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Synthesis of Polycyclic Aromatic Hydrocarbons with Highly Twisted N-Doped Heptalene

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Abstract A series of N-doped heptalene-containing polycyclic aromatic hydrocarbons (PAHs) have been synthesized and characterized in comparison with the N-doped azulene analogs. The crystal structure revealed its highly twisted geometry with a dihedral angle of 105.7° in the cove region of the N-doped dibenzoheptalene backbone. In addition, the electronic structure was both theoretically and experimentally investigated compared with the PAH bearing N-doped azulene unit. Our study provides a new synthetic strategy towards N-doped heptalene-embedded PAHs, and gives insights into the electronic properties of novel π -systems with N-doped nonalternant topologies.

Key words: heptalene, nitrogen doping, non-alternant PAHs, optical properties, fluorescence

Introduction

Polycyclic aromatic hydrocarbons (PAHs) containing nonhexagons have attracted great interests due to their intriguing topological structures and optoelectronic properties.¹ Typically, the introduction of pentagons and heptagons into π -systems brings in novel geometries and unique properties, such as the aromaticity,² open-shell character,³ host–guest interactions⁴ and chirality⁵. Heteroatom doping is another effective strategy to alter the electronic structures of PAHs.⁶ Recently, N-doped PAHs containing odd–membered rings have been developed, which greatly enriched the chemistry of molecular nanocarbons.⁷

Azulene and heptalene (Figure 1) are the representative nonalternant molecules with an aromatic and an antiaromatic character, respectively,⁸ in the planar geometry, which have been widely used as key building blocks in the synthesis of functional π -conjugated systems,⁹ especially for helicenes¹⁰ and curved nanographenes.¹¹ The introduction of azulene unit, generally, resulted in unsymmetrically distrib-





Figure 1 Molecular design of N-doped azulene derivatives 1 and heptalene derivatives $\mathbf{2}$.

uted frontier orbitals, which further affect the physical and chemical properties, including dipole moment and photophysical and redox properties.¹² The heptalene moiety has a significant impact on the molecular geometries and the aromaticity of π -conjugated systems.¹³ By doping one nitrogen (N) atom into these two units, such as azepino[3.2.1-hi]indole I and azabenzo[ef]heptalene II, one of the bridging sp²carbon atoms is replaced by the sp³-N atom. Accordingly, one additional benzene ring is required to fuse the bicycle to guarantee the fully π -conjugated system. Recently, examples of PAHs based on structure I have been successfully synthesized due to the well-established synthetic methodologies.¹⁴ For instance, a typical example is the N-doped nanographenes containing pentagon–heptagon pair(s), including the analogs of 1, facilely synthesized via a ring expansion strategy by our group.^{7b} However, the π -extended derivatives based on structure II are still rarely reported probably due to the high strain when forming the adjacent heptagons. For example, Rickhaus et al. reported the synthesis of dibenzo-azabenzo[ef]heptalene derivatives in the pursuit of azatriseptane.¹⁵ During the preparation of this manuscript, azaheptalene 2 was reported by Ishigaki et al. via a one-pot method, and its chiral property was investigated.¹⁶ Herein, we report the synthesis of a series of π -extended PAHs with N-doped heptalene or N-doped azulene, respectively, which can be viewed as benzannulated I and II, via a different synthetic strategy. Besides, the effects of heteroatom doping at



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different joined nonhexagons on both the geometric and electronic structures have been thoroughly investigated.

