

Five-fold Symmetric Pentaindolo- and Pentakis(benzoindolo)-Corannulenes: Unique Structural Dynamics Derived from the Combination of Helical- and Bowl-Inversions

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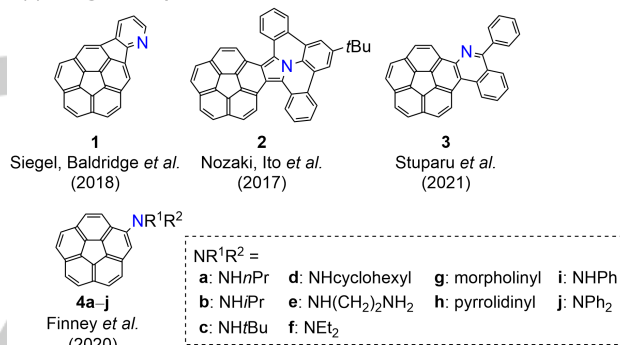
Abstract: Peripherally π -extended corannulenes bearing quintuple azahelicene units, **10** and **11**, were prepared and their dynamic behaviors were studied both experimentally and theoretically. The fused corannulenes were synthesized from sym-pentabromocorannulene in three steps, including Buchwald–Hartwig amination, Pd-catalyzed intramolecular C–H arylation, and *N*-methylation. X-Ray diffraction analysis for **10** displayed a conformer possessing a *P*(*M*) bowl chirality and a *PPMPM* (*PMPMM*) helical chirality, which was found to be the most stable conformer(s). Variable-temperature NMR measurements of **10** and **11** revealed that their structural isomers can be interconvertible in solution, depending on their steric congestion around the helical scaffolds. Automated search for conformers in the equilibrium and transition states by Artificial Force Induced Reaction (AFIR) method revealed their interconversion networks, including bowl-inversion and helical-inversion, the activation barriers of which were estimated to be 2.6–3.6 kcal·mol^{−1} and 9.8–26.9 kcal·mol^{−1}, respectively. These values are smaller than those of the pristine corannulene (12.5 kcal·mol^{−1}) and the corresponding azahelicenes (22.0 and 35.3 kcal·mol^{−1}), respectively. This analysis indicated that the co-existing corannulene and azahelicene moieties influence the conformational dynamics, which leads to mitigation of the activation energy barriers for isomerization.

Introduction

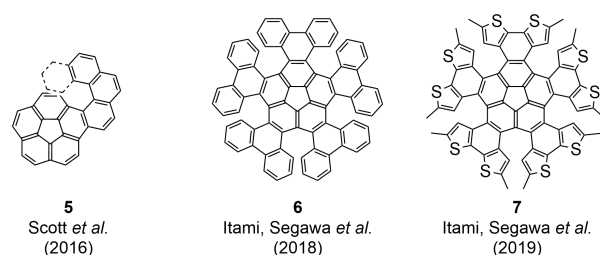
Corannulene (C₂₀H₁₀) is a bowl-shaped hydrocarbon, being a fragment of C₆₀.^[1] Corannulene and its peripherally substituted derivatives have been intensively studied over the years in the field of self-assembly,^[2] organic field-effect transistor (OFET),^[3] organic light emitter,^[4] metal-organic framework (MOF),^[5] and so forth. Corannulenes show characteristic conformational dynamics, which affect the key properties and play important roles in some of the above applications. Therefore, structural modifications of corannulene have also been an attractive area of research, which is getting recognized as an advantage of curved nanographenes.^[6–8] Despite such developments, peripherally heteroarene-fused corannulenes have been limited to azaindenocorannulene **1** reported by Siegel and Baldrige,^[8f] pyrrole-fused corannulene **2** reported by Nozaki and Ito,^[8d,g] and isoquinoline-fused corannulene **3** reported by Stuparu (Chart 1).^[8j] Even simple alkylamino- and arylamino-substituted corannulenes

4a–j have only recently been reported.^[8i] As seen in these examples, nitrogen-incorporation is an effective way for electronic tuning to deliver rich redox chemistry as well as optical response. Furthermore, due to the bowl-shaped 3D structure, azaindenocorannulene **1** is a chiral molecule whose CD and VCD spectra were analyzed both experimentally and theoretically.

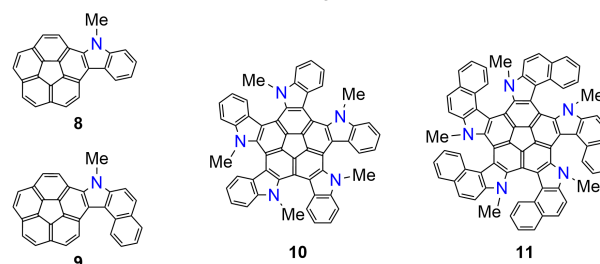
(a) Nitrogen-incorporated corannulenes



(b) Corannulene–Helicene hybrids



(c) This work: Corannulene–Azahelicene hybrids



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Chart 1. (a) Previous reports on nitrogen-incorporated corannulenes **1–4**, (b) corannulene–helicene hybrids **5–7**, and (c) corannulene–azahelicene hybrids **8–11**.

Motivated by these nitrogen-substituted corannulenes, we came up with an idea of the synthesis of azahelicene-incorporated corannulene. Helicenes are *ortho*-fused polycyclic aromatic hydrocarbons with helical structures originating from steric repulsion between the terminal aromatic rings.^[9] Corannulene–helicene hybrids **5** have been synthesized as rare skeletally chiral molecules possessing two kinds of chirality, *i.e.* chirality derived from the helical part and chirality derived from the bowl-shaped curvature.^[10b] Based on the racemization time profiles, their racemization barriers were evaluated, which suggested that bowl and helical chiralities mutually affect the inversion dynamics at the other site. Multiple helicene is another target of interest due to the enhancement of chiroptical properties and interconversion network among various metastable isomers.^[9g,10a,10c–f,11] Segawa and Itami reported quintuple helicenes **6** and **7** based on the corannulene scaffold.^[10c,d] Interestingly, the conformer observed by XRD analysis is a *PPPPP* (*MMMMM*) conformer for **6**,^[10c] but a *PPMPM* (*MMPMP*) conformer for **7** although a *C*₅ symmetric propeller-shaped conformer was predicted to be the most stable for **7**.^[10d] Because the inversion activation energies in **6** and **7** are high (>30 kcal·mol^{−1}) mainly due to the large steric congestion at the periphery, their dynamic behaviors are difficult to analyze in detail.

