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Synthesis of 5,9-Diaza Analogues of [5]- and [6]Helicene and their Chiroptic and Photophysical Characterization

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6,10-Dipropyl-5,9-diaza[5]- and -[6]helicene were synthesized by *ortho*,*ortho'* fusion of *ortho*-teraryldicarboxamides. Key steps in the synthesis of the teraryls are azide formation with subsequent reduction and amidation followed by Suzuki cross couplings. The *ortho* fusions were achieved with phosphorus pentoxide and phosphoryl oxide. The total syntheses could be accomplished with 10% and 3%, respectively, in seven consecutive steps starting with *meta*-dibromobenzene. The helicenes were investigated by UV/Vis and fluorescence spectroscopy and by quantum chemical calculation of, *inter alia*, the HOMO-LUMO gaps. Racemization barriers of the helicenes were calculated, whereupon the optical resolution of 5,9-diaza[6]helicene was attempted and carried out successfully; ECD spectra were measured of its enantiomers.

Introduction

According to the IUPAC definition helicenes[1] are *"ortho*-fused polycyclic aromatic or heteroaromatic compounds in which all rings (minimum five) are angularly arranged so as to give helically shaped molecules, which are thus chiral".[2] This not only allows for the condensation of benzene rings (Figure 1, top) or their hetero analogues,[3] but similarly of, e.g., five-[4] or seven-membered rings.[5] Actually, we consider the IUPAC definition to be not fully suitable for the description of this class of compounds, since the term 'aromatic' is not well-defined and occasionally even antiaromatic rings can be present in helicenes.[4,6] To our understanding helicenes need to be fully conjugated, but not necessarily aromatic. Due to their intrinsic chirality, helicenes (e.g., **A** or **B**) show interesting chiroptic properties and have found numerous applications.[1f] Aza analogues of helicenes have similarly been investigated: They have been used as organocatalysts,[7] proton sponges,[8] or ligands in transition metal complexes,[9] they show enhanced optical properties, e.g., in circularly polarized luminescence (CPL),[10] and change their photophysical properties upon protonation.[11] The intercalation into DNA has been reported for cationic aza-, oxa-, and thiahelicenes.[12] Helicenes consisting of benzene rings (carbohelicenes) and their respective heteroatom analogues are usually prepared by electrocyclization of stilbene-type compounds with subsequent oxidative aromatization.[1b,d,e,13] The synthesis of amino-substituted carbo- and thiahelicenes by electrophilic cyclization of *ortho*,*ortho'* cyanomethyl-substituted terphenyls has been reported by the Prim group.[14] Further methods for the synthesis of aza- and diazahelicenes are transition metal-catalyzed [2+2+2] cyclizations[15] and couplings of *ortho*,*ortho'*-dihalobiaryls[7b,16] or *ortho*-alkynylbiaryls.[15b]

In the recent years we used *ortho*,*ortho'* fusions (Figure 1, bottom) in suitably substituted terphenyls **I** to synthesize diaza[5]helicenes **C** and **D**,[17] indolo[2,3-*c*]carbazoles **E**,[17b] indolophenanthridines,[18] thiahelicenes **F**,[19] and helicene-shaped cyclopenta-fused polyaromatic hydrocarbons **G** and **H**

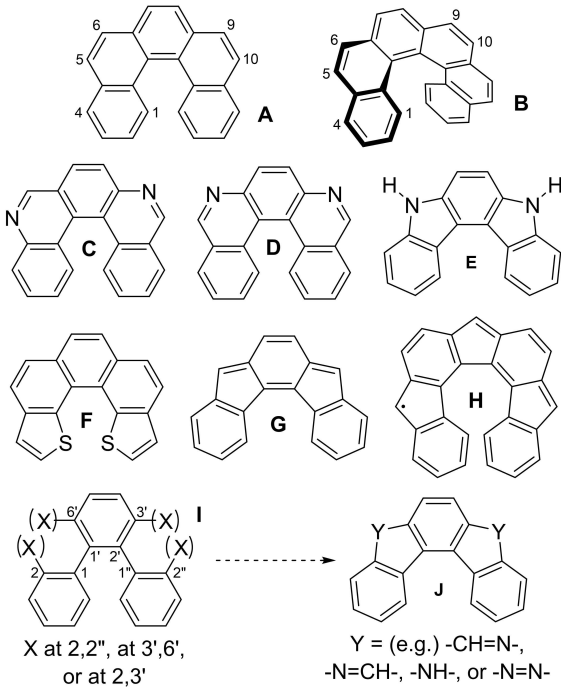

Figure 1. Top row: carbohelicenes, center: structures previously obtained in our group, bottom: general scheme for *ortho*,*ortho'* fusion of terphenyl derivatives to pentahelicenes.

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(CP-PAHs), where the latter were partly obtained as stable radical species (Figure 1, center).[4]

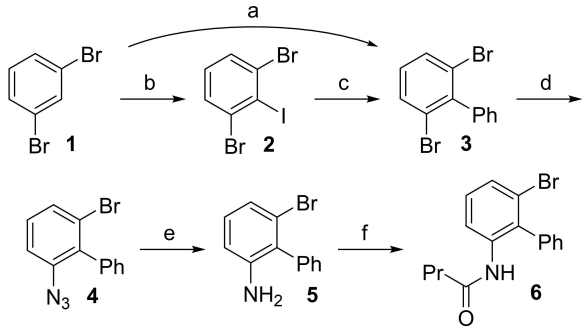
Herein we report on the synthesis of 5,9-diaza[5]- and -[6]helicenes by *ortho*,*ortho*′ fusions in teraryls and on their chiroptic and photophysical characterization.

Results and Discussion

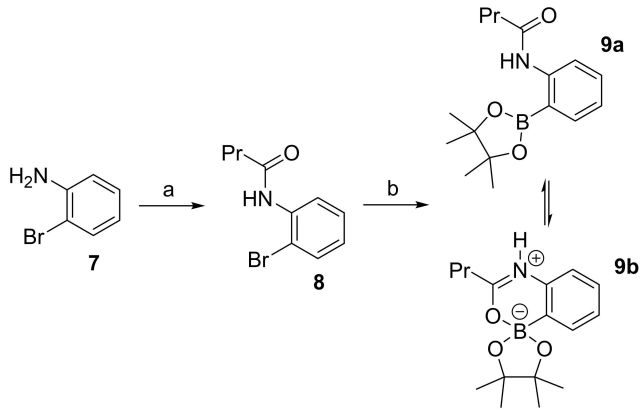
Synthesis of 5,9-diaza[5]helicene 11

A terphenyl precursor **10** suitable for cyclization to the respective helicene **11** could be synthesized by Suzuki coupling of a brominated biphenyl **6** and a phenyl boronate **9**. The former was synthesized starting with *meta*-dibromobenzene (**1**), which was *ortho*-metalated with lithium diisopropylamide (LDA), transferred into a zinc organyl, and reacted with phenyl iodide in a Negishi coupling furnishing dibromobiphenyl **3** (Scheme 1).[20] Since a non-satisfactory 31% yield was achieved with this sequence, we tested a two-step protocol, in which *ortho*-lithiated dibromobenzene was trapped with iodine to yield trihalogenated benzene **2**. Suzuki coupling with phenylboronic acid led to biphenyl **3** with a significantly improved yield of 61% over both steps.[21] As expected, only the iodide position reacted in this cross coupling. Metal-halogen exchange at one of the bromide positions and trapping with tosyl azide led to azide **4**,[22] which was subsequently reduced to the respective amine **5** by hydrogenation. Acylation with butyryl chloride[23] furnished the biphenyl electrophile **6** destined for Suzuki coupling. The thus present propyl group was chosen to allow for a sufficient solubility of all intermediates and products and to facilitate NMR-spectroscopic analyses. It was expected to have no significant influence on the physical and spectroscopic properties of the aimed helicene. We could show in previous syntheses that a wide range of substituents can be introduced into helicenes, when similar protocols are applied.[17]

Boronate **9** was accessible by acylation of *ortho*-bromoaniline (**7**) and subsequent Miyaura coupling using bis(pinacolato)diboron (B_2pin_2) with [1,1′-bis-(diphenylphosphino)-ferrocene]-dichloro-palladium(II) [$PdCl_2$(dppf)] as catalyst (Scheme 2).

