ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Benzo[*f*]benzo[5,6]indolo[3,2-*b*]indole: a stable unsubstituted 4nπ-electron acene with an antiaromatic 1,4-diazapentalene core†

Cite this: *Chem. Commun.*, 2014, 50, 3324

Received 11th December 2013,
Accepted 4th February 2014

DOI: 10.1039/c3cc49418g

www.rsc.org/chemcomm

Li Qiu,[ab] Xuhui Zhuang,[ab] Na Zhao,[ab] Xiao Wang,[a] Zengjian An,[a] Zhenggang Lan*[a] and Xiaobo Wan*[a]

A stable unsubstituted 4nπ-electron acene with an antiaromatic 1,4-diazapentalene core was prepared *via* an unprecedented mild oxidation. Further investigation showed that the stability of such acenes was dependent on the fusion patterns of the peripheryl benzene rings to the centre core.

Pentalenes, a class of antiaromatic hydrocarbons, have aroused tremendous interest recently,[1] 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 the 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 amorphorous product when heated.[4] Despite the fact 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 system[6] 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.

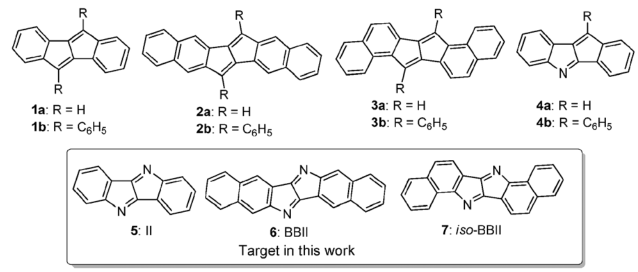
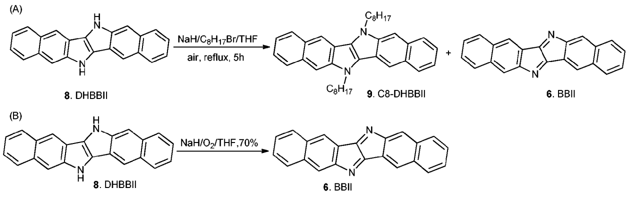


Fig. 1 Structures of acenes containing an antiaromatic pentalene core and its aza-derivatives.

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–C_8H_{17}Br in a 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 $CHCl_3$ or THF and its structure was confirmed to be BBII by NMR and HRMS analysis (Scheme 1, eqn A). We reasoned that it might be formed *via* the oxidation of the dianion of DHBBII by O_2.[5c] The yield of BBII was



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

---

[a] *CAS Key Laboratory of Biobased Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China. E-mail: wanxb@qibebt.ac.cn, lanzg@qibebt.ac.cn; Fax: +86-532-80662740; Tel: +86-532-80662740*

[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. CCDC 976489. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc49418g

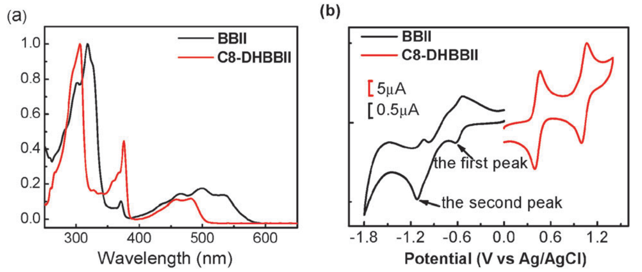
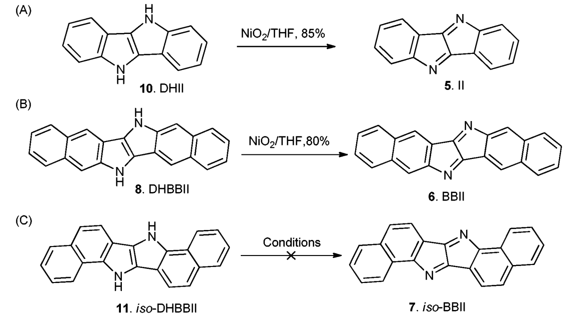


Fig. 2 (a) Normalized UV-vis spectra of C8-DHBBII and BBII in THF. (b) Cyclic voltammetry of BBII (in THF) and C8-DHBBII (in chloroform), electrolyte: NBu_4ClO_4, 0.1 M, scan rate: 0.1 V s^{-1}.