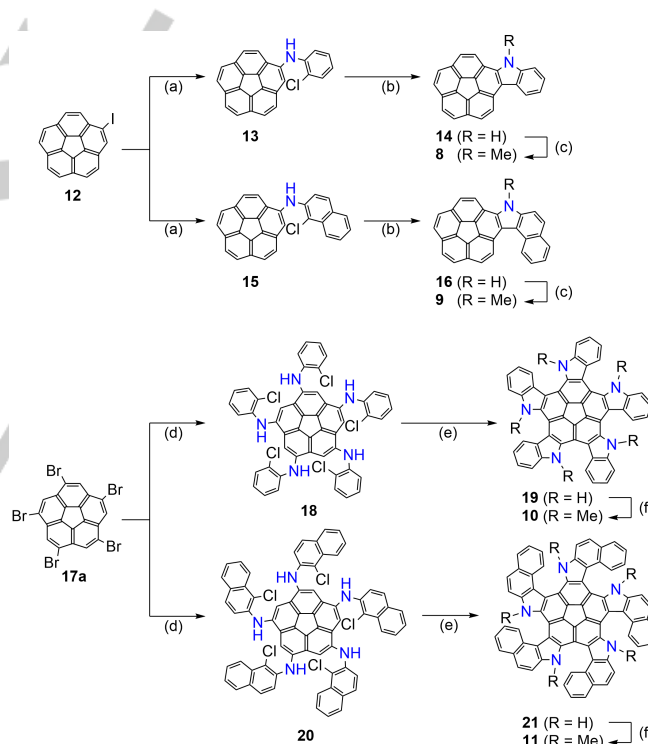
Here we report the synthesis of azahelicene-fused corannulenes **8** and **9**, and quintuply azahelicene-fused corannulenes **10** and **11** to investigate the electronic perturbation by nitrogen-incorporation and to show unique molecular dynamics. Detailed photophysical measurements, redox properties, crystallographic analyses of **8–11** are presented. A special focus will be placed on the unique structural aspects such as contorted geometries and interconversion networks among various structural isomers of **10** and **11**.

Results and Discussion

Synthesis: Recently, we reported the synthesis of *sym*-pentabromo- and *sym*-pentaiodocorannulenes, which opened up a door for unprecedented corannulene derivatives.^[12] Indeed, pentaphosphorylated corannulene was successfully prepared by a Pd-catalyzed cross-coupling reaction from 1,3,5,7,9-pentabromocorannulene (**17a**) or 1,3,5,7,9-pentaiodocorannulene (**17b**) in 31% and 82% yields, respectively. Before testing five-fold amination reactions of **17a**, first we conducted the amination reaction with monoiodocorannulene **12**,^[13] which afforded aminocorannulenes **13** and **15** in moderate yields (Scheme 1). Then, palladium-catalyzed intramolecular C–H arylation of **13** and **15** in the presence of a palladium catalyst and DBU under microwave heating^[14] gave **14** and **16** in 69% and 62% yields, respectively. The pyrrolic NH moiety of **14** and **16** was viable to be methylated to afford **8** and **9** in good yields, which are easier to handle due to the improved solubility compared with the N–H forms (**14** and **16**).

Next, we examined the five-fold peripheral amination reactions of **17a** under the same catalyst system (Pd(dppf)Cl₂·CH₂Cl₂, DPPF, NaOtBu), which afforded pentaaminated corannulenes **18** and **20** in 29% and quantitative yields, respectively. With **18** and **20** in

hand, five-fold intramolecular C–H arylation reactions were conducted, and fully fused products **19** and **21** were obtained after purification by filtration. Pentaindolocorannulene **19** was poorly soluble in common organic solvents, but was slightly soluble in DMSO and DMF. In the ¹H NMR spectrum of **19** in DMSO-*d*₆, a five-fold-symmetric signal pattern was observed; a broad singlet at 12.10 ppm for the five NH protons and multiplets at 7.59–9.22 ppm for the protons on fused-benzo moieties. On the other hand, pentakis(benzoindolo)corannulene **21** was hardly soluble in organic solvents and its characterization by NMR was difficult though the formation of **21** was indicated by mass spectrometry (Figure S36). To improve the solubility, *N*-methylation reactions of **19** and **21** were examined with sodium hydride and iodomethane to afford **10** and **11**. The two-step yields for **10** and **11** are 23% and 21%, respectively. The high-resolution mass spectrometry of **10** and **11** revealed their molecular ion peaks at *m/z* = 765.2892 (calculated for C₅₅H₄₅N₅ = 765.2898 [*M*][−]) and *m/z* = 1015.3675 (calculated for C₇₅H₃₅N₅ = 1015.3680 [*M*][−]). To the best of our knowledge, **10** and **11** are the first examples of PAHs containing five azahelicene moieties and this is the first use of 1,3,5,7,9-pentabromocorannulene **17a** as a key intermediate in multi-step syntheses.



