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U-shaped Helical Azaarenes: Synthesis, Structures and Properties

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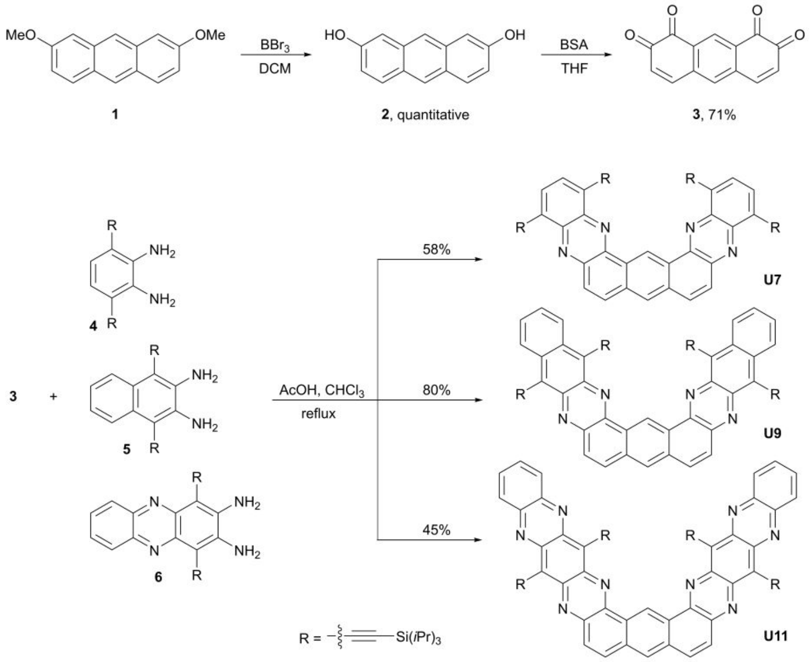
ABSTRACT The synthesis and properties of a series of U-shaped helical azaarenes are reported. Crystal structures of these helical azaarenes were obtained, and the solid-state structures unequivocally exhibited their helicity.

In the past few decades, we have witnessed the rapid progress of N-heteroarenes[1] in organic electronics, especially in organic field effect transistors (OFETs).[2] However, most of the N-heteroarenes are synthesized in linear shape due to the lack of suitable building blocks to construct non-linear backbones.[3] Consequently, the majority of non-linear N-heteroarenes are HAT (1,4,5,8,9,12-hexaazatriphenylene)-based star-shaped azaarenes employing the commercially available hexaketocyclohexane as the building block.[4] Among the existing non-linear N-heteroarenes, helical azaarenes are seldomly reported compared with star-shaped analogues.[5]

Currently, the majority of helical azaarenes are azahelicenes. Although azahelicenes were synthesized prior to carbohelicenes, the latter has received more attention because of their good functionality and the versatile synthetic approaches towards them. Until recently, more interesting properties have been observed in azahelicenes.[6] The incorporation of nitrogen atoms could alter the electronic structure and allow the fine tuning of optoelectrical properties. Based on the nitrogen-containing heterocycles, azahelicenes could be classified into several types: pyridine-containing ones,[7] pyrroles,[8] pyridazine derivatives,[9] etc. It is noteworthy that pyrazine-containing azahelicenes are extremely rare.[10] Such gap prompts us to synthesize novel pyrazine-containing helical azaarenes (**U7**, **U9** and **U11**).

Starting from 2,7-dimethoxyanthracene **1**[11], demethylation using BBr_3 in boiling dichloromethane furnishes **2** in quantitative yield; followed by oxidizing **2** with benzeneseleninic acid anhydride (BSA) to tetraketone **3** in 71% yield. The two-fold condensation reactions between tetraketone **3** and diamines **4**, **5** and **6** gave the helical azaarenes in moderate to good yields (Scheme 1).



Scheme 1. Synthesis of Helical Azaarenes U7, U9 and U11.

