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5-Azadibenzo[*a*,*g*]corannulene†

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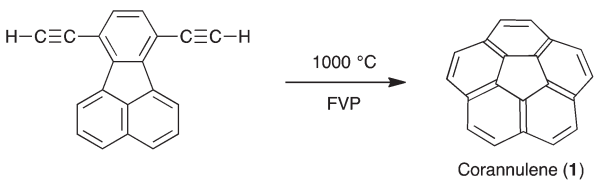
5-Azadibenzo[*a*,*g*]corannulene, the first azacorannulene with a nitrogen on the rim, has been synthesized in seven steps from 4-bromoisoquinoline. The strained pyridine ring opens thermally to a polycyclic aromatic nitrile and hydrolytically to an amino aldehyde with the same polycyclic aromatic hydrocarbon framework.

Introduction

Corannulene (**1**), the first bowl-shaped polycyclic aromatic hydrocarbon, was originally prepared in 1967 by a lengthy synthetic route that produced only milligram amounts of material.[1] The discovery of fullerenes in 1985,[2] however, reawakened interest in corannulene, the smallest fragment of C_{60} that retains geodesic curvature, and stimulated the development of shorter, more efficient syntheses of this fascinating compound in the early 1990s.[3] The flash vacuum pyrolysis (FVP) synthesis introduced by our laboratory (Scheme 1)[3a] was ultimately streamlined to a gram-scale 3-step synthesis[4] and laid the groundwork for FVP syntheses of dozens of other geodesic polyarenes.[5] Today, corannulene is available in kilogram quantities from the solution-phase route reported by Siegel *et al.*[6] Until recently, however, corannulene analogues having one or more nitrogen atoms incorporated into their polycyclic skeletons remained unknown. Herein, we report the synthesis and some properties of the first geodesic heterocycle in which a CH unit on the rim of a corannulene has been replaced by a nitrogen atom.



Scheme 1 Flash vacuum pyrolysis (FVP) synthesis of corannulene (**1**).

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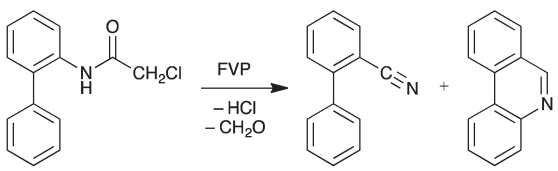
†Electronic supplementary information (ESI) available: NMR spectra of compounds **6**, **9**, **10**, **11**, **12**, **13a**, **13b**, **14a**, **14b**, **15**, **18**, **20**, and **22**; UV-VIS spectra of **6**, then plus acid, then plus base. See DOI: 10.1039/c6qo00831c

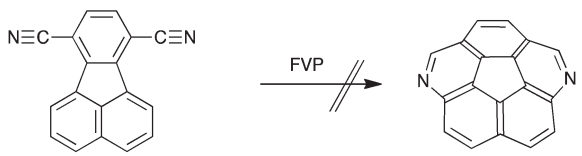
A brief history of azacorannulenes

The first attempt to synthesize an azacorannulene was reported in the Ph.D. dissertation of Matthew S. Bratcher in 1996 and was modelled after the first FVP synthesis of corannulene (Scheme 2, compare with Scheme 1).[7] The formation of 9-phenanthridine as a product from the FVP synthesis of 2-cyanobiphenyl reported earlier by R. F. C. Brown (eqn (1))[8] provided optimism that this double cyclization should work, but it never did. Subsequent molecular orbital calculations at the B3LYP/6-31G** level of theory[9a] revealed the reason: although the double cyclization in Scheme 1 is exothermic by 68 kcal mol^{-1}, the double cyclization in Scheme 2 is endothermic by 18 kcal mol^{-1}.[9b] This dramatic switch in equilibrium thermodynamics probably depends on several factors, such as the relative strengths of π-bonds in nitriles *vs.* alkynes,[10] the relative aromatic stabilization energies of benzene rings *vs.* pyridine rings,[11] the relative lengths of C=C bonds *vs.* C=N bonds,[12] *inter alia*.