Scheme 1. Synthesis of peripherally nitrogen-incorporated corannulenes. Conditions: (a) 2-chloroaniline (for **13**, 1.2 eq.) or 1-chloro-2-aminonaphthalene (for **15**, 1.2 eq.), Pd(dppf)Cl₂·CH₂Cl₂ (5 mol%), DPPF (15 mol%), NaOtBu (1.2 eq.), toluene, 110 °C, 18–24 h, 54% (for **13**) and 62% (for **15**); (b) Pd(PCy₃)₂Cl₂ (30 mol%), DBU (10 eq.), DMA, 250 °C (microwave), 1 h, 69% (for **14**) and 62% (for **16**); (c) CH₃I (50 eq.), NaH (50 eq.), DMF, 0 °C to RT, 1 h, 72% (for **8**) and 73% (for **9**); (d) 2-chloroaniline (for **18**, 10 eq.) or 1-chloro-2-aminonaphthalene (for **20**, 10 eq.), Pd(dppf)Cl₂·CH₂Cl₂ (5 mol%), DPPF (15 mol%), NaOtBu (6.0 eq.), toluene, 110 °C, 40–41 h, 29% (for **18**) and quant. (for **20**); (e) Pd(PCy₃)₂Cl₂ (150 mol%), DBU (50 eq.), DMA, 250 °C (microwave), 1 h; (f) CH₃I (100 eq.), NaH (100 eq.), DMF, 0 °C to RT, 1 h, 23% (for **10**, over 2 steps) and 21% (for **11**, over 2 steps).

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VT NMR measurements: The solubilities of **10** and **11** were drastically improved and well-soluble in halogenated solvents, enabling us to investigate their detailed conformational dynamics in solutions by NMR measurements. (Figure 1 and Figure S23–25) Similarly to **19**, **10** showed a symmetric ^1H NMR spectral pattern in CD_2Cl_2 at 30 °C. A singlet due to the methyl protons was observed at 4.39 ppm and doublets/triplets due to the protons on the fused benzo-scaffolds were observed in the range of 7.48–8.74 ppm. This observation, with the aid of literature information,^[15] suggests that helical-inversions at the peripheral aza[5]helicenes and bowl-inversion of the central corannulene scaffold occur faster than the NMR time scale. Upon cooling the temperature, the ^1H NMR signals became broadened. At –90 °C, we observed five broad singlets around 4.16–4.50 ppm and complicated broad signals in the range of 7.30–8.60 ppm, which indicates that the dynamic structural changes are slower than the NMR time scale at this temperature. On the other hand, pentakis(benzoindolo)corannulene **11** exhibited a C_1 -symmetric ^1H NMR signal pattern, including five singlets at 3.67–4.30 ppm due to the five methyl protons in 1,1,2,2-tetrachloroethane- d_2 at 30 °C (Figure 1b). Upon heating to 135 °C, the five singlets were merged into one broad singlet at 4.28 ppm that was assigned due to the methyl protons. Based on these VT NMR spectra, energy barriers for structural changes are considered to be higher for **11** than those for **10**, which is ascribable to the heavier steric congestion at the terminal azahelicene moiety in **11**. The distinct difference in the activation energy of the observed structural change indicates that this dynamic behavior corresponds mainly to the azahelicene-inversion process. Upon cooling to –90 °C, almost the same signal pattern was observed for **11** with slight signal broadening (Figure 1c). The line broadening was temperature-dependent as indicated by the full width of half maximum (FWHM) values (Figure S25c). This observation would be rationalized by the fast bowl-inversion even at low temperature, which is supported by quantum chemistry calculations (*vide infra*).

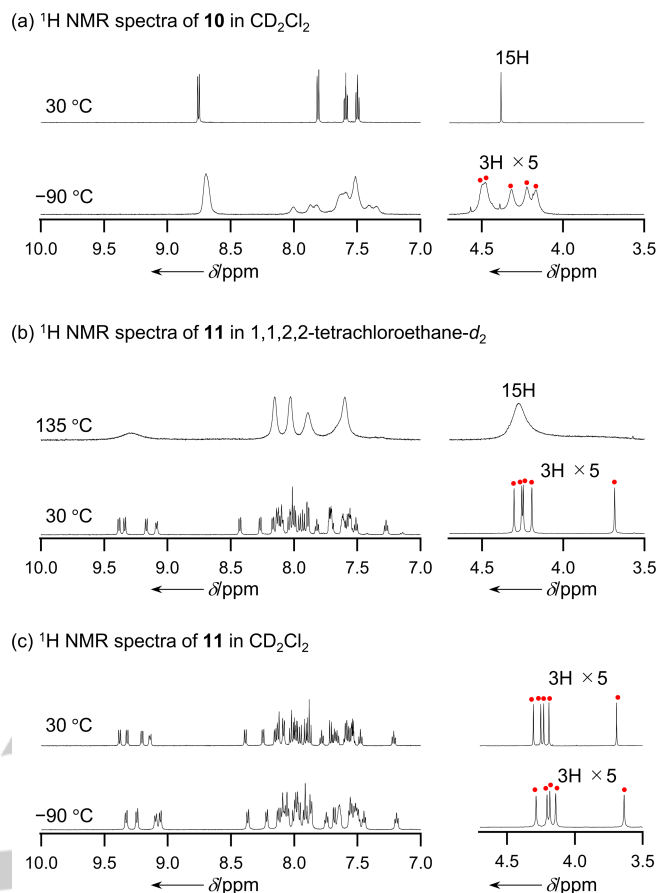


Figure 1. (a) ^1H NMR spectra of **10** in CD_2Cl_2 at 30 °C and –90 °C. (b) ^1H NMR spectra of **11** in 1,1,2,2-tetrachloroethane- d_2 at 30 °C and 135 °C. (c) ^1H NMR spectra of **11** in CD_2Cl_2 at 30 °C and –90 °C.