Comp.	ABS_{max} [nm]	λ_{onset} [nm]	EMS_{max} [nm]	LUMO [ev] mes.[a]/cal.[b]	HOMO [ev] mes.[c]/cal.[b]	gap[ev] mes.[d]/cal.[b]
U7	471	482	478	-3.08/-2.82	-5.65/-5.68	2.57/2.86
U9	561	594	602	-3.27/-3.07	-5.36/-5.25	2.09/2.18
U11	664	701	692	-3.77/-3.53	-5.54/-5.31	1.77/1.78

Table 1. Optical and electronic properties of U7, U9 and U11

[a] $LUMO_{mes.} = -(E_{red(onset)} + 4.8)$ (eV); [b] DFT calculations (B3LYP/6-31G*) using Gaussian 09; TMS groups were used instead of TIPS; [c] $E_{HOMO}=E_{LUMO(CV)} - E_{gap(opt)}$ (eV); [d] gap_{mes} was calculated from 1240nm/λ_{onset}.

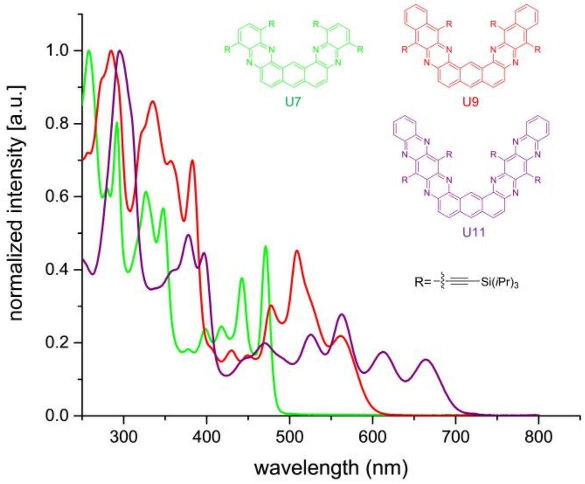


Figure 1. Normalized absorption spectra of **U7**, **U9** and **U11** in dichloromethane (10^{-5} M).

Figure 1 shows the normalized absorption spectra of **U7**, **U9** and **U11**. There is an obvious increase in λ_{max} (Table 1) from **U7** to **U11**, which indicates the size-dependent bathochromic shift in the absorption. Compared with the reported S-shape counterparts[12] (Figure S15), helical azaarenes show small hypsochromic shifts in λ_{max}. It is worth mentioning that the helical azaarenes have almost identical optical band gaps to their constitutional isomers, which exhibits the similarity in their optical properties (Table S1). Unlike the constitutional isomers, cyclic voltammetry of helical azaarenes was performed in DCM at room temperature due to their much-improved solubility. The measured LUMOs of helical azaarenes are apparently shallower than that of S-shaped isomers. This could be ascribed to their twisted helical structures. The two pyrazine units near the centre are highly distorted because of the torsional strain of the helix. Hence, the conjugation in these two pyrazine units is rather weak resulting in smaller π-systems compared to S-shaped azaarenes, which further leads to the shallower LUMOs. Taking **U11** as an example, unlike its S-shaped isomer whose LUMO is deeper than the linear TIPS-TAP,[13] **U11** has a shallower LUMO than TIPS-TAP. The calculated energy levels are in good agreement with the experimental values and also show the same trend (Table 1).

The crystals suitable for X-ray analysis were obtained via slow diffusion of methanol vapor into the chlorobenzene solutions of helical azaarenes. The solid-state structures and stacking patterns are shown in Figure 2. From the crystal structures, one can conclude that the helicity of these azaarenes is caused by the steric hindrance between the two inner TIPS groups. Moreover, all three racemates are racemic compounds, which means that the *P* and *M*-isomers are both present in the crystal with the ratio of 1:1. The packing motifs of **U7**, **U9** and **U11** are similar. *P* and *M*-isomers pack in pairs such that the arms of the helix are on top of each other to different extents in an inverted manner. **U9** has the largest overlapping area and longest stack distance, whereas **U11** possesses the smallest overlapping area but the shortest stack distance. **U7**, on the other hand, bears intermediate overlapping area and stack distance. The TIPS groups strongly hinder the π–π stacking due to their bulkiness, and the helical backbone further obstructs the effective π–π stacking. Consequently, helical azaarenes possess much improved solubility compared with their S-shaped counterparts, and they could be easily dissolved in chlorinated solvents and other common solvents such as dichloromethane, hexane, THF, DMF and toluene.