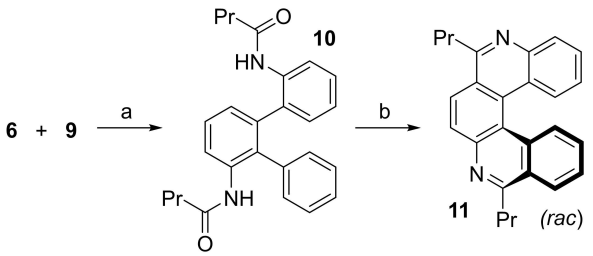


Scheme 1. Synthesis of biphenyl bromide **6**. Conditions: a) LDA, then $ZnCl_2$, then PhI, cat. $Pd(PPh_3)_4$, THF, −78 °C to rt (31%); b) LDA, I_2, THF, −78 °C to rt (71%); c) $PhB(OH)_2$, cat. $Pd(PPh_3)_2Cl_2$, Na_2CO_3, THF/H_2O, 80 °C (86%); d) BuLi, TsN_3, THF, −78 °C to rt (67%); e) H_2, cat. Pd/C, EtOAc, rt (93%); f) butyryl chloride, NEt_3, THF, 0 °C to rt (93%).



Scheme 2. Synthesis of boronated anilide **9**. Conditions: a) butyryl chloride, NEt_3, THF, 0 °C to rt (92%); b) B_2pin_2, cat. $PdCl_2$(dppf), KOAc, dioxane, 85 °C (50%).

The rather poor yield of 50% might be due to a reduced solubility of boronate **9** and thus to an impeded work-up and purification process. It has already been noticed[1a] that intramolecular coordination of the electrophilic boron center and the nucleophilic carbonyl oxygen would lead to a betaine structure **9b** with significantly increased polarity. This assumption is corroborated by an observed de-shielding of the amide proton in ^{1}H NMR spectroscopy (**8**: $\delta = 7.62$ ppm versus **9**: $\delta =$ 9.97 ppm). Anyway, **9** was obtained with 46% yield over two steps.Suzuki coupling of bromide **6** and boronate **9** to terphenyl **10** could be realized with 85% (Scheme 3), where we used a proven protocol with palladium(II) acetate, cesium carbonate, and Buchwald's SPhos ligand (2-dicyclohexylphosphino-2′,6′-dimethoxy[1,1′-biphenyl]).[24] Double cyclization by electrophilic aromatic substitution with dehydrating conditions furnishing diaza[5]helicene **11** was here achieved with a combination of phosphorus pentoxide (P_4O_{10}) and phosphoryl chloride, albeit with only 33% yield.[23] Hendrickson's reagent (Ph_3PO/Tf_2O),[25] which was successfully applied in previous azahelicene syntheses,[17] did not lead to any cyclization in the present case. We previously realized[17a] that *ortho*,*ortho*′ fusion to diazahelicenes using a twofold electrophilic aromatic substitution (S_EAr) may be prevented by formation of electrophilic species (nitrilium or imidocarbenium ions), which strongly deactivate adjacent rings.[25b] Alternatively, the second S_EAr might be complicated because protonated and thus similarly deactivated phenanthridines are formed during the first S_EAr.



Scheme 3. Synthesis of 5,9-diaza[5]helicene **11**. Conditions: a) cat. $Pd(OAc)_2$, Cs_2CO_3, SPhos, dioxane/H_2O, 80 °C (85%); b) P_4O_{10}, $POCl_3$, 110 °C (33%).

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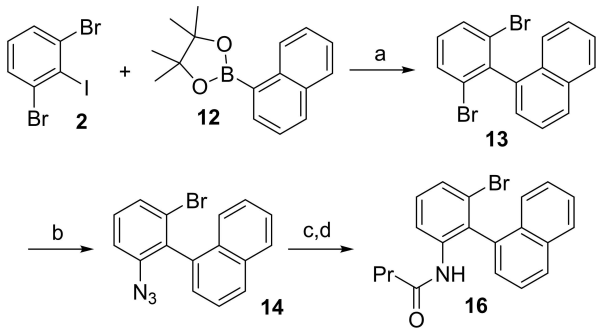
Synthesis of 6,10-disubstituted 5,9-diaza[5]helicene **11** was thus achieved with a total yield of 10% over seven consecutive steps, which is a significant improvement over our previous synthesis, where a total yield of only 2–4% over eleven steps was reached.[17a] As mentioned above, substitution should be rather flexible in this sequence, which would allow the introduction of divers substituents.

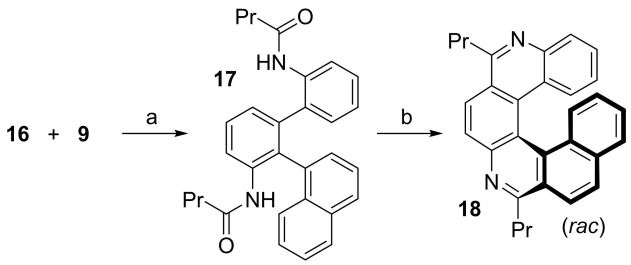
Synthesis of 5,9-diaza[6]helicene 18

Diaza[6]helicene **18** was obtained following a similar strategy: Suzuki coupling of iodide **2** with naphthalene boronate **12**, introduction of an azido group, reduction to the respective amine **15**, and acylation furnished biaryl bromide **16** (Scheme 4). Yields in this sequence were slightly worse than those for the synthesis of the related biphenyl **6**, most probably due to the increased steric hindrance of the naphthalene group.

Suzuki coupling of bromide **16** with boronate **9** furnished teraryl **17** (Scheme 5). Due to the occurrence of rotamers (hampered rotation along the two biaryl bonds), an analysis of this teraryl turned out to be not possible with NMR-spectroscopic methods. Both amide groups of the teraryl were used for *ortho* fusions furnishing 5,9-diaza[6]helicene **18**, which was thus obtained in 3% yield over seven consecutive steps (starting with dibromobenzene **1**). The poor 27% yield of the final double cyclization might be due to the fact that teraryl **17** could be present in four configurations with an assumed



Scheme 4. Synthesis of biaryl bromide **16**. Condition: a) cat. $Pd(PPh_3)_2Cl_2$, LiOH, $MeCN/H_2O$, 80 °C (46%); b) BuLi, TsN_3, THF, −78 °C to rt (68%); c) H_2, cat. Pd/C, EtOAc, rt (→**15**; 88%); d) butyryl chloride, NEt_3, THF, 0 °C to rt (62%).



Scheme 5. Synthesis of 5,9-diaza[6]helicene **18**. Conditions: a) cat. $Pd(OAc)_2$, Cs_2CO_3, SPhos, dioxane/H_2O, 80 °C (82%); b) P_4O_{10}, $POCl_3$, 110 °C (27%).

Properties of 5,9-helicenes 11 and 18

Helicenes with up to seven *ortho*-condensed six-membered rings suffer thermal racemization via a single achiral transition state, while racemization of higher helicenes proceeds via multi-step mechanisms.[26] Racemization even of smaller helicenes can be impeded if substituents are present at the relevant positions (e.g., in 1,12-dimethyl[4]helicene).[12c,27] In the absence of hindering substituents racemization barriers are rather low for small helicenes, e.g. [5]helicenes, while higher helicenes are more and more stable against racemization. We have observed previously, that diastereotopic CH_2 groups directly attached to diaza[5]helicenes show two signals in ^1H NMR spectroscopy, proving a stereochemical integrity of the helicenes on NMR time scales.[17b] Although a resolution of [5]helicenes had been achieved by chromatographic separation of diastereomeric crystals[28] or with special HPLC methods at low temperature,[29] the fast racemization at room temperature prevents resolution of [5]helicene into enantiomerically stable isomers. To gain more precise information, we performed quantum chemical investigations on the racemization barriers of diazahelicenes, where these calculations were performed with the unsubstituted parent diaza[5]- and -[6]helicenes **11′** and **18′**. Details are given in the SI. The racemization barrier of parent 5,9-diaza[5]helicene **11′** was calculated by us to be 89.2 kJ mol^{-1} (Figure 2). This value is somewhat lower than an experimentally determined value for carbo[5]helicene (**A**; 98.3 kJ mol^{-1})[30] and a calculated value for 5,10-diaza[5]helicene (not depicted; 93.3 kJ mol^{-1}).[23] For comparison we furthermore calculated the racemization barrier of 6,9-diaza[5]helicene (**D**), the parent of a number of compounds previously synthesized by us,[17b] to be 92.2 kJ mol^{-1}. Since carbo[5]helicene (**A**) and

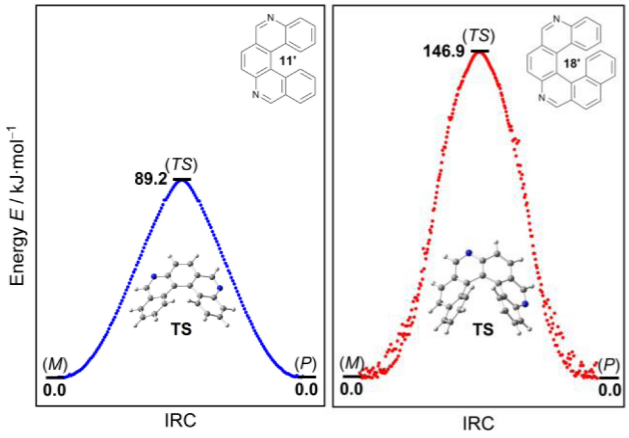


Figure 2. Optimized structures and zero point-corrected energies of enantiomers and transition states (TS) for racemizations as well as intrinsic reaction coordinate (IRC) analyses for diaza[5]helicene **11′** (left) and diaza[6]helicene **18′** (right).