Photophysical properties: The UV/vis absorption and emission spectra of **8–11** are shown in Figure 2.^[16] The absorption edges of fused-corannulenes were more intense than that of the pristine corannulene ($\text{C}_{20}\text{H}_{10}$) as a consequence of the deformation of the structural symmetry and partially allowed HOMO–LUMO transitions (Figure S54–56 and Table S6–10). The absorption spectra of monoaminocorannulenes **4a–f** also exhibited weak absorption bands over 350 nm as seen in **8–11**. In addition, as the unique properties of monoaminocorannulenes **4a–f**, Finney *et al.* pointed out (1) enhanced fluorescence quantum yields^[17] in solution and (2) solid-state emission^[18]. Fused corannulenes **8–11** exhibit red-shifted fluorescence with more than 10 times larger quantum yields ($\Phi_{\text{F,DCM}} = 0.14\text{--}0.25$, DCM = CH_2Cl_2) compared to that of the pristine corannulene ($\Phi_{\text{F,DCM}} = 0.013$). This is in marked contrast to the case of carbohelicene–corannulene hybrid **6** ($\Phi_{\text{F,DCM}} = 0.03$). In addition, emissions of **8–11** were also detected in the solid-state (Figure 2c and Figure S41). While the quantum yields of **9–11** in the solid states ($\Phi_{\text{F,solids}} = 0.022\text{--}0.078$) are lower, the emission spectrum of **8** exhibited comparable efficiencies ($\Phi_{\text{F,solids}} = 0.16$ vs $\Phi_{\text{F,DCM}} = 0.17$). Among **8–11**, significantly red-shifted solid-state-emission of **9** at around 600 nm is considered to result from the stronger intermolecular interaction.^[19] Moreover, low-temperature phosphorescence was observed for **8–11** in frozen 2-methyl-THF at –196 °C (Figure 2d). The phosphorescence lifetimes (τ_{p}) were determined to be 2.9, 3.3, 2.2, and 1.4 s based on the single-exponential curve-fittings in

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phosphorescence decay profiles. (see Figure S42–45 for details) It is noteworthy that the low-temperature-phosphorescence lifetime of **9** is as long as those of cyclic carbazoles ($\tau_p = 3.33$ – 3.41 s in 2-methyl-THF at -196 °C) reported recently.^[20] In the current case, the spin-orbit-coupling process may be enhanced due to the non-planar structures.^[21]

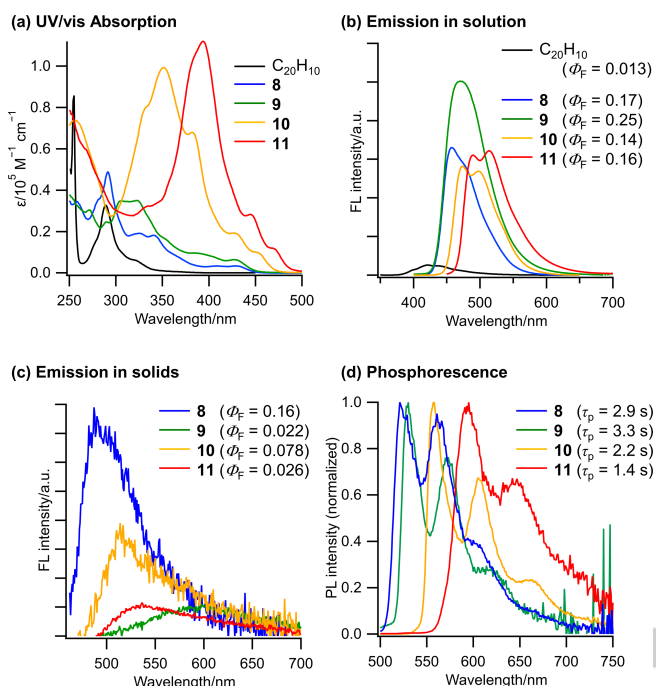


Figure 2. (a) UV/vis absorption spectra in CH_2Cl_2 . (b) Fluorescence spectra in CH_2Cl_2 . (c) Fluorescence spectra in solid state. (d) Phosphorescence spectra in 2-methyl-THF at -196 °C.

Electrochemical properties: The redox potentials determined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) are summarized in Table 1. Upon peripheral π -extension with indole and benzindole moieties, the reduction potentials ($E_{\text{red},1}$) are not significantly affected while the first oxidation potentials ($E_{\text{ox},1}$) become smaller.^[22] As a result, electrochemical HOMO–LUMO gaps (ΔE) are decreased to as little as 2.76 eV for **11**. This tendency is consistent with HOMO–LUMO gaps estimated by DFT calculations (see Figure S55).

Table 1. The oxidation potentials ($E_{\text{ox},1}$ – $E_{\text{ox},3}$), reduction potentials ($E_{\text{red},1}$), electrochemical HOMO–LUMO gaps (ΔE), and theoretical HOMO–LUMO gaps ($e(\text{HOMO-LUMO})$) are summarized for corannulene $\text{C}_{20}\text{H}_{10}$ and the fused corannulenes **8**–**11**. The redox potentials are shown (Conditions) Solvent: benzonitrile, Supporting electrolyte: 0.1 M $n\text{Bu}_4\text{N}^+\text{PF}_6^-$, Working electrode: Glassy carbon, Counter electrode: Pt, Reference electrode: Ag/AgClO_4 , Scan rate: 0.05 V/s.

compd.	$E_{\text{ox},3}$ [V] ^[a]	$E_{\text{ox},2}$ [V] ^[a]	$E_{\text{ox},1}$ [V] ^[a]	$E_{\text{red},1}$ [V] ^[a]	ΔE [eV] ^[b]	$e(\text{HOMO-LUMO})$ [eV] ^[c]
$\text{C}_{20}\text{H}_{10}$	-	-	-	-2.40 ^[22]	-	4.35
8	-	0.88	0.77	-2.34	3.11	3.59
9	-	-	0.62	-2.32	2.94	3.49
10	0.94	0.72	0.44	-2.40	2.84	3.37

11 - 0.61 0.38 -2.38 2.76 3.18

[a] Redox potentials are shown against ferrocene/ferrocenium ion couple. [b] $\Delta E = e(E_{\text{ox},1} - E_{\text{red},1})$. [c] MO energy levels were calculated at the B3LYP-D3(BJ)/def2-SVP level.