Results and Discussion

The synthetic methodologies toward tribenzo[*b.d.f*]azepine derivatives have been well established,17 which provide guidance to the synthesis of N-containing heptalenes. Initially, the direct synthesis of **2** starting from dibromo-aniline **3** was attempted using palladium (Pd)-catalyzed double annulations (Route A, Scheme 1). However, it failed to obtain 2; instead, mono-annulated product 5 was obtained in 21-58% yield. Therefore, a stepwise synthetic strategy (Routes B and C) from 5 towards 2 was adopted. Copper-catalyzed Ullmann reaction of 5-^tBu with 4 successfully afforded triarylated amine 6. However, the subsequent Pd-catalyzed direct arylation gave **1-**^{*t*}**Bu** with one newly formed pentagon in a total yield of 54% over two steps. There was no reaction further using the Scholl reaction of **1**-^{*t*}**Bu** toward 10 in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)/trifluoromethanesulfonic acid (TfOH). Pdcatalyzed decarboxylative annulation of 2-aminobenzoic acids with cyclic hypervalent diaryliodonium reagents has been reported to construct N-doped seven-membered rings.¹⁸ Inspired by this method, cyanation of **5** with CuCN, followed by hydrolysis with a strong base, afforded the precursors 8 with the carboxylic acid functional group in a total yield of 47-66%. Finally, the desired N-doped heptalenecontaining 2 was successfully obtained via Pd-catalyzed decarboxylative annulation in a yield of 6 – 16%. All the targets



Scheme 1 Synthesis of N-doped azulene-containing PAH 1 and N-doped heptalene derivatives 2.

were soluble in common organic solvents and were unambiguously characterized by NMR and high-resolution mass spectrometry.

Single crystals of **2-**^t**Bu** suitable for X-ray diffraction analvsis were obtained by slow evaporation of the chloroform/ acetonitrile solutions (Figure 2). Compound 2-^tBu demonstrates a highly twisted structure of C_2 symmetry with a dihedral angle (C1-C2-C3-C4) of 105.7°, which is much larger than that of the cove region in the heptalene-embedded PAHs (46.9°).^{11b} This further supports the large racemization barrier for **2** (49.4 kcal \cdot mol⁻¹, Figure S5), which indicates a high configurational stability that allows for chiral separation.¹⁶ Bond length analysis on the N-doped heptagonal rings indicates an obvious bond length alternation on the C-C bonds due to π -localization of fused benzene rings (Figure 2a), and the C–N bond lengths (1.42 Å) are shorter than the C-N single bond length (1.48 Å). A pair of enantiomers of 2-'Bu with different helical chirality exist in the packing model, in which they are aligned on the *ac* plane (Figure 2c). Owing to the twisted structure and the bulky *tert*-butyl group, no obvious π - π interaction between molecules was observed in the solid state.



Figure 2 Top view (a) and side view (b) of **2-**^t**Bu** with thermal ellipsoids at the 30% probability level. (c) Molecular packing of the enantiomers **2-**^t**Bu**. *P*-helical is shown in blue; *M*-helical is shown in pink. Hydrogen atoms are omitted for clarity.

Theoretical calculations on **1-**^{*t*}**Bu** and **2-**^{*t*}**Bu** were carried out at the B3LYP/6–31 G(d,p) levels to gain insight into the differences on the electronic structures. Compound **2-**^{*t*}**Bu** exhibits slightly higher HOMO (-5.19 eV) and LUMO (-1.00 eV) energy levels than those of **1-**^{*t*}**Bu** (HOMO: -5.25 eV, LUMO: -1.10 eV) (Figure S2). The HOMO of **2-**^{*t*}**Bu**

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is located on the inner backbone, and the LUMO is distributed on the peripheral rings around the N atom. The embedded N atom in both 1-^tBu and 2-^tBu contributes little to their LUMOs. Nuclear-independent chemical shift (NICS: Figure 3a) calculations of both compounds were further performed. The values of the pentagon and heptagon in **1**-^{*t*}**Bu** are -9.7 and 14.4. respectively, suggesting the weak aromatic character for the pentagon and an antiaromatic character for the heptagon. Interestingly, the two heptagons in 2-'Bu have small values of 9.8, indicating a weak antiaromatic character. The weak aromatic/antiaromatic characters of these non-hexagonal rings could be attributed to the π -localization of the peripherally fused benzene rings. These results are further supported by the anticlockwise ring current flow in the heptagons and the diatropic ring current circuits in the peripheral benzene rings as shown in the anisotropy of the induced current density (ACID; Figure 3b) maps.



Figure 3 (a) NICS(1)_{zz} values and (b) ACID plots of **1**-^t**Bu** (left) and **2**-^t**Bu** (right).