5,10-diaza[5]helicene are not stable against racemization at room temperature,[1a,23,28,31] we did not attempt an optical resolution for diaza[5]helicene **11**. As expected, racemization barrier of the parent 5,9-diaza[6]helicene **18'** was significantly higher; it was calculated to be 146.9 kJ mol^{-1}. It thus can be estimated that racemization of **18'** is $1.3 \cdot 10^{10}$ times slower (at 25 °C) than interconversion of **11'**. This value is close to an experimentally determined value of 149 kJ mol^{-1} for carbo[6]helicene (**B**)[32] and to a calculated value for 5,12-diaza[6]helicene (151 kJ mol^{-1}),[23,30] where both helicenes could successfully be separated into their enantiomers. Trying a resolution of diaza[6]helicene **18** thus seemed to be promising.

Resolution of 5,9-diaza[6]helicene **18** was achieved with analytical and later on with semi-preparative HPLC on a chiral phase, i.e., on modified amylose phase, using an isogradic hexane/iPrOH mixture as eluent (details are given in the SI). Both enantiomers were base line-separated and thus could be isolated as enantiomerically pure fractions, which were characterized by electronic circular dichroism (ECD) spectroscopy (Figure 3).[33] Comparison of these spectra with a spectrum calculated with TD-DFT allowed the unambiguous assignment of a *P* configuration to fraction 1 and an *M* configuration to fraction 2. We furthermore calculated an ECD spectrum of protonated (*P*)-**18** and found it to have an overall similar shape. Further details are given in the SI.

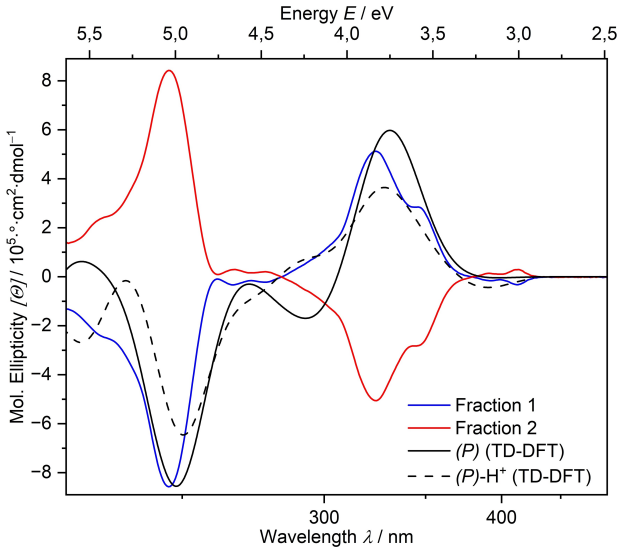


Figure 3. ECD-spectra of enantiomers of diaza[6]helicene **18**: measured (red, blue) in CH_2Cl_2 at 25 °C, calculated *P* enantiomer (black), calculated protonated *P* enantiomer (black, dashed).

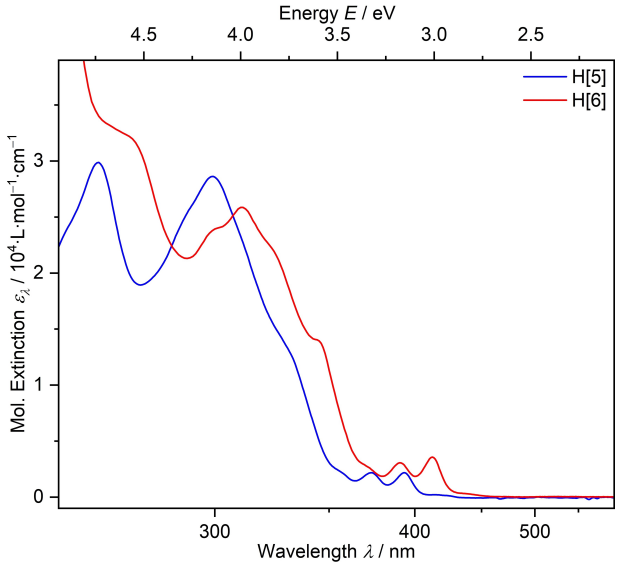


Figure 4. UV/Vis spectra of diaza[5]helicene **11** (blue) and diaza[6]helicene **18** (red) in CH_2Cl_2 at 20 °C.

For a photophysical characterization we at first measured UV/Vis spectra of helicenes **11** and **18** (Figure 4). Both spectra are quite similar, where a slight redshift of about 10–20 nm is observed for all bands of 5,9-diaza[6]helicene **18**.

Bands with weak intensity can be recognized in the region of 360–430 nm [log(ε) $<$3.6] while significant absorption maxima appear at 299 nm (for **11**) and at 310 nm (for **18**). Several shoulders to these bands can furthermore be recognized. For comparison we calculated the respective transitions in TD-DFT calculations and conclude that the low-energy transitions are essentially due to HOMO-LUMO transitions. Contribution of these orbitals to the low-energy band is 72% for **11** and 87% for **18**. The small intensity is reflected by small oscillator strengths for these transitions: $f \approx 0.06$ (**11**) and $f \approx 0.09$ (**18**). Further details to measured and calculated UV/Vis spectra are given in the SI.

The frontier orbitals are π orbitals spreading over the entire helicene framework (Figure 5); the low-energy transitions are thus $\pi \rightarrow \pi^*$ transitions. The calculated HOMO-LUMO gap of diaza[6]helicene **18** is 4.15 eV and is thus 0.31 eV smaller than the HOMO-LUMO gap of diaza[5]helicene **11** (4.46 eV). This reflects the bathochromic shift observed for **18**.

Photophysical emission of the helicenes was determined by measuring fluorescence spectra (Figure 6). For excitation we chose a low-energy wavelength with high extinction, i.e., diaza[5]helicene **11** was irradiated at 300 nm and diaza[6]helicene **18** at 310 nm. The spectra showed typical Stokes shifts into the range of 400–450 nm, which is in accordance with a blue fluorescence of the compounds visible to the naked eye. Again, a bathochromic shift of the fluorescence of **18** is observed in comparison with that of pentahelicene **11**. Diaza[5]helicene **11** showed fluorescence bands at 402 and 422 nm, while the hexahelicene analogue **18** shows bands at 425 and 446 nm.

Participation of the nitrogen lone pairs (and the respective molecular orbitals, c.f. Figure 5) was investigated by titration experiments: UV/Vis and fluorescence spectra were recorded after addition of trifluoroacetic acid (TFA). Successive addition of TFA (up to 8 equiv. in 7 steps) to diaza[5]helicene **11** during measuring UV/Vis spectra (Figure 7) revealed isosbestic points at 256, 265, 287, and 315 nm. Since absorption maxima at 262 and 299 nm are gradually decreasing, it can be assumed that these are due to a participation of $n \rightarrow \pi^*$ transitions. A similar behavior is observed for diaza[6]helicene **18**: An absorption maximum at 310 nm (between isosbestic points at 292 and 327 nm) is vanishing during addition of TFA.