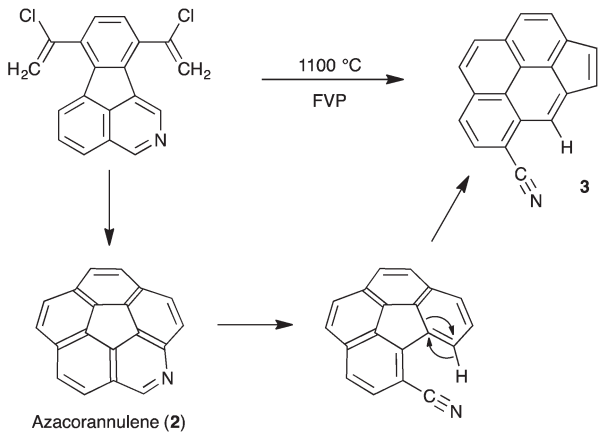


(1)

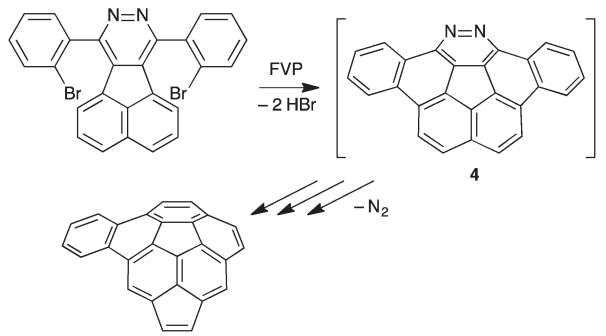
The second attempt to synthesize an azacorannulene was reported by P. W. Rabideau at the spring 1998 national meeting of the American Chemical Society in Boston but was never published.[13] Adopting our strategy of using α-chlorovinyl



Scheme 2 Unsuccessful attempt at FVP synthesis of a diazacorannulene.



Scheme 3 Unsuccessful attempt at FVP synthesis of azacorannulene (**2**).



Scheme 4 Unsuccessful attempt at FVP synthesis of a diazadibenzocorannulene.

groups as FVP precursors for ethynyl groups,[4] Rabideau attempted to synthesize the parent azacorannulene (**2**) but obtained instead the isomeric nitrile (**3**). Most likely, the synthesis worked, but the strained pyridine ring busted open by the reverse of the thermal cyclization shown in eqn (1).‡ Further relief of strain was achieved by a 5/6-ring switching process, a common rearrangement at temperatures of 1100 °C or more (Scheme 3).[14] We encountered a similar thermal sensitivity of the title compound but were able to fine-tune our FVP conditions well enough to minimize it (see below).

An attempt to synthesize a dibenzo-derivative of 1,2-diazacorannulene (**4**) was reported in 2006 and may also have worked, but the desired product did not survive the FVP high temperatures and lost the N_2 unit (Scheme 4).[15]

Very recently, two separate research groups in Japan have successfully synthesized substituted derivatives of a pentabenzoazacorannulene in which the nitrogen atom is located at a 5-membered ring hub position (**5**, Fig. 1).[16] These remarkable compounds are the first "nitrogen-doped" geodesic polyarenes with a nitrogen atom embedded at an interior position. The

‡ FVP of isoquinoline produces 2-vinylbenzonitrile.[7]

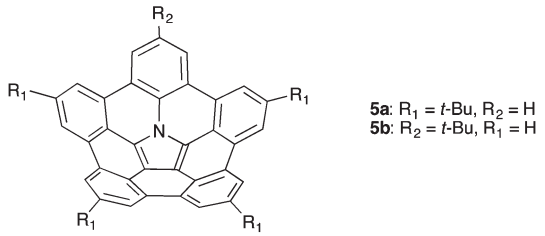


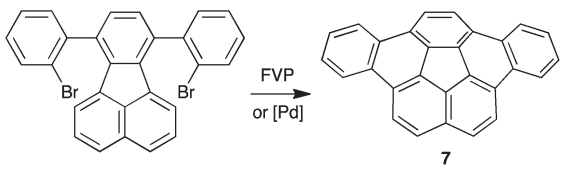
Fig. 1 Pentabenzoazacorannulenes with an embedded nitrogen atom.

