentalene core, such as II and *iso*-BBII, and to investigate their structure-stability relationship. We envisioned that II and *iso*-BBII could be synthesized in the same manner as BBII. However, the oxidation of DHII under similar conditions gave a messy mixture, although a suspicious new yellow spot (later proved to be II) was observed on TLC at the beginning but faded gradually as the reaction proceeded. These observations suggested that II was unstable under such oxidation conditions and underwent further decomposition. Other oxidants

were then explored. Using DDQ or TCQ as the oxidant gave similar results, while using PbO₂ as the oxidant only gave a crude II (¹HNMR spectrum, ESI[†]) in low yield (45%).^{5c} Another mild oxidant, nickel peroxide (NiO₂),¹⁴ was then considered.^{14a} Fortunately, upon treatment of DHII with NiO₂, pure II was obtained as a bronze-coloured solid in 85% yield, just by washing the crude product with appropriate amount of ether (Scheme 2, EqA). Compared with BBII, II was stable only at solid state under ambient conditions and decomposed fast under acidic conditions (even as mild as silica gel), evidenced by the time-dependent UV-vis spectroscopy of them in acidic solution (Fig. S4, ESI[†]). TGA showed that II decomposed at 200 °C, 50 °C lower than that of BBII (Fig. S1, ESI[†]). Nevertheless, similar to BBII, II exhibits a pair of semi-reversible reduction waves in THF with the first $^{red}E_{1/2}$ at -0.54 V (Fig. S3, ESI[†]), indicating its excellent electron affinity. NiO₂ was also applied to the conversion of DHBII to BBII successfully and in 80% yield (Scheme 2, EqB). However, to our surprise, all attempts to synthesize *iso*-BBII via the oxidation of *iso*-DHBII under the above conditions were unsuccessful (Scheme 2, EqC). In all cases, decomposition of *iso*-DHBII was observed, and no *iso*-BBII was isolated, implying that *iso*-BBII was even much less stable than II.



Scheme 2. Optimized synthesis of II (A), BBII (B) and attempts to synthesize *iso*-BBII (C) (Conditions include (1) NaH/O₂; (2) DDQ or TCQ; (3) PbO₂; (4) NiO₂).

Comparing the structures of II, BBII and *iso*-BBII, we realized that fusing more aromatic rings to the antiaromatic 1,4-diazapentalene core did not necessarily lead to better stability. The fusion pattern should also play a very important role. This possibility stimulated us to investigate their structure-stability relationship *in silico*. The electronic and photo-physical properties of the three diazapentalenes were calculated with the DFT(B3LYP/6-31+G*) method embedded in the Gaussian 09 software package.¹⁵ The calculated UV-spectra match well with the experimental one (Fig. S5, ESI[†]), and the observed complexity in the long wavelength absorption region of BBII (Fig. 2a) might due to near overlap of HOMO-1 → LUMO and HOMO → LUMO transitions.¹⁶ The resultant molecular orbitals and energy diagrams are shown in Fig. 3. According to the calculation, the symmetry of the HOMO and LUMO of both II and *iso*-BBII are mismatched (Fig. 3), hence the transition between them is symmetry-forbidden, indicating that they are typical 4nπ-electron systems.^{2b, 2c} On the other hand, the HOMO → LUMO transition is symmetry-allowed for BBII, which implies its antiaromatic character is quite diluted. Conclusively, the location of the fusion is important to determine the frontier orbital

symmetry: fusing a benzene ring linearly to II causes the frontier orbital symmetry change, while fusing a benzene ring angularly to II does not.

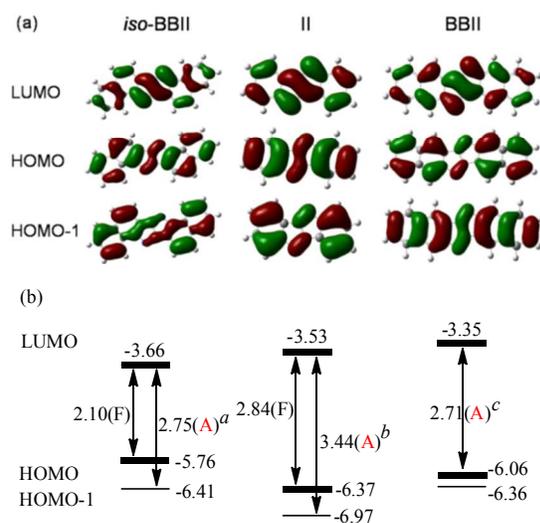


Fig. 3. (a) : Molecular orbitals and (b) : energy diagrams (eV) of *iso*-BBII (left), II (middle) and BBII (right) (A: transition is symmetry allowed; F: transition is symmetry forbidden; *a*: oscillator strength(os)=0.08, *b*: os=0.27; *c*: os=0.65)