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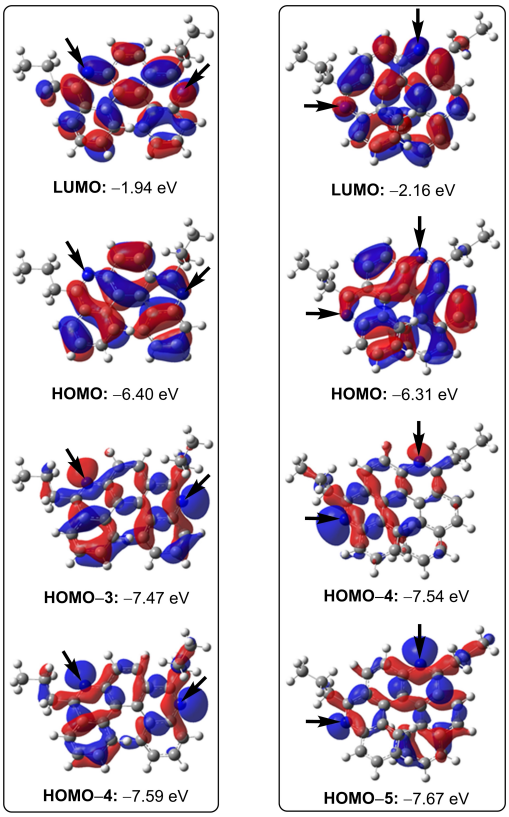

Figure 5. Frontier molecular orbitals of diaza[5]helicene **11** (left) and diaza[6]helicene **18** (right; iso values $\alpha = 0.02$) and their energies (two top rows); molecular orbitals with contribution of the nitrogen lone pairs (bottom rows), where arrows indicate positions of the nitrogen atoms.

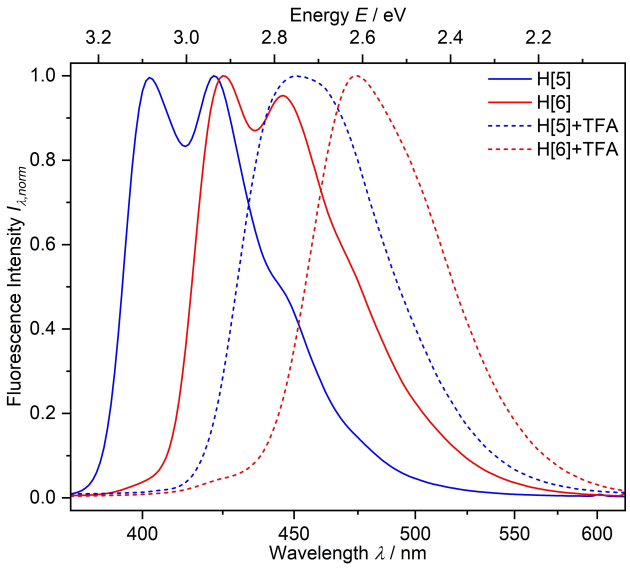

Figure 6. Normalized fluorescence spectra of diaza[5]helicene **11** (blue) and diaza[6]helicene **18** (red) in CH_2Cl_2 at 20 °C; dashed curves: the respective spectra after addition of 8 equiv. TFA.

Fluorescence spectra were similarly measured after addition of eight equivalents of TFA (Figure 6, dashed curves). For both helicenes a shift of about 0.25 eV towards lower energies is

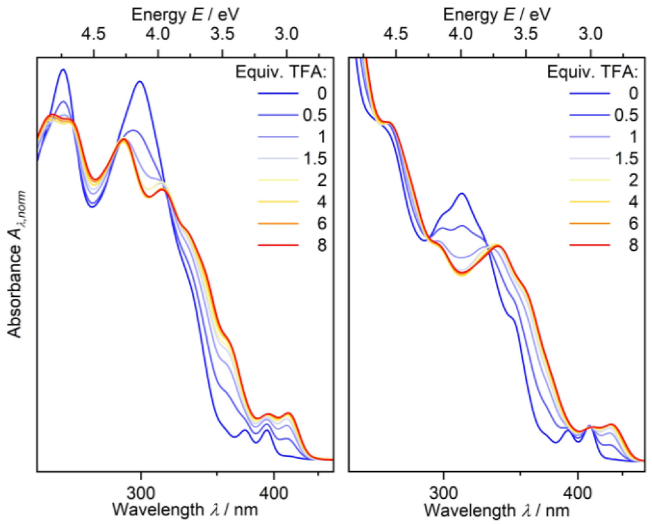

Figure 7. UV/Vis spectra of diaza[5]helicene **11** (left) and diaza[6]helicene **18** (right) in CH_2Cl_2 at 20 °C during addition of TFA.

observed, which goes in line with a visible change of a blue to a turquoise blue fluorescence. Addition of TFA furthermore leads to a loss of the fine structure and only one broad band is observed for both helicenes (**11**: 451 nm; **18**: 475 nm). A redshift in absorption and emission spectra had similarly been observed for further aza helicenes described in literature.[11]

Conclusions

It turned out that *ortho* fusion of suitably substituted teraryls allowed for the concise and high-yielding synthesis of 5,9-diaza[5]- and -[6]helicenes. The possibility of an optical resolution makes the diaza[6]helicene particularly suitable for possible applications. Here, the chiroptic properties might favorably augment its advantageous optical properties, which are reflected by a small HOMO-LUMO gap of only 4.1 eV.

Experimental Section

General

Technical solvents (CH_2Cl_2 and hexane) were distilled prior to use. EtOAc, Et_2O, EtOH, and MeCN were purchased as HPLC-grade solvents and used without further purification. THF and dioxane were dried over sodium, CH_2Cl_2 was dried over CaH_2, and these solvents were distilled prior to use. Flash column chromatography[34] was carried out using Merck SiO_2 60 (230–400 mesh) and thin layer chromatography (TLC) was carried out using commercially available Merck F_{254} pre-coated sheets. ^1H and ^{13}C NMR spectra were recorded with Bruker Avance 400 or Avance Neo instruments. Chemical shifts are given in ppm and are referenced by using the residual signals of the solvent as internal standard. IR spectra were recorded with a Bruker Alpha FT-IR-spectrometer using the ATR technique and mass spectra were recorded with a Finnigan MAT-95 mass spectrometer. UV/Vis data were recorded with an Agilent Cary 60 spectrophotometer,

fluorescence data were collected using a Horiba Fluoromax-4. ECD spectra were measured on a Jasco J-815 spectropolarimeter. In all cases quartz glass cuvettes were used and the temperature of the samples was kept at 20 °C for absorption and fluorescence spectra and at 25 °C for ECD spectra. Optical resolution of **18** was carried out on an Agilent HPLC-1000 system. Amylose SA columns [amylose tris(3,5-dimethylphenylcarbamate)] were used as stationary phase (analytical scale: 250×4.60 mm, 5 μm; semi-preparative scale: 250×30 mm, 10 μm) and an isogradic mixture of hexane and iPrOH (98:2) served as eluent.

1,3-Dibromo-2-iodobenzene (2)

Following a published procedure,[21] nBuLi (2.5 M in hexane, 8.6 mL, 21.6 mmol, 1.02 equiv) was added dropwise at −78 °C within 10 min to a solution of iPr_2NH (2.98 mL, 2.15 g, 21.2 mmol, 1.00 equiv) in anhydrous THF (56 mL) and stirring was continued for 15 min. Dibromobenzene **1** (2.56 mL, 5.00 g, 21.2 mmol, 1.00 equiv) was added dropwise within 15 min at this temperature and stirring was continued for 2 h. A solution of I_2 (5.58 g, 22.0 mmol, 1.04 equiv) in anhydrous THF (9 mL) was added, the cooling bath was removed, and the mixture was stirred for 15 h at rt. Aqueous $Na_2S_2O_3$ solution (10%; 50 mL) was added and the mixture was extracted with Et_2O (3×50 mL). The combined organic layers were dried ($MgSO_4$), concentrated at reduced pressure, and recrystallized from EtOH/H_2O (25:1; ca. 27 mL) to yield **2** as colorless crystalline platelets (5.41 g, 15.0 mmol, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.55 (d, ^3J = 8.0 Hz, 2 H, 2×ArH), 7.08 (d, ^3J = 8.0 Hz, 1 H, ArH). The NMR data are in full agreement with published data.[21]

2,6-Dibromo-1,1'-biphenyl (3)

By Suzuki coupling: $PdCl_2(PPh_3)_2$ (78 mg, 111 μmol, 0.01 equiv) was added under an argon atmosphere to a degassed (ultrasonication for 15 min) solution of iodide **2** (4.00 g, 11.1 mmol, 1.00 equiv), $PhB(OH)_2$ (1.42 g, 11.6 mmol, 1.05 equiv), and Na_2CO_3 (2.34 g, 22.1 mmol, 1.99 equiv) in THF/H_2O (1:1; 80 mL). The solution was stirred for 15 h at 80 °C and cooled to rt, half-concentrated brine (160 mL) was added, and the mixture was extracted with EtOAc (3×80 mL). The combined organic layers were dried (Na_2SO_4), concentrated at reduced pressure, and purified by column chromatography (silica gel, hexane) to yield **3** as a colorless solid (2.97 g, 9.52 mmol, 86%).