then improved to 70% using pure O_2 as the oxidant (Scheme 1, eqn B).[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 thermostability (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 comparison. The UV-vis spectra (Fig. 2a) show that the band absorption edge is 512 nm for C8-DHBBII 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 voltammogram of C8-DHBBII exhibits a pair of reversible oxidation waves with ${}^{\text{ox}}E_{1/2}$ of 0.43 V and 1.03 V, respectively, in chloroform. BBII, on the other hand, shows a pair of reduction waves with ${}^{\text{red}}E_{1/2}$ of −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 might also be due to the high reactivity of the radical anion generated in the reduction process, since this possibility could not be ruled out under our experimental conditions. Nevertheless, the cyclic voltammetry demonstrates that BBII is a good electron-acceptor, while C8-DHBBII is a good electron-donor. Compared with its parent pentalene analogues, BBII displays better electron affinity. For example, the first ${}^{\text{red}}E_{1,1/2}$ of **2b** is −1.52 V,[2e] 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 DHBBII to BBII represents a striking example that an aromatic electron-donor could be converted to an antiaromatic electron-acceptor under mild conditions.[13]

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 a 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 PbO_2 as the oxidant only gave a crude II (^{1}HNMR spectrum, ESI†) in low yield (45%).[5e] Another mild oxidant, nickel peroxide (NiO_2),[14] was then considered.[14a] Fortunately, upon treatment of DHII with NiO_2, pure II was obtained as a bronze-coloured solid in 85% yield, just by washing the crude product with an appropriate amount of ether (Scheme 2, eqn A). Compared with BBII, II was stable only in the 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 ${}^{\text{red}}E_{1/2}$ of −0.54 V (Fig. S3, ESI†), indicating its excellent electron affinity. NiO_2 was also applied to the conversion of DHBBII to BBII successfully and in 80% yield (Scheme 2, eqn B). However, to our surprise, all attempts to synthesize iso-BBII *via* the oxidation of iso-DHBBII under the above conditions were unsuccessful (Scheme 2, eqn C). In all cases, decomposition of iso-DHBBII 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/O_2; (2) DDQ or TCQ; (3) PbO_2; (4) NiO_2).

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 by 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 be due to the 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 symmetries of the HOMO and LUMO of both II and iso-BBII are mismatched (Fig. 3), hence the transition between them is

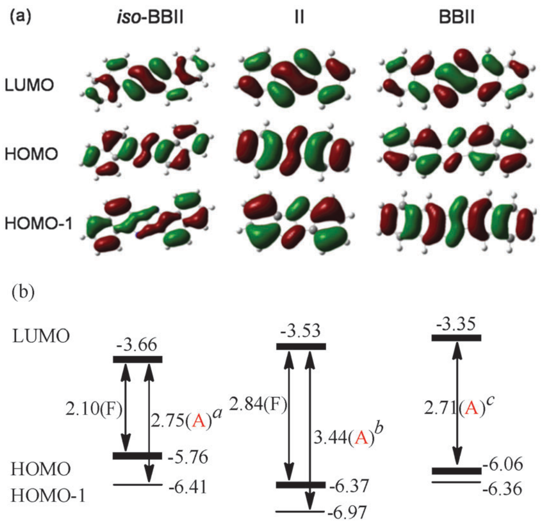


Fig. 3 (a) Molecular orbitals and (b) energy diagrams (eV) of iso-BBII (left), II (middle) and BBII (right) (A: transition is symmetry allowed; F: transition is symmetry forbidden; (*a*) oscillator strength (os) = 0.08, (*b*) os = 0.27; (*c*) os = 0.65).

symmetry-forbidden, indicating that they are typical 4nπ-electron systems.[2b,2e] 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.

The antiaromaticty 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 the 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 a 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 diffraction studies, however, only the single crystal of II was obtained (ESI†), and BBII could not form a 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.

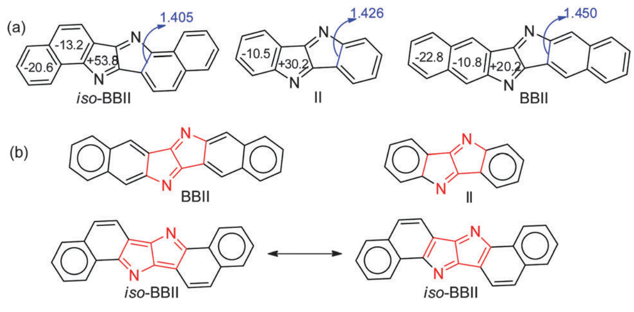


Fig. 4 (a) NICS(1)$_{zz}$ values (black colored) and representative bond lengths (blue colored, in Å) of iso-BBII, II and BBII; (b) resonance structures analysis of BBII, II and iso-BBII.