The photophysical and electrochemical properties of **1-**^{*t*}**Bu** and **2** were further compared (Figure 4 and Table 1).¹⁹ Compound **1**-^{*t*}**Bu** shows two major absorptions at 310 nm and 350 nm. Compound 2 with different substituents exhibit identical absorptions with a hypsochromically shifted wavelength maximum at 315 nm (Figure 4a). All compounds have a blue emission in solution. Interestingly, the emissions of 2, ranging from 446 nm to 459 nm, are more redshifted compared to those of **1-**^{*t*}**Bu** (438 nm), probably due to the large conformation changes upon photoexcitation.²⁰ Cyclic voltammetry measurements of these two compounds 1-^tBu and 2-'Bu in dichloromethane revealed one reversible oxidation wave $(E_{1/2}^{ox})$ at 0.79 V and 0.76 V, respectively. The HOMO energy levels are estimated to be -5.49 eV for 1-^tBu and -5.48 eV for 2-^tBu, respectively, which are much higher than those of other N-doped analogs.7b



Figure 4 (a) Absorptions (solid line) and emissions (dashed line) of compounds 1-^tBu and 2 measured in dichloromethane at 298 K. (b) Cyclic voltammograms of 1-^tBu and 2-^tBu in anhydrous dichloromethane with *n*-Bu₄NPF₆ (0.1 M) as the electrolyte versus Fc/Fc⁺. Scan rate: $0.1 V \cdot s^{-1}$.

Table 1 Photophysical and electrochemical properties of $1\mbox{-}^t\!Bu$ and 2

Compound	λ_{ab}^{a} (nm)	λ _{em} ª (nm)	$E_{1/2}^{0x} {}^{b}$ (V)	HOMO ^c (eV)	$E_g^{\mathrm{opt}d}$
1- ^t Bu	350	438	0.79	-5.49	3.17
2-Н	315	447	-	-	3.34
2-Cl	315	459	-	-	3.34
2- ^t Bu	315	446	0.76	-5.48	3.34

^aMeasured in dichloromethane $(1.0 \times 10^{-5} \text{ M})$. ${}^{b}E_{1/2}^{vx}$ is the half-wave potential of the oxidative waves with potentials vs. Fc/Fc⁺ couple. ^cHOMO energy levels were calculated according to the equation: HOMO = $-(4.8 + E_{onset}^{vx})$, where E_{onset}^{vx} values are the onset potentials of the first oxidative redox wave. ^dObtained from the edge of the absorption spectra according to $E_{0}^{opt} = (1240)\lambda_{onset}$).

Conclusions

In summary, we demonstrated the synthesis and characterization of a series of N-doped heptalene derivatives, which can be viewed as the benzannulation of four benzene rings with an azabenzo[*ef*]heptalene core. The crystal structure revealed the molecular backbone possessing a highly twisted geometry with a dihedral angle of 105.7°, and theoretical calculations suggested the weak antiaromatic charac-



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ter for the inner heptagons. In addition, the π -extended Ndoped heptalene exhibited similar electronic structures of the N-doped azulene analogs, such as the redox properties and molecular orbital energy levels. Our research reported herein opens a new door for the synthesis of novel graphene nanostructures with N-doped heptalene, and related works are ongoing in our group.

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Supporting Information

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Conflict of Interest

The authors declare no conflict of interest.