X-Ray crystallographic analysis: Single crystals of **8**–**10** and **14**–**16** were obtained by a vapor diffusion method and their structures were unambiguously determined by X-ray diffraction analysis (Figure S46–51 and Table S5). The obtained structures of **8** and **9** are shown in Figure 3 and that of **10** in Figure 4. The chirality definition of **8** and the helicene chirality definition of **9** are introduced in conjunction with Figure 3. A bowl-shaped molecule with a desymmetrizing element can be inherently chiral as reported for hemibuckybowl^[23] and azaindene-fused corannulene **1**.^[8f] Although this type of chirality is out of the scope of conventional annotation of molecular chirality, enantiomers can be distinguished by extended application of Cahn–Ingold–Prelog rule using *P* or *M* as proposed by Scott *et al.*^[23] Siegel *et al.* have proposed alternative labels for chiral bowls of this sort;^[8f] according to their definition, the bowl designated *P* by Scott *et al.* would be labeled as the 𐄂 enantiomer, and the bowl designated *M* by Scott *et al.* would be labeled as the 𐄃 enantiomer. Hereafter, this kind of chirality will be referred to as bowl chirality and expressed with *P* or *M*, following the definition by Scott *et al.* In Figure 3c, the two molecules included in a unit cell are both designated as *P* enantiomers. This observation indicates the spontaneous chiral resolution of **8** upon crystallization as the first case of corannulene derivatives, to the best of our knowledge. In addition to the bowl chirality, benzoindolocorannulene **9** owns the helical chirality around the aza[5]helicene moiety (Figure 3e). For example, the helical chirality of **9** shown in Figure 3d and 3e is assigned as *M* using a general definition of chirality for helicenes.^[9] In the unit cell of **9**, a pair of the enantiomers were found (Figure 3f). Similarly, in the crystal structure of **10**, a pair of enantiomers were observed that is expressed as *P*,*PMPMM* (i.e. the bowl chirality is *P* and the helical chirality is *PMPMM*) and *M*,*PPMPM* (i.e. the bowl chirality is *M* and the helical chirality is *PPMPM*) conformers. In the previous quintuple-helicene–corannulene hybrids, the conformers of **6** and **7** can be fully expressed by five *P/M* (helicities) since each peripheral π -extension unit possesses a C_s -like symmetric element (phenanthrene unit for **6** and etheno-bithiophene unit for **7**). In contrast, in order to uniquely assign a conformer of pentaazahelicene–corannulene hybrids **10** and **11** in this work, six *P/M* are required for describing bowl chirality and helical chirality due to the incorporation of the nitrogen atoms asymmetrically into the π -extension frameworks. These molecules can be regarded as a rare example possessing bowl chirality and multiple helical chirality in the same molecules. The bowl-depth values, which are defined by the distance between the centroid of the central five-membered ring and the mean plane of the ten carbon atoms on the rim, are 0.868 Å for **8**, 0.802 Å for **9**, and 0.482 Å for **10** (Figure S57). The bowl depth value of **10** is obviously shallower than those of **8**, **9**, and the pristine corannulene $\text{C}_{20}\text{H}_{10}$ (0.862, 0.889 Å).^[24,25] The strain around the azahelicene moieties are evaluated by considering the averaged dihedral angles. For example, dihedral angles of **8** denoted as a–b–c–d and b–c–d–e are -0.95° and 18.13° , respectively, and the average (ϕ_{ave}) is 8.59° (Table S2–4). The ϕ_{ave} for **9** is -17.07° , while the five averaged values for **10** are 14.83° , 6.99° , -13.98° , 14.95° , and -12.87° .

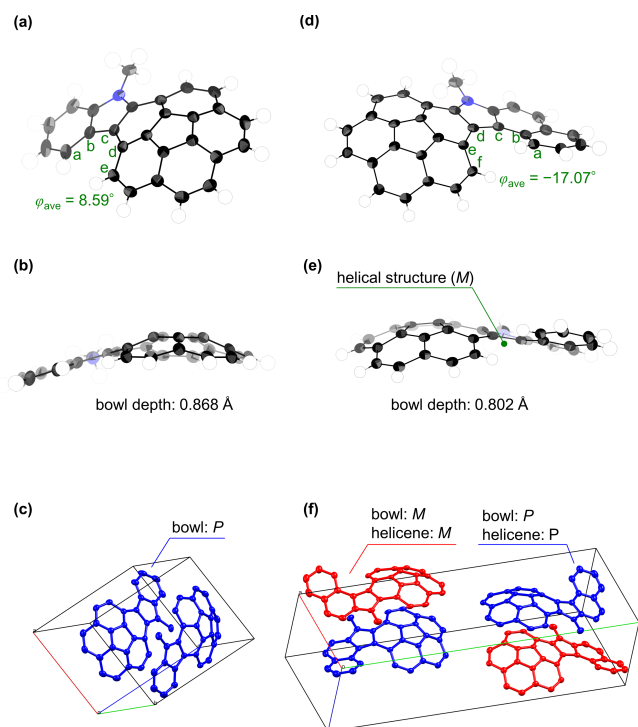


Figure 3. X-Ray crystal structures. (a) Perspective view, (b) side view, and (c) packing structure of **8**. (d) Perspective view, (e) side view, and (f) packing structure of **9**. Hydrogen atoms were omitted for clarity in (c) and (f). The thermal ellipsoids were scaled at 50% probability level.