penta-*peri*-benzannulation is a clever design principle that gives these compounds an even number of trigonal carbon atoms, thus allowing the nitrogen atom to accommodate a pair of π-electrons. Without such benzannulation, the neutral parent $C_{19}H_{10}N$ azacorannulene might exhibit radical-like reactivity, similar to that of the azafullerene $C_{59}N$.[17]

Results and discussion

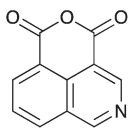
FVP synthesis of 5-azadibenzo[*a*,*g*]corannulene (6)

Scheme 5 outlines our successful seven-step synthesis of 5-azadibenzo[*a*,*g*]corannulene (**6**), which relies on FVP to impose curvature in the final step. The last three steps of this pathway closely resemble those used in our first synthesis of the analogous geodesic hydrocarbon, dibenzo[*a*,*g*]corannulene (**7**, eqn (2)),[7] whereas the first four steps follow procedures developed by Rabideau *et al.* for their synthesis of the azacorannulene precursor shown in Scheme 3.[13,18]



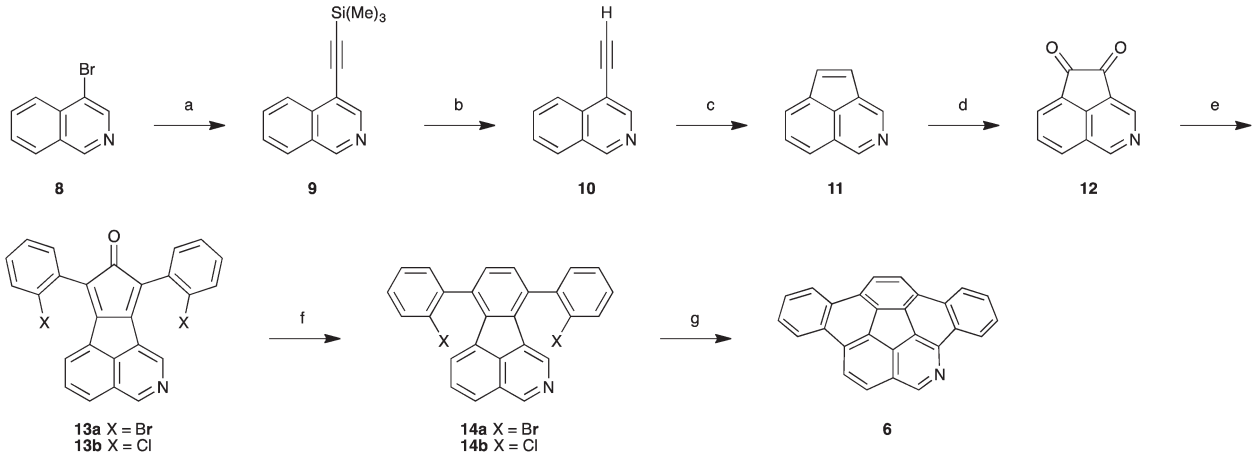
(2)

The synthesis begins with a Sonogashira coupling of 4-bromoisoquinoline (**8**) and trimethylsilylacetylene to give 4-(trimethylsilylethynyl)isoquinoline (**9**).[19] Desilylation of the protected acetylene with KOH affords 4-ethynylisoquinoline (**10**), which can be cyclized under FVP conditions to give the heterocyclic analogue of acenaphthylene **11**. Oxidation of **11** with benzeneselenic anhydride in chlorobenzene then affords α-diketone **12**.[18] From this last reaction, a minor side product was isolated, the ^{1}H NMR spectrum of which looks very similar to that of **12**. Further analysis by mass spectrometry led to the identification of this compound as anhydride **15**, a product of overoxidation.