This trend was also verified by NICS(1)$_{zz}$ calculation,[18] which provided a quantitative comparison of 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 that 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 in diluting 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 that 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 the 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) π electron-rich donors (DHII and DHBBII) to 4nπ electron-deficient acceptors (II and BBII) was achieved under mild oxidation conditions, and BBII exhibits excellent stability. We further discovered that the antiaromatic character of the 1,4-diazapentalene core could not be simply diluted by fusing the 4nπ 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 4nπ systems.

This work was supported by the ''100 Talents'' program from the Chinese Academy of Sciences and the National Science Foundation of China (21174157, 21103213, 91233106).

Notes and references

1 H. Hopf, *Angew. Chem., Int. Ed.*, 2013, **52**, 12224.

2 (*a*) M. Saito, M. Nakamura and T. Tajima, *Chem.–Eur. J.*, 2008, **14**, 6062; (*b*) T. Kawase, A. Konishi, Y. Hirao, K. Matsumoto, H. Kurata and T. Kubo, *Chem.–Eur. J.*, 2009, **15**, 2653; (*c*) Z. U. Levi and T. D. Tilley, *J. Am. Chem. Soc.*, 2009, **131**, 2796; (*d*) H. Zhang, T. Karasawa, H. Yamada, A. Wakamiya and S. Yamaguchi, *Org. Lett.*, 2009, **11**, 3076; (*e*) T. Kawase, T. Fujiwara, C. Kitamura, A. Konishi, Y. Hirao, K. Matsumoto, H. Kurata, T. Kubo, S. Shinamura, H. Mori, E. Miyazaki and K. Takimiya, *Angew. Chem., Int. Ed.*, 2010, **49**, 7728; (*f*) Z. U. Levi and T. D. Tilley, *J. Am. Chem. Soc.*, 2010, **132**, 11012; (*g*) M. Saito, *Symmetry*, 2010, **2**, 950; (*h*) T. Maekawa, Y. Segawa and K. Itami, *Chem. Sci.*, 2013, **4**, 2369; (*i*) J. Zhao, K. Oniwa, N. Asao, Y. Yamamoto and T. Jin, *J. Am. Chem. Soc.*, 2013, **135**, 10222.

3 (*a*) G. M. Badger, *Aromatic Character and Aromaticity*, Cambridge University Press, New York, 1969; (*b*) D. Lloyd, *Non-Benzenoid Conjugated Carbocyclic Compounds*, Elsevier, New York, 1984, p. 377; (*c*) L. A. Paquette, *Topics in Current Chemistry*, Springer-Verlag, New York, 1984, vol. 119, p. 58.

4 (*a*) K. Brand, *Ber. Dtsch. Chem. Ges.*, 1912, **45**, 3071; (*b*) C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 1952, 2263; (*c*) C. C. Chuen and S. W. Fenton, *J. Org. Chem.*, 1958, **23**, 1538.

5 (*a*) W. Treibs, *Naturwissenschaften*, 1961, **48**, 130; (*b*) W. Treibs, *Chimia*, 1968, **22**, 467; (*c*) S. Hünig and H. C. Steinmetzer, *Tetrahedron Lett.*, 1972, **13**, 643; (*d*) J. J. Eisch and T. Abraham, *Tetrahedron Lett.*, 1976, **17**, 1647; (*e*) S. Hünig and H.-C. Steinmetzer, *Justus Liebigs Ann. Chem.*, 1976, 1090.

6 (*a*) B. A. Hess Jr, L. J. Schaad and C. W. Holyoke Jr, *Tetrahedron*, 1975, **31**, 295; (*b*) I. Gutman, M. Milun and N. Trinajstic, *J. Am. Chem. Soc.*, 1977, **99**, 1692.

7 (*a*) C. J. Tonzola, M. M. Alam, W. Kaminsky and S. A. Jenekhe, *J. Am. Chem. Soc.*, 2003, **125**, 13548; (*b*) M. Winkler and K. N. Houk, *J. Am. Chem. Soc.*, 2007, **129**, 1805; (*c*) B. Gao, M. Wang, Y. Cheng, L. Wang, X. Jing and F. Wang, *J. Am. Chem. Soc.*, 2008, **130**, 8297; (*d*) Y.-Y. Liu, C.-L. Song, W.-J. Zeng, K.-G. Zhou, Z.-F. Shi, C.-B. Ma, F. Yang, H.-L. Zhang and X. Gong, *J. Am. Chem. Soc.*, 2010, **132**, 16349; (*e*) Z. Liang, Q. Tang, R. Mao, D. Liu, J. Xu and Q. Miao, *Adv. Mater.*, 2011, **23**, 5514; (*f*) Z. Liang, Q. Tang, J. Xu and Q. Miao, *Adv. Mater.*, 2011, **23**, 1535; (*g*) O. Tverskoy, F. Rominger, A. Peters, H.-J. Himmel and U. H. F. Bunz, *Angew. Chem., Int. Ed.*, 2011, **50**, 3557.