References and Notes

- (a) Fei, Y.; Liu, J. Adv. Sci. 2022, 9, 2201000. (b) Pun, S. H.; Miao, Q. Acc. Chem. Res. 2018, 51, 1630. (c) Liu, Y.; Ma, Z.; Wang, Z.; Jiang, W. J. Am. Chem. Soc. 2022, 144, 11397. (d) Wang, J.; Gámez, F. G.; Marín-Beloqui, J.; Diaz-Andres, A.; Miao, X.; Casanova, D.; Casado, J.; Liu, J. Angew. Chem. Int. Ed. 2023, 62, e202217124.
- (2) (a) Ong, A.; Tao, T.; Jiang, Q.; Han, Y.; Ou, Y.; Huang, K. W.; Chi, C. Angew. Chem. Int. Ed. **2022**, 61, e202209286. (b) Fei, Y.; Fu, Y.; Bai, X.; Du, L.; Li, Z.; Komber, H.; Low, K.-H.; Zhou, S.; Phillips, D. L.; Feng, X.; Liu, J. J. Am. Chem. Soc. **2021**, 143, 2353.
- (3) (a) Horii, K.; Kishi, R.; Nakano, M.; Shiomi, D.; Sato, K.; Takui, T.; Konishi, A.; Yasuda, M. *J. Am. Chem. Soc.* **2022**, *144*, 3370. (b) Konishi, A.; Yasuda, M. *Chem. Lett.* **2021**, *50*, 195. (c) Wu, F.; Ma, J.; Lombardi, F.; Fu, Y.; Liu, F.; Huang, Z.; Liu, R.; Komber, H.; Alexandropoulos, D. I.; Dmitrieva, E.; Lohr, T. G.; Israel, N.; Popov, A. A.; Liu, J.; Bogani, L.; Feng, X. *Angew. Chem. Int. Ed.* **2022**, *61*, e202202170.

(4) Mora-Fuentes, J. P.; Codesal, M. D.; Reale, M.; Cruz, C. M.; Jiménez, V. G.; Sciortino, A.; Cannas, M.; Messina, F.; Blanco, V.; Campaña, A. G. Angew. Chem. Int. Ed. 2023, 62, e202301356.