By Negishi coupling: Following a published protocol,[20] BuLi (2.5 M in hexane; 4.3 mL, 10.8 mmol, 1.02 equiv) was added dropwise within 10 min under an argon atmosphere to a cooled (−78 °C) solution of iPr_2NH (1.49 mL, 1.08 g, 10.7 mmol, 1.00 equiv) in anhydrous THF (40 mL). The mixture was stirred for 15 min and dibromobenzene **1** (1.28 mL, 2.50 g, 10.6 mmol, 1.00 equiv) was added dropwise within 15 min. Stirring was continued for 2 h at this temperature and $ZnCl_2$ (1.73 g, 12.7 mmol, 1.20 equiv) was added with positive argon pressure. The mixture was stirred for a further 30 min and warmed within 1 h to rt. PhI (1.20 mL, 2.16 g, 10.6 mmol,1.00 equiv) and $Pd(PPh_3)_4$ (612 mg, 530 μmol, 0.05 equiv) were added and stirring was continued for 15 min. Saturated aqueous NH_4Cl solution (10%; 20 mL) was added and the mixture was extracted with Et_2O (3×40 mL). The combined organic layers were dried ($MgSO_4$), concentrated at reduced pressure, and purified by column chromatography (silica gel, hexane) to yield **3** as a colorless solid (1.02 g, 3.27 mmol, 31%). R_f = 0.50 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.64 (d, ^3J = 8.0 Hz, 2 H, 2×ArH), 7.50–7.39 (m, 3 H, 3×ArH), 7.24–7.20 (m, 2 H, 2×ArH), 7.07 (t, ^3J = 8.0 Hz, 1 H, ArH). The NMR data are in full agreement with published data.[35]

2-Azido-6-bromo-1,1'-biphenyl (4)

BuLi (2.5 M in hexane; 3.5 mL, 8.75 mmol, 1.09 equiv) was added dropwise within 10 min under an argon atmosphere to a cooled (−78 °C) solution of biphenyl **3** (2.50 g, 8.01 mmol, 1.00 equiv) in anhydrous THF (65 mL). Stirring was continued for 1 h and a solution of $TosN_3$[36] (1.74 g, 8.82 mmol, 1.10 equiv) in anhydrous THF (15 mL) was added dropwise. The solution was warmed to rt within 15 h, saturated aqueous NH_4Cl solution (60 mL) was added, and the mixture was extracted with EtOAc (3×60 mL). The combined organic layers were washed with H_2O (60 mL) and brine (60 mL), dried ($MgSO_4$), concentrated at reduced pressure, and purified by column chromatography (silica gel hexane) to yield **4** as a pale yellow oil (1.46 g, 5.33 mmol, 67%). R_f = 0.40 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.48–7.41 (m, 4 H, 4×ArH), 7.25–7.17 (m, 4 H, 4×ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 140.0 (C_q), 137.4 (C_q), 134.7 (C_q), 130.0 (2×CH), 129.7 (CH), 129.1 (CH), 128.3 (CH), 128.3 (2×CH), 125.5 (C_q), 117.7 (CH); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3056 (w), 2136 (w), 2095 (s), 1558 (m), 1450 (w), 1429 (s), 1291 (s), 1159 (w), 1116 (w), 1072 (w), 1007 (w); MS (FAB): *m/z* (%) = 273.1 (5) $[M]^+$, 245.1 (10) $[M–N_2]^+$, 166.1 (100) $[M–N_2Br]^+$; HRMS: *m/z* calcd. for $C_{12}H_8{}^{79}BrN_3$ $[M]^+$: 272.9896, found: 272.9894.

6-Bromo-[1,1'-biphenyl]-2-amine (5)

Pd/C (10%; 143 mg, i.e., 14.3 mg Pd) was added to a solution of azide **4** (1.41 g, 5.14 mmol, 1.00 equiv) in EtOAc (10 mL) and an H_2-filled balloon was attached. The slurry was stirred for 17 h at rt until completion of the reaction (as monitored by TLC) and filtered over celite. The filtrate was concentrated at reduced pressure to yield **5** as a brown solid (1.19 g, 4.80 mmol, 93%) containing minor amounts of impurities. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.52–7.43 (m, 3 H, 3×ArH), 7.31–7.26 (m, 2 H, 2×ArH), 7.08 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 1 H, ArH), 7.01 (t, ^3J = 7.9 Hz, 1 H, ArH), 6.71 (dd, ^3J = 7.9 Hz, ^4J = 1.2 Hz, 1 H, ArH), 3.53 (bs, 2 H, NH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 145.7 (C_q), 138.1 (C_q), 130.1 (2×CH), 129.5 (CH), 129.2 (2×CH), 128.2 (C_q), 128.1 (CH), 124.6 (C_q), 122.3 (CH), 114.1 (CH); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3377 (w), 1608 (m), 1559 (w), 1461 (m), 1436 (w), 1290 (w), 1006 (w), 872 (w), 764 (w), 730 (w), 701 (m), 566 (w); MS (FAB): *m/z* (%) = 249.0 (100) $[M]^+$, 247.0 (97) $[M]^+$, 225.2 (15), 169.1 (52) $[M–Br]^+$; HRMS: *m/z* calcd. for $C_{12}H_{10}{}^{79}BrN$ $[M]^+$: 246.9991, found: 246.9991.

N-(6-Bromo-[1,1'-biphenyl]-2-yl)butanamide (6)

A solution of butanoyl chloride (1.99 mL, 2.04 g, 19.2 mmol, 4.00 equiv) in anhydrous THF (8 mL) was added dropwise within 15 min to a cooled (0 °C) solution of amine **5** (1.19 g, 4.80 mmol, 1.00 equiv) and Et_3N (1.90 mL, 1.38 g, 13.6 mmol, 2.83 equiv) in anhydrous THF (40 mL). Stirring was continued for 15 h at rt, H_2O (150 mL) was added, and the mixture was extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were washed with 1 M NaOH (50 mL), H_2O (50 mL), and brine (50 mL), dried ($MgSO_4$), concentrated at reduced pressure, and purified by column chromatography (silica gel, CH_2Cl_2) to yield **6** as a light brown solid (1.42 g, 4.46 mmol, 93%). R_f = 0.2 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.35 (d, ^3J = 8.3 Hz, 1 H, ArH), 7.55–7.52 (m, 2 H, 2×ArH), 7.50–7.47 (m, 1 H, ArH), 7.43–7.41 (m, 1 H, ArH), 7.26–7.22 (m, 3 H, 3×ArH), 6.79 (bs, 1 H, NH), 2.06 (t, ^3J = 7.4 Hz, 2 H, CH_2), 1.48 (sext, ^3J = 7.4 Hz, 2 H, CH_2), 0.84 (t, ^3J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 171.1 (CO), 137.2 (C_q), 136.9 (C_q), 132.3 (C_q), 129.9 (2×CH), 129.7 (CH), 129.4 (2×CH), 128.9 (CH), 127.95 (CH), 123.7 (C_q), 119.7 (CH), 39.9 (CH_2), 18.8 (CH_2), 13.7 (CH_3); IR (ATR): $\tilde{\nu}$ (cm^{-1}) 3256 (w), 2962 (w), 1649 (m), 1556 (w), 1513 (m), 1433 (m), 1358 (w), 1282 (w), 1197 (w), 1173 (w), 1129 (w), 1070 (w), 1007 (w), 963 (w), 917 (w), 866 (w), 812 (w), 775 (w), 759 (m), 739

(w), 695 (m), 622 (w), 553 (w); MS (FAB): *m/z* (%) = 318.1 (100) $[M+1]^+$, 249.0 (24) $[M–C_4H_5O]^+$, 169.1 (14); HRMS: *m/z* calcd. for $C_{16}H_{17}{}^{79}BrNO$ $[M+1]^+$: 318.0488, found: 318.0490.