15

Double aldol condensation of **12** with 1,3-bis(2-bromophenyl) propan-2-one or 1,3-bis(2-chlorophenyl)propan-2-one gives substituted cyclopentadienones, **13a** and **13b**, respectively, as



Scheme 5 (a) Trimethylsilylacetylene, $(Ph_3P)_2PdCl_2$, CuI, Et_3N, 70 °C, 95% yield. (b) KOH, CH_3OH, 73% yield. (c) FVP, 950 °C, 50% yield. (d) $(PhSeO)_2O$, PhCl, 62% yield. (e) 1,3-Bis(2-C_6H_4X)acetone, KOH, CH_3OH, 90% yield (X = Br or Cl). (f) Norbornadiene, reflux, 82% yield (X = Br) and 65% (X = Cl). (g) FVP, 1000 °C, X = Br, 28% yield.

purple solids. Heating these intermediates in refluxing 2,5-norbornadiene promotes a Diels–Alder/decarbonylation/retro-Diels–Alder sequence that generates substituted indenoisoquinolines **14a** and **14b**, respectively.§ [20]

FVP of the dibromo compound (**14a**) at 1000 °C gives 5-azadibenzo[*a*,*g*]corannulene (**6**) as the major product in 28% isolated yield. Mechanistically, each cyclization is probably initiated by homolytic cleavage of an Ar–Br bond, thereby generating a reactive aryl radical that adds to the π-system of the ring across the bay region.[21] The lower bond dissociation energy of Ar–Br bonds (~80 kcal mol^{-1}) relative to those of Ar–Cl bonds (~95 kcal mol^{-1})[22] makes the dibromo intermediate (**14a**) the logical choice for FVP experiments. The dichloro intermediate (**14b**) was prepared to use as a starting material for the attempted solution-phase synthesis of 5-azadibenzo[*a*,*g*]corannulene (**6**) discussed below. In our experience, aryl chlorides perform better than aryl bromides in Pd-catalysed intramolecular arylation reactions.[23]

Spectroscopic properties of 5-azadibenzo[*a*,*g*]corannulene (6)

High resolution mass spectrometry of the FVP product confirmed the expected $C_{27}H_{13}N$ molecular formula, and the ^{1}H NMR spectrum left no doubt that the compound was the desired 5-azadibenzo[*a*,*g*]corannulene (**6**). Fig. 2 shows the low field region of the ^{1}H NMR spectrum of **6**, where all of the signals appear. The furthest downfield singlet (a) at δ 9.45 ppm comes from the lone hydrogen *ortho* to the nitrogen. The one-hydrogen multiplet at δ 9.05 corresponds to the bay region proton (b). Its downfield shift relative to the signals for the other three bay region hydrogens (*c*, δ 8.60) is the consequence of a through-space repulsive interaction with the nitrogen lone pair of electrons.[24] Finally, the two doublets (δ 8.00 and 8.22) are very similar in chemical shift and coupling constant to the corresponding two-spin system (δ 8.02 and 8.30) in the ^{1}H NMR spectrum of the hydrocarbon analogue, dibenzo[*a*,*g*]corannulene (**7**),[23] lending further support to the structural assignment.

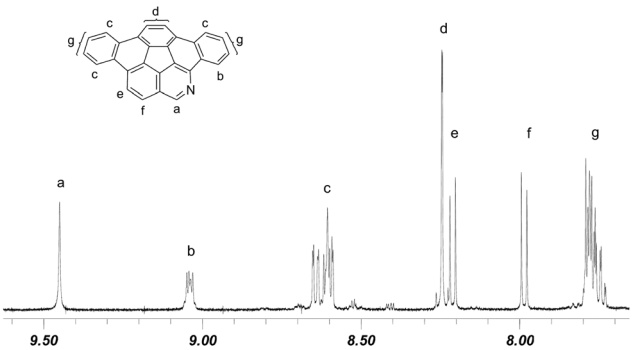


Fig. 2 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 5-azadibenzo[*a*,*g*]corannulene (**6**).