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- (5) Rickhaus, M.; Mayor, M.; Juríček, M. Chem. Soc. Rev. 2017, 46, 1643.
- (6) (a) Wang, X. Y.; Yao, X. L.; Narita, A.; Mullen, K. Acc. Chem. Res. 2019, 52, 2491. (b) Wang, W. F.; Hanindita, F.; Tanaka, Y.; Ochiai, K.; Sato, H.; Li, Y. X.; Yasuda, T.; Ito, S. Angew. Chem. Int. Ed. 2023, 62, e202218176. (c) Yu, Y.; Wang, L.; Lin, D. Q.; Rana, S.; Mali, K. S.; Ling, H. F.; Xie, L. H.; De Feyter, S.; Liu, J. Z. Angew. Chem. Int. Ed. 2023, 62, e202303335. (d) Borissov, A.; Maurya, Y. K.; Moshniaha, L.; Wong, W. S.; Zyla-Karwowska, M.; Stepien, M. Chem. Rev. 2022, 122, 565.
- (7) (a) Nebauer, J.; Neiß, C.; Krug, M.; Vogel, A.; Fehn, D.; Ozaki, S.; Rominger, F.; Meyer, K.; Kamada, K.; Guldi, D. M.; Görling, A.; Kivala, M. Angew. Chem. Int. Ed. 2022, 61, e202205287. (b) Luo, H.; Liu, J. Angew. Chem. Int. Ed. 2023, 62, e202302761. (c) Chaolumen; Stepek, I. A.; Yamada, K. E.; Ito, H.; Itami, K. Angew. Chem. Int. Ed. 2021, 60, 23508. (d) Krzeszewski, M.; Dobrzycki, Ł.; Sobolewski, A. L.; Cyrański, M. K.; Gryko, D. T. Angew. Chem. Int. Ed. 2021, 60, 14998. (e) Qiu, Z.-L.; Chen, X.-W.; Huang, Y.-D.; Wei, R.-J.; Chu, K.-S.; Zhao, X.-J.; Tan, Y.-Z. Angew. Chem. Int. Ed. 2022, 61, e202116955.
- (8) (a) Vogel, E.; Kerimis, D.; Allison, N. T.; Zellerhoff, R.; Wassen, J. Angew. Chem. Int. Ed. 1979, 18, 545. (b) Dauben, H. J., Jr.; Bertelli, D. J. J. Am. Chem. Soc. 1961, 83, 4659.
- (9) Xin, H.; Hou, B.; Gao, X. Acc. Chem. Res. 2021, 54, 1737.
- (10) (a) Ma, J.; Fu, Y.; Dmitrieva, E.; Liu, F.; Komber, H.; Hennersdorf, F.; Popov, A. A.; Weigand, J. J.; Liu, J.; Feng, X. *Angew. Chem. Int. Ed.* **2020**, 59, 5637. (b) Duan, C.; Zhang, J.; Xiang, J.; Yang, X.; Gao, X. *Angew. Chem. Int. Ed.* **2022**, 61, e202201494.
- (11) (a) Yamamoto, K.; Saitho, Y.; Iwaki, D.; Ooka, T. Angew. Chem. Int. Ed. **1991**, 30, 1173. (b) Ogawa, N.; Yamaoka, Y.; Takikawa, H.; Yamada, K.-i.; Takasu, K. J. Am. Chem. Soc. **2020**, 142, 13322. (c) Han, Y.; Xue, Z.; Li, G.; Gu, Y.; Ni, Y.; Dong, S.; Chi, C. Angew. Chem. Int. Ed. **2020**, 59, 9026.
- (12) (a) Anderson, A. G., Jr.; Steckler, B. M. J. Am. Chem. Soc. 1959, 81, 4941. (b) Michl, J.; Thulstrup, E. W. Tetrahedron 1976, 32, 205. (c) Shevyakov, S. V.; Li, H.; Muthyala, R.; Asato, A. E.; Croney, J. C.; Jameson, D. M.; Liu, R. S. H. J. Phys. Chem. A 2003, 107, 3295.
- (13) (a) Lindner, H. J.; Kitschke, B. Angew. Chem. Int. Ed. 1976, 15, 106.
 (b) Boyd, G. V. Tetrahedron 1966, 22, 3409.
- (14) (a) Michalsky, I.; Gensch, V.; Walla, C.; Hoffmann, M.; Rominger, F.; Oeser, T.; Tegeder, P.; Dreuw, A.; Kivala, M. *Chem. Eur. J.* 2022, 28, e202200326. (b) Ito, M.; Kawasaki, R.; Kanyiva, K. S.; Shibata, T. *Eur. J. Org. Chem.* 2016, 2016, 5234. (c) Wagner, J.; Zimmermann Crocomo, P.; Kochman, M. A.; Kubas, A.; Data, P.; Lindner, M. *Angew. Chem. Int. Ed.* 2022, 61, e20220232.
- (15) Zhang, K.; El Bitar Nehme, M.; Hope, P. A.; Rickhaus, M. Helv. Chim. Acta. **2023**, 106, e202200195.
- (16) Nishimura, Y.; Harimoto, T.; Suzuki, T.; Ishigaki, Y. Chem. Eur. J. 2023, 29, e202301759.
- (17) (a) Fang, M.-Y.; Chen, L.-P.; Huang, L.; Fang, D. M.; Chen, X.-Z.; Wang, B.-Q.; Feng, C.; Xiang, S.-K. J. Org. Chem. 2021, 86, 9096.
 (b) Cheng, C.; Tu, D.; Zuo, X.; Wu, Z.; Wan, B.; Zhang, Y. Org. Lett. 2021, 23, 1239.
- (18) Hu, T.; Ye, Z.; Zhu, K.; Xu, K.; Wu, Y.; Zhang, F. Org. Lett. **2020**, *22*, 505.
- (19) The UV-Vis spectroscopy was performed on the Agilent Cary 60. The photoluminescence spectra were measured on Cary Eclipse Fluorescence Spectrofluorometer, Agilent Cary G9800AA. Cyclic voltammetry (CV) measurements were carried out on a CHI660E

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(CH Instruments, USA) in a three-electrode cell in an anhydrous dichloromethane (DCM) solution of tetrabutylammonium hexa-fluorophosphate (n-Bu4NPF6, 0.1 M) with a scan rate of 100 mV/ s at room temperature. All potentials were further calibrated

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against ferrocene/ferrocenium (Fc/Fc+).
(20) (a) Qiu, S.; Zhang, Z.; Wang, Z.; Qu, D.-H.; Tian, H. *Precis. Chem.* **2023**, *1*, 129. (b) Chen, Y.; Tseng, S.-M.; Chang, K.-H.; Chou, P.-T. J. Am. Chem. Soc. **2022**, 144, 1748.