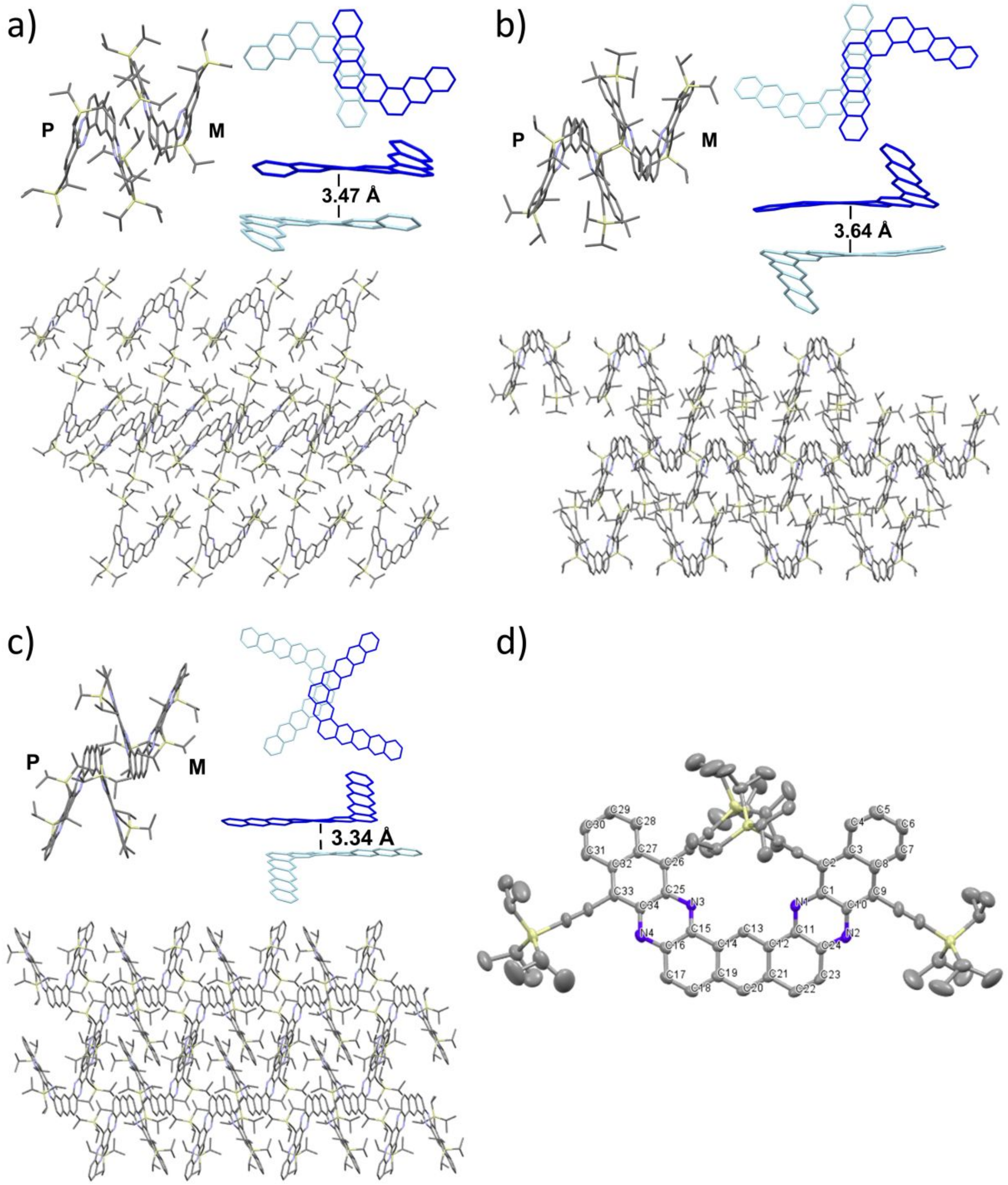


Figure 2 Crystal structures and packing motifs of **U7** (a), **U9** (b) and **U11** (c). ORTEP plot of **U9** (d). Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids drawn at the 50% probability level.