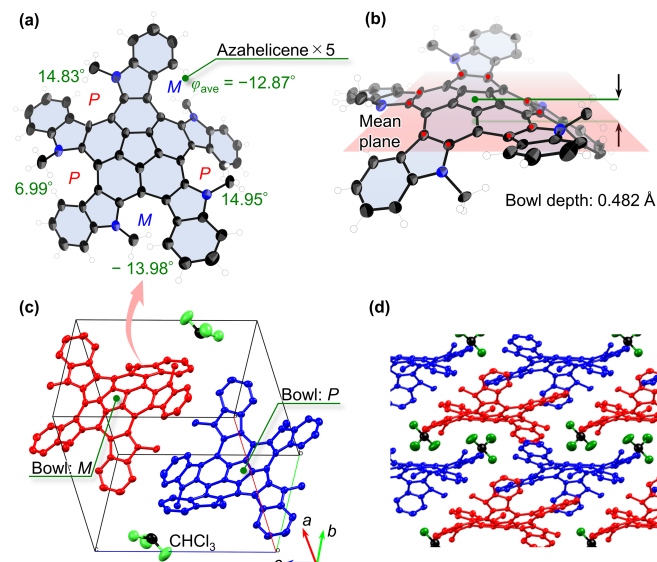


Figure 4. X-Ray crystal structure of **10**. (a) Top view and helicities in each azahelicene scaffold. (b) Side view and the bowl-depth. (c) Representation in a unit cell. (d) Packing structure viewed along the b-axis. The thermal ellipsoids are scaled at 50%. The solvent molecules are omitted for clarity in (a) and (b), and the hydrogen atoms are omitted for clarity in (c) and (d). Red and blue molecules in (c) and (d) represent **10-M,PPMPM** and **10-P,PPMPM**, respectively. In (a) and (b), one of the enantiomers (**10-M,PPMPM**) is shown.

Theoretical calculations: To gain further insights into the distorted corannulene cores of **10** and **11**, we performed DFT calculations for the most stable isomers of **10** and **11** at the B3LYP-D3(BJ)/def2-SVP level.^[26–28] Table 2 summarizes

structural parameters such as the bond lengths, bowl-depths, and average dihedral angles. Slight elongation of the rim bonds (labeled as v) is observed, whereas other bond lengths i–iv are almost intact. As observed in the crystal structure, the bowl-depths in penta-fused corannulenes tend to be shallower than that of the pristine corannulene (0.580 Å for **10** and 0.485 Å for **11**). This tendency has been seen in the previously reported fused corannulenes.^[10] The smaller bowl depth of **10** in the crystal structure (0.482 Å) may be ascribed to the crystal packing force. Furthermore, the strain around azahelicenes of **10** and **11** were evaluated by considering the DFT-constructed azahelicene fragments **frg-10** and **frg-11**. As a reference, the averaged dihedral angles (ϕ_{ave}) of **frg-10** and **frg-11** are 12.89° and 14.77°, respectively. Quintuple helicenes **10** and **11** own five sets of dihedral angles. In the quintuple helicenes with the bowl chirality of *M*, the *M*-twisted azahelicenes (C and E in Table 2) of **10** show slightly larger absolute ϕ_{ave} values, while the *P*-twisted azahelicenes (A and C) of **11** show larger ϕ_{ave} values as compared to those of the fragments. The strain energies were estimated by using homodesmotic reaction models (Table S24).^[29] The ΔH value of **11** (19.8 kcal·mol^{−1}) is larger than that of **10** (14.1 kcal·mol^{−1}), which is consistent with the larger steric bulkiness of the fused benzoindolo scaffolds. However, the strain energies of quintuple azahelicenes are less than five times of the ΔH values of single azahelicenes ($\Delta H = 4.4$ kcal·mol^{−1} for **frg-10** and 5.4 kcal·mol^{−1} for **frg-11**).

Table 2. Comparison of the structural parameters of **10-M,PPMPM**, **11-M,PPMPM**, **frg-10-P**, **frg-11-P**, and the pristine corannulene (C₂₀H₁₀) based on the DFT-optimized structures at the B3LYP-D3(BJ)/def2-SVP level. The most stable conformers **10-M,PPMPM** and **11-M,PPMPM** (*vide infra*) are chosen here for detailed analysis.

Quintuple azahelicene–corannulene hybrids					
Single azahelicenes (reference compounds)					
Corannulene					
	10	11	frg-10	frg-11	C₂₀H₁₀
i [Å] ^[a]	1.421	1.419	1.428	1.428	1.422
ii [Å] ^[a]	1.390	1.387	1.377	1.378	1.388

iii [Å] ^[a]	1.451	1.453	1.418	1.419	1.454
iv [Å] ^[a]	1.455	1.462	1.424	1.425	
v [Å] ^[a]	1.442	1.453	1.414	1.418	1.390
bowl depth [Å]	0.580	0.485	-	-	0.901
$\varphi_{\text{ave}}(\text{A})^{\circ[\text{b}]}$	12.84	15.51	12.89	14.77	-
$\varphi_{\text{ave}}(\text{B})^{\circ[\text{b}]}$	9.10	-13.26	-	-	-
$\varphi_{\text{ave}}(\text{C})^{\circ[\text{b}]}$	-14.36	15.87	-	-	-
$\varphi_{\text{ave}}(\text{D})^{\circ[\text{b}]}$	13.57	-13.46	-	-	-
$\varphi_{\text{ave}}(\text{E})^{\circ[\text{b}]}$	-13.87	-11.59	-	-	-

[a] The averaged bond lengths. [b] The averaged dihedral angles in each azahelicene.