N-(2-Bromophenyl)butanamide (8)

A solution of butanoyl chloride (4.81 mL, 4.94 g, 46.4 mmol, 4.00 equiv) in anhydrous THF (20 mL) was added dropwise within 15 min to a cooled (0 °C) solution of aniline **7** (2.00 g, 11.6 mmol, 1.00 equiv) and Et_3N (4.60 mL, 3.33 g, 32.9 mmol, 2.83 equiv) in anhydrous THF (100 mL). Stirring was continued for 15 h at rt, H_2O (360 mL) was added, and the mixture was extracted with CH_2Cl_2 (3×120 mL). The combined organic layers were washed with 1 M NaOH (120 mL), H_2O (120 mL), and brine (120 mL), dried ($MgSO_4$), concentrated at reduced pressure, and purified by column chromatography (silica gel, hexane/EtOAc, 4:1) to yield **8** as a pale yellow solid (2.58 g, 10.7 mmol, 92%). R_f = 0.45 (hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.37 (d, ^3J = 8.3 Hz, 1 H, ArH), 7.62 (bs, 1 H, NH), 7.53 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 1 H, ArH), 7.31 (td, ^3J = 7.9, ^4J = 1.5 Hz, 1 H, ArH), 6.97 (td, ^3J = 7.7, ^4J = 1.6 Hz, 1 H, ArH), 2.41 (t, ^3J = 7.5 Hz, 2 H, CH_2), 1.79 (sext, ^3J = 7.4 Hz, 2 H, CH_2), 1.04 (t, ^3J = 7.4 Hz, 3 H, CH_3). The NMR data are in full agreement with published data.[37]

N-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl] butanamide (9)

Bromide **8** (1.00 g, 4.13 mmol, 1.00 equiv), B_2pin_2 (1.15 g, 4.53 mmol, 1.10 equiv), and KOAc (1.01 g, 10.3 mmol, 2.50 equiv) were placed in a flask and the mixture was degassed by three cycles of evacuation for 10 min and refilling with argon. Anhydrous dioxane (20 mL) was added and the mixture was degassed by ultrasonication for 15 min. Pd(dppf)Cl_2·CH_2Cl_2 (270 mg, 330 μmol, 0.08 equiv) was added, the mixture was stirred for 15 h at 85 °C and cooled to rt. EtOAc (40 mL) was added and the mixture was filtered over celite. The filtrate was concentrated at reduced pressure and purified by column chromatography (silica gel, CH_2Cl_2/EtOAc, 10:1) to yield **9** as a colorless solid (595 mg, 2.06 mmol, 50%). Traces of pinacol were removed in high vacuum at 60 °C. R_f = 0.2 (CH_2Cl_2/EtOAc, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.97 (bs, 1 H, NH), 8.15 (d, ^3J = 8.3 Hz, 1 H, ArH), 7.73 (dd, ^3J = 7.5 Hz, ^4J = 1.7 Hz, 1 H, ArH), 7.40–7.33 (m, 1 H, ArH), 7.12–7.05 (m, 1 H, ArH), 2.22 (t, ^3J = 7.5 Hz, 2 H, CH_2), 1.76–1.69 (m, 2 H, CH_2), 1.37 (s, 12 H, 4×CH_3), 0.97 (t, ^3J = 7.4 Hz, 3 H, CH_3). The NMR data are in full agreement with published data.[23]

N,N'-([1,1':2',1''-Terphenyl]-2,3'-diyl)dibutanamide (10)

Following a published protocol,[24d] $Pd(OAc)_2$ (23 mg, 100 μmol, 0.07 equiv) and SPhos (86 mg, 210 μmol, 0.15 equiv) were added to a degassed (ultrasonication for 15 min) solution of bromide **6** (439 mg, 1.38 mmol, 1.00 equiv), boronate **9** (520 mg, 1.80 mmol, 1.30 equiv), and Cs_2CO_3 (1.35 g, 4.14 mmol, 3.00 equiv) in dioxane (30 mL) and H_2O (5 mL). The mixture was stirred for 15 h at 80 °C and cooled to rt. Half-concentrated brine (35 mL) was added and the mixture was extracted with EtOAc (3×35 mL). The combined organic layers were dried (Na_2SO_4), concentrated at reduced pressure, and purified by column chromatography (silica gel, hexane/EtOAc, 3:2; then silica gel, CH_2Cl_2/MeOH, 50:1) to yield **10** as a colorless solid (467 mg, 1.17 mmol, 85%). R_f = 0.4 (hexane /EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.46 (d, ^3J = 8.3 Hz, 1 H, ArH), 8.12 (d, ^3J = 8.3 Hz, 1 H, ArH), 7.48 (t, ^3J = 7.9 Hz, 1 H, ArH), 7.28–7.20 (m, 3 H, ArH and/or NH), 7.18–6.86 (m, 8 H, ArH and/or NH), 2.16–2.09 (m, 4 H, 2×CH_2), 1.65–1.49 (m, 4 H, 2×CH_2), 0.95–0.85 (m, 6 H, 2×CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 171.3 (CO), 170.8 (CO), 137.6 (C_q), 136.3 (C_q), 135.2 (C_q), 135.2 (C_q), 131.8 (C_q), 130.7 (CH), 130.6 (CH), 130.5 (C_q), 129.3 (CH), 129.0 (CH), 129.0 (CH), 128.9 (CH), 128.3 (CH), 128.3 (CH), 125.9 (CH), 123.3 (CH), 121.3 (CH), 120.5 (CH), 40.0 (CH_2), 39.9 (CH_2), 19.0 (CH_2), 18.9 (CH_2), 13.8 (CH_3), 13.7 (CH_3); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1679 (w), 1515 (w), 1172 (w), 808 (w), 752 (w), 707 (w); MS (FAB): *m/z* (%) = 401.3 (100) $[M+1]^+$, 331.3 (96), 261.2 (40); HRMS: *m/z* calcd. for $C_{26}H_{29}N_2O_2$ $[M+1]^+$: 401.2224, found: 401.2222.

6,10-Dipropyl-5,9-diaza[5]helicene, 6,10-Dipropyldibenzo [*a*,*k*][3,7]phenanthroline (11)

Following a published protocol,[23] terphenyl **10** (60 mg, 150 μmol, 1.00 equiv), P_4O_{10} (553 mg, 1.95 mmol, 13.0 equiv), and $POCl_3$ (17 mL) were placed under an argon atmosphere in a pressure vial and heated to 110 °C for 16 h. The mixture was cooled to rt, H_2O (2 mL) was added dropwise, and the mixture was poured in portions into ice-cooled 5 M NaOH (300 mL). The precipitate was collected by filtration, dissolved in CH_2Cl_2 (30 mL), washed with H_2O (2×30 mL), dried ($MgSO_4$), concentrated at reduced pressure, and purified by column chromatography (silica gel, hexane/EtOAc, 4:1) to yield **11** as a pale yellow solid (18 mg, 49 μmol, 33%). R_f = 0.13 (hexane/EtOAc, 8:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.56 (d, ^3J = 8.4 Hz, 1 H, ArH), 8.38 (dd, ^3J = 8.4 Hz, ^4J = 1.3 Hz, 1 H, ArH), 8.31 (d, ^3J = 8.8 Hz, 1 H, ArH), 8.28 (dd, ^3J = 8.2 Hz, ^4J = 1.3 Hz, 1 H, ArH), 8.18 (dd, ^3J = 8.3 Hz, ^4J = 1.3 Hz, 1 H, ArH), 8.14 (d, ^3J = 8.7 Hz, 1 H, ArH), 7.68–7.60 (m, 2 H, 2×ArH), 7.52–7.46 (m, 1 H, ArH), 7.29–7.24 (m, 1 H, ArH), 3.56–3.35 (m, 4 H, 2×CH_2), 2.12–1.97 (m, 4 H, 2×CH_2), 1.17 (t, J = 7.3 Hz, 6 H, 2×CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 164.1 (C_q), 161.7 (C_q), 145.8 (C_q), 144.6 (bs, C_q, clearly visible only in an HMBC spectrum), 133.6 (C_q), 131.1 (C_q), 129.2 (CH), 128.9 (CH), 128.7 (CH), 128.5 (CH), 128.0 (CH), 127.7 (CH), 127.6 (CH), 125.8 (CH), 125.5 (CH), 125.4 (C_q), 124.9 (C_q), 124.4 (CH), 124.3 (C_q), 119.3 (C_q), 38.7 (CH_2), 38.2 (CH_2), 23.6 (CH_2), 23.0 (CH_2), 14.6 (2×CH_3); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2956 (w), 1573 (w), 1374 (w), 757 (w); UV/Vis (CH_2Cl_2): λ_{max} (nm) [ε] = 262 [29800], 299 [28600], 329 [shoulder, 13600], 355 [shoulder, 2400], 372 [2200], 393 [2200]; MS (FAB): *m/z* (%) = 447.4 (33), 365.3 (100) $[M+1]^+$; HRMS: *m/z* calcd. for $C_{26}H_{25}N_2$ $[M+1]^+$: 365.2012, found: 365.2011.