The interplane angles of **U7**, **U9** and **U11** are 38.9^0, 48.2^0 and 39.7^0, respectively. The sum of torsional angels increases from 52.7^0 to 82.0^0 as the helical skeleton becomes larger. Unlike the common helicenes, where all the aromatic rings are fused inward encircling the axis, there are only two phenanthrene segments folding inward in the as-obtained helical azaarene molecules. Thus, although the interplane angle of **U9** is significantly larger than that of **U7**, there is little difference in the sum of their torsional angles. Upon close inspection on their torsional angles (Table S2), it is found that the largest torsional angles of **U7**, **U9** and **U11** are almost identical. More interestingly, all of those largest torsional angles belong to the phenanthrene segments, which substantiates the similarity in helical skeletons among the as-obtained helical azaarenes. Although the helicity of U-shaped azaarenes is clearly shown here, one should not mistreat the U-shaped helical azaarenes as azahelicenes, since they do not comply with the definition of helicenes. Instead, the U-shaped azaarenes might unveil another bulky-substituent-induced helical configuration other than the traditional helicenes.

In conclusion, a series of helical azaarenes have been prepared by the condensation reactions between tetraone **3** and diamines **4** – **6**. The optical and electronic properties of as-obtained compounds were investigated and compared with their S-shaped constitutional isomers. Helical skeletons of those helical azaarenes were unequivocally revealed by the single crystal X-ray analysis.

EXPERIMENTAL SECTION

Materials. Reagents and solvents for synthesis were, if not otherwise specified, purchased from Sigma Aldrich and used without further purification. THF and DCM were dried over sodium and CaH_2 respectively, then freshly distilled prior to use. Technical grade dichloromethane (DCM) and hexane for column chromatography were purchased from Aik Moh and used as received. Benzeneseleninic anhydride was purchased from ACROS Organics. Compounds **1**[11], **4**[14], **5**[14] and **6**[15] were synthesized according to the reported literature.

Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 300 NMR spectrometer at ambient temperature with tetramethylsilane (TMS) as an internal standard. High resolution mass spectrum (HRMS) was performed on a Waters Q-Tof premier mass spectrometer. UV-Vis absorbance was recorded on UV-Vis-NIR spectrometer Cary 5000. Cyclic voltammetry measurements were conducted on a CHI 604E electrochemical workstation, where platinum wires were used as bath counter electrode and reference electrode and glassy carbon (diameter: 1.6 mm; area: 0.02 cm^2) was employed as working electrode. Ferrocene was used as an external standard. Potentials were recorded versus Fc$^+$/Fc in anhydrous DCM with tetrabutylammonium hexafluorophosphate (TBAPF$_6$, 0.1 M) as supporting electrolyte at a scan rate of 100 m Vs^{-1}. After the acquirement of E_{Fc} (0.25 eV in our setup), the value of LUMO can be calculated applying empirical formulas $E_{\mathrm{LUMO}} = -[4.8 - E_{\mathrm{Fc}} + E_{\mathrm{re}}^{\mathrm{onset}}]$ eV. Optical bandgaps were calculated from 1240 nm/λ_{onset}. The value of HOMO level is then obtained using $\mathrm{E_{HOMO} = E_{LUMO} - E_{gap(opt)}}$ (eV). Crystal structure analysis was accomplished using diffractometers with Mo Kα radiation. The heat source used in this work was an oil bath over the Heidolph Hei-Tec magnetic stirrer, equipped with Pt 1000 temperature probe.