8 Dibenzo-1,4-diazapentalene was characterized only by UV/vis and IR spectra in references **5a**, **5b** and **5c**. Although MS and ^{1}H-NMR spectra were given in **5e**, HRMS and ^{13}C-NMR data were not available. Moreover, according to **5e**, the description of dibenzo-1,4-diazapentalene was inaccurate in **5a** and **5b**.

9 (*a*) A. J. Matzger and K. P. C. Vollhardt, *Tetrahedron Lett.*, 1998, **39**, 6791; (*b*) C. S. Wannere, D. Moran, N. L. Allinger, B. A. Hess, L. J. Schaad and P. v. R. Schleyer, *Org. Lett.*, 2003, **5**, 2983; (*c*) U. H. F. Bunz, *Chem.–Eur. J.*, 2009, **15**, 6780.

10 L. Qiu, C. Yu, N. Zhao, W. Chen, Y. Guo, X. Wan, R. Yang and Y. Liu, *Chem. Commun.*, 2012, **48**, 12225.

11 IR spectroscopy was used to determine that the obtained BBII was free of starting material (Page S30, ESI†), since the existence of residual starting material could not be detected by NMR.

12 T. Nishinaga, T. Ohmae and M. Iyoda, *Symmetry*, 2010, **2**, 76.

13 (*a*) S. Miao, P. v. R. Schleyer, J. I. Wu, K. I. Hardcastle and U. H. F. Bunz, *Org. Lett.*, 2007, **9**, 1073; (*b*) S. Miao, S. M. Brombosz, P. v. R. Schleyer, J. I. Wu, S. Barlow, S. R. Marder, K. I. Hardcastle and U. H. F. Bunz, *J. Am. Chem. Soc.*, 2008, **130**, 7339; (*c*) J. I. Wu, C. S. Wannere, Y. Mo, P. v. R. Schleyer and U. H. F. Bunz, *J. Org. Chem.*, 2009, **74**, 4343.

14 (*a*) S. Tanaka, K. Satake, A. Kiyomine, T. Kumagai and T. Mukai, *Angew. Chem., Int. Ed.*, 1988, **27**, 1061; (*b*) D. N. Kyosuke Satake and M. Kimura, *Heterocycles*, 1998, **48**, 433.

15 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. M. B. Barone, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li and H. P. Hratchian, *et al.*, Gaussian 09, Gaussian, Inc., Wallingford, CT, 2009.

16 The calculations indicate that the longest absorption of BBII ($S_0 \rightarrow S_1$ band) is attributed to HOMO − 1 → LUMO transition (main contribution 49.6%), which is symmetry-forbidden. An allowed transition ($S_0 \rightarrow S_2$ band) is attributed to HOMO → LUMO transition (main contribution 48.2%) occurs at higher energy. However, due to their energy proximity, near overlap of both transitions might occur, which is consistent with the observed complexity in the long wavelength absorption region of BBII (Fig. 2a). This phenomenon is quite similar with that of its parent pentalene analogue **2b** (see ref. 2e).

17 S. Lu, M. Drees, Y. Yao, D. Boudinet, H. Yan, H. Pan, J. Wang, Y. Li, H. Usta and A. Facchetti, *Macromolecules*, 2013, **46**, 3895.

18 (*a*) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. v. E. Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317; (*b*) P. v. R. Schleyer, H. Jiao, N. J. R. v. E. Hommes, V. G. Malkin and O. L. Malkina, *J. Am. Chem. Soc.*, 1997, **119**, 12669; (*c*) P. von Ragué Schleyer, M. Manoharan, Z.-X. Wang, B. Kiran, H. Jiao, R. Puchta and N. J. R. van Eikema Hommes, *Org. Lett.*, 2001, **3**, 2465; (*d*) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Chem. Rev.*, 2005, **105**, 3842; (*e*) H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Org. Lett.*, 2006, **8**, 863.