4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (12)

Following a published protocol,[38] BuLi (2.5 M in hexane; 12.6 mL, 31.4 mmol, 1.30 equiv) was added dropwise within 10 min under an argon atmosphere to a cooled (−78 °C) solution of 1-bromonaphthalene (5.00 g, 24.1 mmol, 1.00 equiv) in anhydrous THF (56 mL) and the mixture was stirred for 1 h at this temperature. iPrOBpin (6.40 mL, 5.84 g, 31.4 mmol, 1.30 equiv) was added dropwise within 10 min, the cooling bath was removed, and the mixture was stirred for 15 h at rt. H_2O (50 mL) and saturated aqueous NH_4Cl solution (50 mL) were added, the layers were separated, and the aqueous layer was extracted with EtOAc (2×50 mL). The combined organic layers were dried (Na_2SO_4), concentrated at reduced pressure, and purified by column chromatography (silica gel, hexane/EtOAc, 10:3) to yield **12** as a colorless solid (5.67 g, 22.3 mmol, 93%) containing traces of pinacol. R_f = 0.32 (hexane/EtOAc, 8:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.77 (d, ^3J = 8.4 Hz, 1 H, ArH), 8.11–8.05 (m, 1 H, ArH), 7.94 (d, ^3J = 8.2 Hz, 1 H, ArH), 7.84 (d, ^3J = 8.0 Hz, 1 H, ArH), 7.54 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1 H, ArH), 7.48 (t, ^3J = 7.5 Hz, 2 H, 2×ArH), 1.43 (s, 12 H, 4×CH_3). The NMR data are in full agreement with published data.[38]

1-(2,6-Dibromophenyl)naphthalene (13)

Following a published protocol,[39] $Pd(PPh_3)_4$ (1.28 g, 1.11 mmol, 0.10 equiv) was added under an argon atmosphere to a degassed (ultrasonication for 15 min) solution of iodide **2** (4.00 g, 11.1 mmol, 1.00 equiv), boronate **12** (2.82 g, 11.1 mmol, 1.00 equiv), and $LiOH{\cdot}H_2O$ (1.86 g, 44.3 mmol, 4.00 equiv) in MeCN (280 mL) and H_2O (28 mL). The mixture was heated to 80 °C for 15 h and cooled to rt. Half-saturated brine (40 mL) and EtOAc (50 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (3×30 mL) and the combined organic layers were dried (Na_2SO_4), concentrated at reduced pressure, and purified by column chromatography (silica gel, hexane) to yield **13** as a colorless solid (1.84 g, 5.08 mmol, 46%). R_f = 0.43 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.96–7.92 (m, 2 H, 2×ArH), 7.72 (d, ^3J = 8.0 Hz, 2 H, 2×ArH), 7.58 (dd, ^3J = 8.3 Hz, ^3J = 7.1 Hz, 1 H, ArH), 7.51 (ddd, ^3J = 8.1 Hz, ^3J = 6.7 Hz, ^4J = 1.3 Hz, 1 H, ArH), 7.49–7.43 (m, 1 H, ArH), 7.35–7.32 (m, 2 H, 2×ArH), 7.18 (t, ^3J = 8.0 Hz, 1 H, ArH). The NMR data are in full agreement with published data.[39]

1-(2-Azido-6-bromophenyl)naphthalene (14)

BuLi (2.5 M in hexane; 0.80 mL, 2.00 mmol, 1.20 equiv) was added dropwise within 10 min under an argon atmosphere to a cooled (−78 °C) solution of dibromide **13** (600 mg, 1.66 mmol, 1.00 equiv) in anhydrous THF (14 mL) and stirring was continued for 1 h at that temperature. A solution of $TosN_3$ (360 mg, 1.83 mmol, 1.10 equiv) in anhydrous THF was added, the mixture was warmed to rt within 15 h, and saturated aqueous NH_4Cl solution (20 mL) was added. The mixture was extracted with EtOAc (3×20 mL) and the combined organic layers were washed with H_2O (30 mL) and brine (30 mL), dried ($MgSO_4$), concentrated at reduced pressure, and purified by column chromatography (silica gel, hexane) to yield **14** as a pale yellow oil (365 mg, 1.13 mmol, 68%). R_f = 0.31 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.98–7.92 (m, 2 H, 2×ArH), 7.61–7.49 (m, 3 H, 3×ArH), 7.43 (td, ^3J = 7.6 Hz, ^3J = 6.8 Hz, ^4J = 1.3 Hz, 1 H, ArH), 7.38–7.31 (m, 3 H, 3×ArH), 7.29–7.25 (m, 1 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 140.9 (C_q), 135.3 (C_q), 133.6 (C_q), 133.0 (C_q), 131.6 (C_q), 130.1 (CH), 129.0 (CH), 128.9 (CH), 128.7 (CH), 127.7 (CH), 126.6 (CH), 126.5 (C_q), 126.2 (CH), 125.4 (CH), 125.2 (CH), 117.6 (CH); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3052 (w), 2095 (s), 1561 (m), 1433 (m), 1392 (m), 1292 (s), 1102 (m), 839 (w), 799 (m), 774 (s), 737 (m), 708 (m), 484 (w); MS (FAB): *m/z* (%) = 323.1 (14) $[M]^+$, 295.0 (16) $[M–N_2]^+$, 217.1 (38) $[M–N_2Br]^+$, 154.1 (100) [3-NBA; matrix]; HRMS: *m/z* calcd. for $C_{16}H_{10}{}^{79}BrN_3$ $[M]^+$: 323.0053, found: 323.0052.

3-Bromo-2-(naphthalen-1-yl)aniline (15)

Pd/C (10%; 35 mg, i.e., 3.5 mg Pd) was added to a solution of azide **14** (300 mg, 925 µmol, 1.00 equiv) in EtOAc (2 mL) and an H_2-filled balloon was attached. The slurry was stirred for 17 h at rt until completion of the reaction (as monitored by TLC) and filtered over celite. The filtrate was concentrated at reduced pressure to yield **15** as a brown solid (244 mg, 818 µmol, 88%) containing minor amounts of impurities. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.94–7.92 (m, 2 H, 2×ArH), 7.59 (dd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, 1 H, ArH), 7.52 (dd, ^3J = 7.9 Hz, ^3J = 6.3 Hz, 2 H, 2×ArH), 7.45–7.41 (m, 2 H, 2×ArH), 7.16 (d, ^3J = 7.9 Hz, 1 H, ArH), 7.11 (t, ^3J = 7.9 Hz, 1 H, ArH), 6.80–6.79 (m, 1 H, ArH), 3.62 (bs, 2 H, NH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 146.1 (C_q), 135.6 (C_q), 134.1 (C_q), 131.5 (C_q), 129.9 (CH), 128.8 (CH), 128.6 (CH), 128.1 (CH), 126.8 (CH), 126.4 (CH), 126.2 (C_q), 126.1 (CH), 125.6 (C_q), 125.2 (CH), 122.5 (CH), 114.3 (CH); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3385 (w), 1606 (w), 1558 (w), 1504 (w), 1441 (w), 1391 (w), 1292 (w), 1037 (w), 1015 (w), 959 (w), 879 (w), 863 (w), 801 (w), 776 (m), 736 (w), 641 (w); MS (FAB): *m/z* (%) = 299.1 (100) $[M]^+$, 219.1 (70) $[M–Br]^+$; HRMS: *m/z* calcd. for $C_{16}H_{12}N^{79}Br$ $[M]^+$: 297.0148, found: 297.0150.