The antiaromaticity evolution of the three compounds could also be explained by the bond length evolution on the central 1,4-diazapentalene core, which can be regarded as an indicator of π -delocalization.^{2e, 17} The bond lengths of the 1,4-diazapentalene core in all three compounds were calculated at B3LYP/6-31+G* level (Fig. S7, ESI[†]). As shown in Fig. 4a, there is a clear trend for the bond-length evolution of the 5-6 fusion of the three diazapentalenes: with the increase of the stability, the bond length increases from 1.405 Å (*iso*-BBII) to 1.426 Å (II) and then to 1.450 Å (BBII), indicating that this bond has the most single bond character in BBII, but the least in *iso*-BBII. The longer bond length reflects the less contribution from the 8π cyclic conjugation of the diazapentalene, and vice versa.^{2e} As the consequence, BBII has the least and *iso*-BBII has the most antiaromatic character at their diazapentalene core. We tried to provide experimental evidence by single-crystal X-ray diffractions studies, however, only the single crystal of II was obtained (ESI[†]), and BBII could not form single crystal due to its poor solubility. Single crystal analysis revealed that the bond-length of the 5-6 fusion in II (1.412 Å) was shorter than the one (1.425 Å) observed in dibenzopentalene 1b, and matched fairly well with the calculated value (1.426 Å). Additionally, the stability evolution could be explained by Clar's sextet rule. As shown in Fig. 4b, when considering the resonance structures with two Clar's sextets (real benzene rings), which are the major resonance contributors, the central diazapentalene moiety (shown in red) of BBII does not present a typical structure of [8]annulene. In contrast, the central diazapentalene moiety of *iso*-BBII (shown in red) has two resonance structures, both resembling the antiaromatic [8]annulene. Therefore the diazapentalene moiety in *iso*-BBII is more antiaromatic than that in BBII. In the case of II, while it possesses only one major

resonance contributor, the π electron delocalization was not as effective as BBII, and its stability lies between BBII and *iso*-BBII.

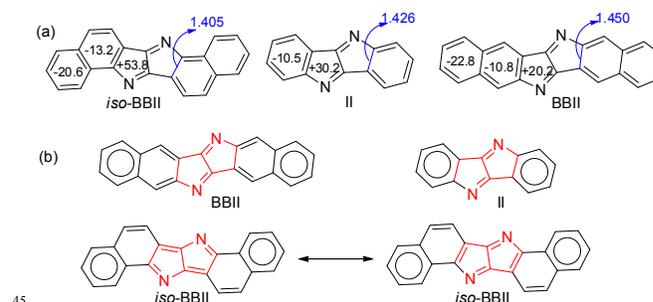


Fig. 4. (a): NICS(1)_{zz} values (black colored) and representative bond lengths (blue colored, in Å) of *iso*-BBII, II and BBII; (b) Resonance structures analysis of BBII, II and *iso*-BBII.

This trend was also verified by NICS(1)_{zz} calculation¹⁸, which provided a quantitative comparison on the antiaromaticity evolution. The results are shown in Fig. 4a. While there is no obvious difference in the aromaticity of the benzene ring directly fused with the diazapentalene core, the antiaromaticity of the diazapentalene core varies significantly. The most positive value (+53.8) of *iso*-BBII indicates its diazapentalene core is the most antiaromatic, and the intermediate one (+30.2) of II reflects its moderate antiaromaticity, while the least positive one (+20.2) of BBII demonstrates the least antiaromaticity. Compared with II, the antiaromatic character of the diazapentalene 8π system is much more diluted in BBII, but much more localized in *iso*-BBII. The NICS(1)_{zz} value of *iso*-BBII is close to that of bare 1,4-diazapentalene(+55.8, Fig. S8, ESI[†]), showing that the fused aromatic ring in *iso*-BBII has little effect to dilute the antiaromatic character of the central diazapentalene core. Thus, as a result, BBII displays the highest stability, and II possesses a fair stability, while *iso*-BBII is not stable enough to be prepared. This is also in accordance with the result from the bond-length calculation and experimental results, and again indicates the fusion pattern is important to determine whether fusing an aromatic ring will stabilize the antiaromatic core or not.

Furthermore, to elucidate the effect of inclusion of N atoms into the parent pentalene core on structure–property relationship, the electronic structure, band gap and antiaromaticity of the parent pentalenes 2a and 3a are compared with the diazapentalenes BBII and *iso*-BBII. Several conclusions could be drawn: (1). the inclusion of N atoms does not influence the symmetry of the orbitals (Fig. S9, ESI[†]), but drastically lowers the energy level of both HOMO and LUMO and reduces the HOMO-LUMO gaps (Table S2, ESI[†]), and resultant UV-vis spectra are different (Fig. S6, ESI[†]); (2). NICS calculation shows no obvious difference in antiaromaticity between BBII and 2a, or between *iso*-BBII and 3a. However, we could not further compare the stability of BBII and 2a, since 2a has not been made yet.

In summary, an expedient conversion from $(4n+2)\pi$ electron-rich donors (DHII and DHHBII) to $4n\pi$ electron-deficient acceptors (II and BBII) was achieved under mild oxidation conditions, and BBII exhibit excellent stability. We further discovered that the antiaromatic character of the 1,4-diazapentalene core could not be simply diluted by fusing the $4n\pi$ ring with more aromatic rings. The location of the fusion has

dramatic effects on the stability of the resultant linear acenes, as evidenced by the fact that BBII is much more stable than II, while its (2, 3)-isomer *iso*-BBII is much less stable than II and could not be prepared. Theoretical calculations explained these experimental results clearly from several aspects, including the change of the frontier orbital symmetry, bond-length evolution, resonance structure and the change in antiaromaticity. These results may be useful for the design of other novel stabilized $4n\pi$ systems.

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