2,7-Dihydroxyanthracene (2). In a heatgun-dried Schlenk flask purged with argon, **1** (477 mg, 2 mmol, 1 eq) was dispersed in dry DCM (30 ml). The suspension was cooled to 0 °C using an ice/water bath, followed by the dropwise addition of BBr$_3$ (1 ml, 5 eq). Then the cooling bath was removed, and the mixture was heated to reflux in an oil bath for 4h. After being cooled to 0 °C again, ice-cold water was carefully added to the mixture to quench the unreacted BBr$_3$. The resulting slurry was extracted with diethyl ether (3 x 50 ml), and the organic phase was combined and dried with sodium sulfate. The removal of solvent under reduced pressure gave **2** as light brown solid (420 mg, quant.). mp 159 °C; ^{1}H NMR (300 MHz, Acetone-*d$_6$*) δ = 8.49 (s, 2H), 8.18 (s, 1H), 7.84 (s, 1H), 7.76 (d, J = 9.1 Hz, 2H), 7.07 (d, J = 2.3 Hz, 2H), 6.96 (dd, J = 9.1, 2.4 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, DMSO-*d$_6$*) δ = 154.7, 133.2, 129.8, 125.9, 125.3, 119.8, 118.9, 105.9;IR $\nu_{\max}$ 3392, 3218, 1632, 1592, 1547, 1455, 1410, 1378, 1330, 1275, 1227, 1198, 1169, 1137, 972, 893, 843, 798, 745, 648, 591, 549, 476, 422 cm^{-1}; HRMS (ESI) *m/z* [M + H]$^+$ calcd for $C_{14}H_{11}O_2$ 211.0759, found 211.0758.

Anthracene-1,2,7,8-tetraone (3). In a heatgun-dried round bottom flask, benzeneseleninic acid anhydride (1.8 g, 5 mmol) was suspended in dry THF (80 ml) under argon. To the stirring suspension in an oil bath, a solution of **2** (0.5 g, 2.38 mmol) in dry THF (40 ml) was added dropwise at 50 °C. After the addition, heat was turned off, and the resulting deep red solution was allowed to stand overnight. Upon the completion of reaction, the solvent was removed *in vacuo*. The residual was washed with hot diethyl ether (15 ml), and DCM (10 ml) then dried *in vacuo*. **3** was obtained as deep reddish brown solid (403 mg, 71%). This product was used directly in next step without further purification. ^{1}H NMR (300 MHz, THF-d_8) δ = 6.81 (s, 1H), 5.86 (s, 2H), 5.83 (s, 1H), 4.77 (d, J = 10.2 Hz, 2H); ^{13}C{^{1}H} NMR was not taken due to the poor solubility of **3** in common solvents; IR ν_{max} 3052, 1706, 1665, 1602, 1586, 1429, 1322, 1261, 1230, 1177, 1166, 1124, 1088, 945, 914, 838, 796, 675, 524 cm^{-1}; HRMS (ESI) *m/z* [M + H]$^+$ calcd for $C_{14}H_{11}O_2$ 211.0759, found 211.0758.

General procedure (GP). To a round bottom flask equipped with a condenser, **3** (20 mg, 0.084 mmol) and diamine (0.2 mmol) were added to a solvent mixture of chloroform (5 ml) and acetic acid (15 ml). The stirring solution was heated to 100 °C in an oil bath for 1 d. The mixture was cooled to RT, and the solvent was removed *in vacuo*. This crude product was further purified by column chromatography on silica gel using a Hexane/DCM solvent mixture.