N-[3-Bromo-2-(naphthalen-1-yl)phenyl]butanamide (16)

A solution of butanoyl chloride (0.29 mL, 298 mg, 2.80 mmol, 4.00 equiv) in anhydrous THF (13 mL) was added dropwise within 15 min to a cooled (0 °C) solution of amine **15** (210 mg, 704 µmol, 1.00 equiv) and Et_3N (0.28 mL, 203 mg, 2.01 mmol, 2.86 equiv) in anhydrous THF (7 mL). Stirring was continued for 15 h at rt, H_2O (60 mL) was added, and the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with 1 M NaOH (20 mL), H_2O (20 mL), and brine (20 mL), dried ($MgSO_4$), concentrated at reduced pressure, and purified by column chromatography (silica gel, hexane/EtOAc, 4:1; then silica gel, CH_2Cl_2) to yield **16** as a light brown solid (160 mg, 434 µmol, 62%). R_f = 0.22 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.43 (d, ^3J = 8.3 Hz, 1 H, ArH), 8.00 (d, ^3J = 8.3 Hz, 1 H, ArH), 7.96 (d, ^3J = 8.2 Hz, 1 H, ArH), 7.62 (dd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, 1 H, ArH), 7.56–7.50 (m, 2 H, 2×ArH), 7.46–7.32 (m, 4 H, 4×ArH), 6.62 (s, 1 H, NH), 1.90–1.79 (m, 2 H, CH_2), 1.28–1.15 (m, 2 H, CH_2), 0.61 (t, ^3J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 171.1 (CO), 137.9 (C_q), 134.2 (C_q), 134.0 (C_q), 131.3 (C_q), 130.4 (C_q), 130.0 (CH), 129.5 (CH), 128.7 (CH), 128.2 (CH), 128.1 (CH), 127.3 (CH), 126.8 (CH), 125.9 (CH), 125.0 (CH), 124.7 (C_q), 119.8 (CH), 39.6 (CH_2), 18.6 (CH_2), 13.3 (CH_3); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3410 (w), 2960 (w), 1683 (m), 1566 (s), 1502 (s), 1443 (s), 1388 (m), 1287 (m), 1171 (m), 1077 (m), 801 (m), 776 (s), 741 (m), 576 (m), 471 (w); MS (FAB): *m/z* (%) = 368.1 (100) $[M+1]^+$, 297.0 (25) $[M–C_4H_5O]^+$, 218.1 (14) $[M–C_4H_7OBr]^+$; HRMS: *m/z* calcd. for $C_{20}H_{19}{}^{79}BrNO$ $[M+1]^+$: 368.0645, found: 368.0646.

N,*N*'-{2'-(Naphthalen-1-yl)-[1,1'-biphenyl]-2,3'-diyl}dibutanamide (17)

Following a published protocol,[24d] $Pd(OAc)_2$ (6 mg, 27 µmol, 0.08 equiv) and SPhos (22 mg, 54 µmol, 0.16 equiv) were added to a degassed (ultrasonication for 15 min) solution of bromide **16** (126 mg, 342 µmol, 1.00 equiv), boronate **9** (129 mg, 446 µmol, 1.30 equiv), and Cs_2CO_3 (335 mg, 1.03 mmol, 3.00 equiv) in dioxane (6 mL) and H_2O (1 mL). The mixture was stirred for 15 h at 80 °C and cooled to rt. Half-concentrated brine (7 mL) was added and the mixture was extracted with EtOAc (3×7 mL). The combined organic layers were dried (Na_2SO_4), concentrated at reduced pressure, and purified by column chromatography (silica gel, hexane/EtOAc, 2:1; then silica gel, CH_2Cl_2/MeOH, 50:1) to yield **17** as a colorless solid (127 mg, 282 µmol, 82%). **17** was obtained as a mixture of rotamers not analyzable with NMR spectroscopy. R_f = 0.35 (hexane/EtOAc, 4:1); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2960 (w), 1658 (w), 1579 (w), 1509 (m), 1459 (w), 1439 (w), 1387 (w), 1283 (w), 1184 (w), 1074 (w), 803 (w), 779 (w), 753 (m), 542 (w), 495 (w); MS (FAB): *m/z* (%) = 451.3 (100) $[M+1]^+$, 381.3 (63) $[M–C_4H_5O]^+$, 311.2 (68) $[M–2×C_4H_5O]$; HRMS: *m/z* calcd. for $C_{30}H_{31}N_2O_2$ $[M+1]^+$: 451.2380, found: 451.2378.

6,10-Dipropyl-5,9-diaza[6]helicene, 2,6-Dipropylbenzo[*a*]naphtho[2,1-*k*][3,7]phenanthroline (18)

Following a published protocol,[23] terphenyl **17** (200 mg, 444 µmol, 1.00 equiv), P_4O_{10} (2.20 g, 7.75 mmol, 17.5 equiv), and $POCl_3$ (67 mL) were placed under an argon atmosphere in a pressure vial and heated to 110 °C for 16 h. The mixture was cooled to rt, H_2O (10 mL) was added dropwise, and the mixture was poured in portions into ice-cooled 5 M NaOH (890 mL). The precipitate was collected by filtration, dissolved in CH_2Cl_2 (100 mL), washed with H_2O (2×50 mL), dried ($MgSO_4$), concentrated at reduced pressure, and purified by column chromatography (silica gel, hexane/EtOAc, 8:1) to yield **18**

as a pale yellow solid (50 mg, 121 μmol, 27%). R_f = 0.16 (hexane/EtOAc, 8:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.46 (d, ^3J = 8.8 Hz, 1 H, ArH), 8.28 (d, ^3J = 8.7 Hz, 1 H, ArH), 8.26 (d, ^3J = 8.9 Hz, 1 H, ArH), 8.08–8.05 (m, 2 H, 2×ArH), 7.90 (dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz, 1 H, ArH), 7.66 (d, ^3J = 8.5 Hz, 1 H, ArH), 7.42–7.34 (m, 2 H, 2×ArH), 7.30 (dd, ^3J = 8.5 Hz, ^4J = 1.3 Hz, 1 H, ArH), 6.84 (ddd, ^3J = 8.4 Hz, ^3J = 6.8 Hz, ^4J = 1.3 Hz, 1 H, ArH), 6.69 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.4 Hz, 1 H, ArH), 3.59–3.47 (m, 4 H, 2×CH_2), 2.19–2.03 (m, 4 H, 2×CH_2), 1.24 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.20 (t, ^3J = 7.3 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 163.2 (C_q), 161.6 (C_q), 146.8 (C_q), 144.2 (bs, C_q, clearly visible only in an HMBC spectrum), 133.2 (C_q), 132.9 (C_q), 132.3 (C_q), 129.1 (CH), 128.9 (CH), 128.8 (CH), 128.8 (CH), 128.5 (C_q), 128.1 (CH), 127.9 (CH), 127.8 (CH), 126.9 (CH), 126.0 (CH), 125.9 (CH), 124.5 (CH), 124.2 (C_q), 124.0 (C_q), 123.3 (C_q), 121.9 (CH), 116.6 (C_q), 38.9 (CH_2), 38.5 (CH_2), 23.5 (CH_2), 23.4 (CH_2), 14.7 (CH_3), 14.7 (CH_3); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2957 (w), 1566 (w), 1484 (w), 1451 (w), 1377 (w), 1308 (w), 1237 (w), 804 (w), 752 (m), 649 (w), 611 (w); UV/Vis (CH_2Cl_2): λ_{max} (nm) [ε] = 270 [shoulder, 32400], 300 [shoulder, 24000], 310 [25900], 323 [shoulder, 22200], 344 [shoulder, 14100], 370 [shoulder, 2800], 390 [3100], 412 [3600]; MS (FAB): *m/z* (%) = 415.3 (100) $[M+1]^+$; HRMS: *m/z* calcd. for $C_{30}H_{27}N_2$ $[M+1]^+$: 415.2169, found: 415.2168.

Supporting Information

The authors have cited additional references within the Supporting Information.[40–49]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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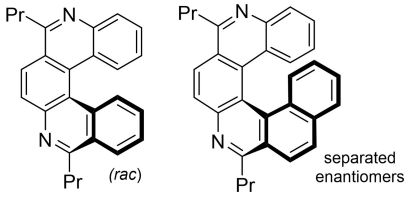

5,9-Diaza[5]- and -[6]helicenes were synthesized by *ortho*,*ortho'* fusion of *ortho*-teraryls. The [6]helicene could be resolved in its enantiomers. Photophysical properties of both compounds were determined by measurements and calculations.

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Synthesis of 5,9-Diaza Analogues of [5]- and [6]Helicene and their Chiroptic and Photophysical Characterization