Exploration of the interconversion network by GRRM: To rationalize the dynamic behaviors of bowl-inversion and azahelicene-inversion, computational approaches have been applied to **10** and **11**. In the initial attempts to explore their interconversion network, DFT calculations with manually constructed input structures were found to be difficult for us in obtaining transition states. Then, we decided to utilize the recently developed GRRM17 program^[30] with the SC-AFIR/PM7 method^[31] for the automatic exploration of all the possible structures in the equilibrium state (EQ) and transition state (TS) of **10** and **11**, and reoptimized them at the B3LYP-D3(BJ)/def2-SVP level.^[26–28] Subsequently, IRC calculations were performed to further confirm whether the transition states connect the different equilibrium structures. Although there are a few examples in the utilization of GRRM for conformational analysis of π -conjugated molecules,^[32] this is the first application of GRRM to comprehensive exploration of a number of EQs, TSs, and isomerization pathways of non-planar aromatic compounds. As a result of the computational approach, we obtained 12 EQs and 24 TSs for **10**, and 10 EQs and 14 TSs for **11** (Figure S58–61 and Table S25,26).^[33] All EQs including mirror-inverted structures (*i.e.* enantiomers) are distinctively expressed with six *PIM* signs as defined above. For example, *M,PPPPP* is the mirror-inverted structure of *P,MMMMM* and the mirror-inverted structure of *P,PPMPM* is *M,PMPMM*. In Figure 5a and 5b, a simplified version of the interconversion network of **10** and **11** are summarized and the relative free energies of the EQs and TSs are shown in kcal·mol⁻¹.^[34] The most stable conformers of **10** (*i.e.*, *10-M,PPMPM* and *10-P,PMPMM*) are the same as those found in the crystal structure. In the interconversion network of **10**, the pathways can be categorized into three patterns: (1) helical-

inversion, (2) bowl-inversion, and (3) mixed helical- and bowl-inversion. Here, it is worth noting that bowl-inversion pathways of **10** and **11** connect different conformers, while the conformations of corannulene–helicene hybrids **6** and **7** are the same before and after bowl-inversions because of their molecular symmetry. The activation barriers for bowl-inversion of **10** are 3.6 kcal·mol⁻¹ (from *M,PPMPM* to *P,PMPMM*) and 8.7 kcal·mol⁻¹ (from *P,PMPMM* to *M,PPMPM*). These barriers are lower than those for helical-inversion (9.8–17.0 kcal·mol⁻¹). The TS structures of the mixed helical/bowl-inversion are similar to those of helical-inversion, and their energies (15.0 and 16.5 kcal·mol⁻¹) are also close to those of pure helicene-inversions. In the case of **11**, the energy differences among possible EQs are smaller, while the TS energies for helical inversion are more energetically demanding (17.9–26.9 kcal·mol⁻¹). In contrast, the activation barrier for the bowl-inversion of **11** is smaller (2.6 kcal·mol⁻¹). Based on these computational results, VT NMR spectra (Figure 1 and Figure S23–25) would be rationalized as follows: (i) Helical/bowl-inversion of **10** rapidly occurs around room temperature to give averaged signal patterns, while some of the helical-inversions are frozen at -90 °C, resulting in broadened signals; (ii) Helical-inversions of **11** are accelerated at elevated temperatures, affording broadened five-fold-symmetric signal patterns at 135 °C. (iii) All helical-inversion of **11** are slower than the NMR time scale below 50 °C whereas bowl-inversion with the low activation barrier (2.6 kcal·mol⁻¹) is likely to occur rapidly even at -90 °C.^[35] To compare the structural dynamics with the simplified fragmental skeletons, namely, the pristine corannulene, **frg-10**, and **frg-11**, the activation barriers (E_a) for their conversion were estimated at the B3LYP-D3(BJ)/def2-SVP level^[26–28] (Figure 5c). Interestingly, the isomerization barriers for **10** (3.6–8.7 kcal·mol⁻¹ for bowl-inversions and 9.8–17.0 kcal·mol⁻¹ for helical(+bowl)-inversions relative to the most stable EQ) are smaller than those of corannulene (12.5 kcal·mol⁻¹) and **frg-10** (22.0 kcal·mol⁻¹), respectively. This result indicates that the co-existing corannulene and azahelicene moieties mutually lower the energy barriers. It is more significant in the case of **11**: the energy barriers of **11** (2.6 kcal·mol⁻¹ for bowl-inversions and 17.9–26.9 kcal·mol⁻¹ for helical-inversions relative to the most stable EQ) are smaller than those of corannulene (12.5 kcal·mol⁻¹) and **frg-11** (35.3 kcal·mol⁻¹), respectively. This mutual reduction of the barriers was previously estimated for **5–7** by kinetic studies and DFT calculations. However, it could be said that the landscape has been revealed more in detail in quintuple azahelicene-corannulene hybrids **10** and **11**, and the energy reduction due to cooperative helical and bowl-inversion was found to be more significant as compared to single helicene-corannulene hybrid **5**.^[10]