U7. GP was applied to **3** (20 mg) and **4** (94 mg). Column chromatography (Hexane/DCM = 5:1) yielded **U7** as a yellow crystalline solid (54 mg, 58 %). mp 337 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.99 (s, 1H), 8.37 (s, 1H), 8.17 (d, J = 9.3 Hz, 2H), 8.02 (d, J = 9.3 Hz, 2H), 7.99 (s, 4H), 1.29 (s, 42H), 1.23 – 1.14 (m, 6H), 1.02 (dd, J = 10.8, 6.9 Hz, 36H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 144.2, 143.4, 143.1, 141.4, 134.3, 133.5, 133.4, 133.3, 130.2, 129.2, 127.1, 125.7, 125.0, 123.6, 104.0, 103.8, 101.7, 100.3, 18.93, 18.87, 11.7, 11.6; IR ν_{max} 2943, 2891, 2865, 2152, 1491, 1462, 1350, 1319, 1243, 1213, 1127, 1060, 1033, 1017, 996, 922, 884, 846, 790, 700, 677, 587, 544, 500, 462, 419 cm^{-1}; HRMS(ESI) *m/z* [M + H]$^+$, calcd for $C_{70}H_{95}N_4Si_4$, 1104.6630, found 1104.6643.

U9. GP was applied to **3** (20 mg) and **5** (104 mg). Column chromatography (Hexane/DCM = 4:1) yielded **U9** as a red crystalline solid (81 mg, 80 %). mp > 350 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 11.01 (s, 1H), 8.91 – 8.74 (m, 4H), 8.28 (s, 1H), 8.10 (d, J = 9.4 Hz, 2H), 7.98 (d, J = 9.4 Hz, 2H), 7.80 – 7.66 (m, 4H), 1.36 (s, 42H), 1.23 – 1.14 (m, 6H), 1.03 (t, J = 7.3 Hz, 36H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 145.3, 144.3, 141.0, 139.3, 135.0, 134.8, 134.7, 133.9, 130.5, 129.7, 127.9, 127.8, 127.61, 127.56, 127.50, 126.3, 121.5, 120.0, 109.3, 107.3, 103.1, 102.8, 18.99, 18.95, 11.71, 11.67; IR ν_{max} 3060, 2942, 2890, 2864, 2135, 1614, 1517, 1463, 1386, 1342, 1315, 1246, 1217, 1115, 1043, 1014, 995, 920, 883, 827, 762, 747, 678, 597, 571, 513, 484, 414 cm^{-1}; HRMS(ESI) *m/z* [M + H]$^+$ calcd for $C_{78}H_{99}N_4Si_4$, 1204.6943, found 1204.6902.

U11. GP was applied to **3** (20 mg) and **6** (114 mg). Column chromatography (Hexane/DCM = 2:1) yielded **U11** as a dark purple crystalline solid (49 mg, 45 %). mp > 350 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 11.00 (s, 1H), 8.34 – 8.25 (m, 4H), 8.23 (s, 1H), 8.10 (d, J = 9.4 Hz, 2H), 7.98 (d, J = 9.4 Hz, 2H), 7.91 – 7.83 (m, 4H), 1.41 (s, 42H), 1.26 – 1.17 (m, 6H), 1.09 (dd, J = 7.0, 2.9 Hz, 36H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 146.4, 145.3, 145.13, 145.07, 143.2, 142.91, 142.88, 141.2, 135.4, 135.0, 131.8, 131.6, 130.73, 130.68, 130.5, 130.0, 128.0, 127.1, 123.7, 121.6, 113.6, 111.0, 103.1, 102.8, 19.02, 18.93, 11.83, 11.80; IR ν_{max}3063, 2942, 2890, 2864, 2348, 1613, 1530, 1501, 1461, 1382, 1356, 1314, 1246, 1228, 1188, 1128, 1071, 1042, 1020, 996, 921, 883, 754, 720, 677, 588, 512, 460, 415; HRMS(ESI) *m/z* [M + H]$^+$, calcd for $C_{82}H_{99}N_8Si_2$, 1309.7061, found 1309.7117.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI:

HRMS, NMR spectra, PL spectra, cyclic voltammetry, details of X-ray crystal structures and computational details (PDF)

Crystallographic data of **U7**, **U9** and **U11** (CIF)

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Notes

The authors declare no competing financial interest

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SYNOPSIS