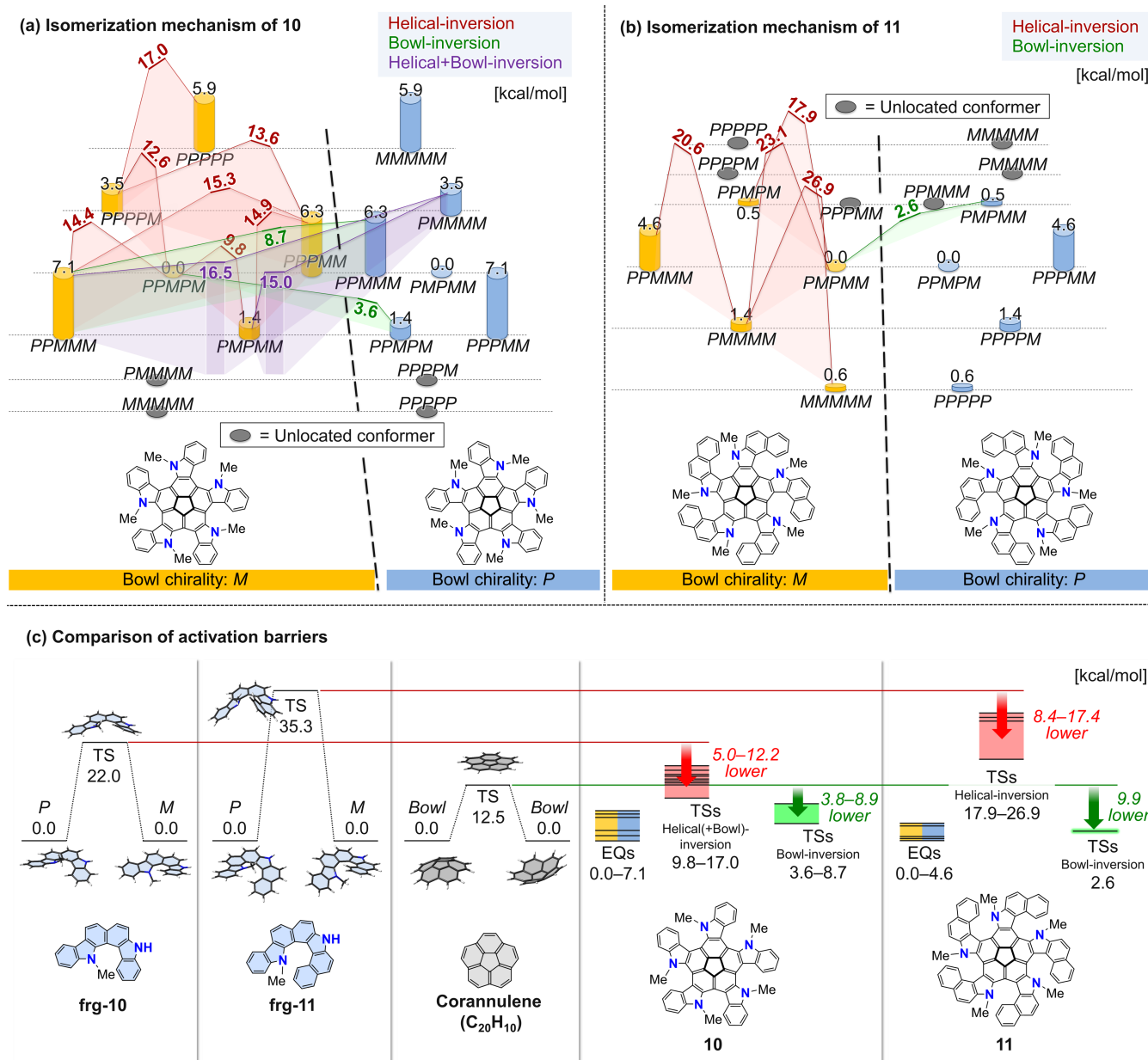


Figure 5. Relative free energies of equilibrium conformers/transition states and simplified representation of the interconversion networks of (a) **10** and (b) **11** at 298.15 K. (c) Interconversion pathways of **frg-10**, **frg-11**, and the pristine corannulene for comparison.

Conclusion

Corannulene–azahelicene hybrids **10** and **11** were synthesized for the first time from *sym*-pentabromocorannulene in three steps, including Buchwald–Hartwig amination, Pd-catalyzed intramolecular C–H arylation, and *N*-methylation. In contrast to the previously reported corannulene–carbohelicene hybrids, nitrogen-incorporated analogues in this work show emission with higher quantum yields as well as solid-state fluorescence and low-temperature phosphorescence with second-order lifetimes. Furthermore, owing to the embedded nitrogen atoms and hence the lowered molecular symmetry, the azahelicene–corannulene hybrids **10** and **11** possess several conformers originating from

five helical chiralities at the periphery and a chirality derived from the bowl-shaped curvature at the center. In spite of such complexity, full interconversion networks were revealed by using GRRM method, the result of which is consistent with the experimental observation by VT-NMR measurements. The strain energies, structural deformation, and inversion dynamics are discussed in detail in comparison with the pristine corannulene and the corresponding azahelicene fragments. Extensive studies on nitrogen-incorporated contorted nanographenes are actively in progress in our laboratory.

Acknowledgements

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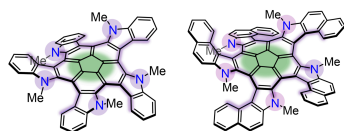
Keywords: corannulene • azahelicene • dynamic conformational change • helical chirality • bowl chirality

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- [33] Some expected EQs such as **10-M,PM MMM** (**10-P,PPPPM**) were unlocated not simply due to the error termination of the calculations but due to the undesired bowl inversion during the geometry optimization steps, which afford diastereomers with different chirality compared with the original input structures.
- [34] Some conformers are connected by more than one pathway, but in Figure 5, only one of the pathways with lower activation energies is shown for clarity. For example, **10-M,PPMPM** and **10-M,PPPPM** are connected by two transition states: **10-TS-M,PPPPM-h-M,PPMPM** (14.1 kcal·mol^{−1}) and **10-TS-M,PPPPM-h-M,PPMPM** (12.6 kcal·mol^{−1}), depending on which helicene is involved in inversion. Here, the helical chirality of the helicene involving inversion is expressed in underlined P/M, and -h- means the two conformers are connected via helicene inversion. In this example, the latter TS has lower energy, so in Figure 5a, only interconversion pathway through **10-TS-M,PPPPM-h-M,PPMPM** is shown. For full representation of the interconversion networks, see Figure S58,61.
- [35] In the ¹H NMR spectrum of **11** at room temperature, the most upfield-shifted singlet signal around 3.7 ppm is assigned as the methyl protons in azahelicene D in **11-M,PPMPM** (Table 2) and ones in the corresponding azahelicene in **11-P,PPMPM**, according to the simulated ¹H chemical shifts. See Table S27–30 and Figure S62 for detail.

Entry for the Table of Contents

**Quintuple-Aza-Helicene–
Corannulene Hybrids**

- Helicities (*P* or *M*) $\times$ 5
- +
- Bowl-shaped Curvature

➡ Unique Dynamic Behaviors

Peripherally π -extended corannulenes with five azahelicene units were prepared and their unique structural dynamics were studied both experimentally and theoretically. This motif contains many conformational isomers due to the helical- and bowl-chiralities. The interconversion networks among possible conformers were explored by using GRRM17 program, which revealed that the co-existing corannulene and azahelicene moieties lower the activation energy barriers for some isomerization processes.