A comparison between the ^{1}H NMR chemical shifts obtained experimentally for azabowl **6** with those derived from theoretical calculations (GIAO/B3LYP/6-31G**)[9,25] reinforces the assignment (Table 1). All but one of the observed chemical shifts agrees with those calculated within an absolute deviation of 0.15 ppm. The only large disparity between the experimental

Table 1 Comparison of calculated (GIAO/B3LYP/6-31G**) and experimental ^{1}H NMR chemical shifts from 5-azadibenzo[*a*,*g*]corannulene (**6**)

	Chemical shifts (ppm)		
	Experimental	Calculated	Absolute deviation
a	9.461	9.609	0.148
b	**9.051**	**9.424**	**0.373**
c	8.663–8.599	8.680–8.639	<0.040
d	8.254	8.353	0.099
e	8.221	8.163	0.058
f	7.994	8.070	0.076
g	7.801–7.738	7.819–7.746	<0.018

§ Rotations around the aryl–aryl bonds in **13a**, **13b**, **14a**, and **14b** are slow on the NMR timescale, which gives rise to NMR signals from two atropisomers for each compound.

and computed shifts (~0.37 ppm) is seen for the hydrogen across the bay region from the nitrogen, labelled as (b). This discrepancy can be explained by the presence of solvent in the experimental NMR; the GIAO program does not take into account solvent effects. In this case, the chemical shift for the hydrogen is calculated to be significantly further downfield than is actually observed. Traces of water in the solvent, or solvent molecules themselves ($CDCl_3$), may hydrogen bond to the lone pair of electrons on the nitrogen, making it less capable of deshielding the hydrogen (b). As a result, the observed signal appears at higher field than the chemical shift predicted by gas phase calculations.

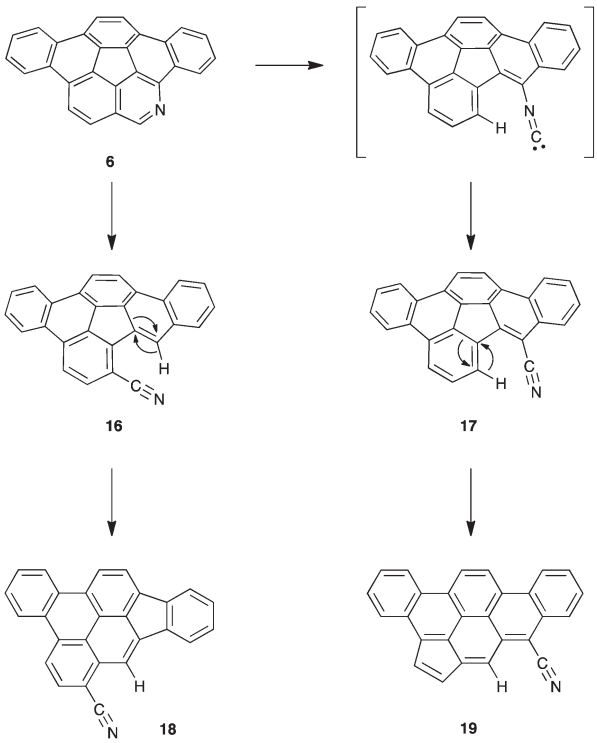
The identification of **6** in the complex mixture of FVP products was aided considerably by comparison of its calculated UV-VIS absorption spectrum with the spectra of the various components of the mixture, obtained with a diode array detector, as they emerged from a reverse phase HPLC column (Fig. 3).[26] The calculated and experimental UV-VIS absorption spectra do not completely align, but the general trends in the absorptions follow similar patterns. Overall, the experimental spectrum is slightly red-shifted relative to the calculated spectrum; maxima are seen at 235, 276, and 324 nm in the experimental spectrum, whereas the predicted spectrum shows corresponding maxima at 228, 270, and 312 nm. Thus, although UV-VIS absorption spectral calculations are not perfect, their value as an aid in locating the desired product in a mixture is demonstrated by our isolation of the previously unknown 5-azadibenzo[*a*,*g*]corannulene (**6**) from a crude mixture using HPLC-UV analysis.

Facile thermal opening of the 5-azadibenzo[*a*,*g*]corannulene pyridine ring

The highest yield of **6** (28%) was obtained when the FVP hot zone was held at 1000 °C, with the flow rate of nitrogen carrier gas adjusted to give an operating pressure of 0.5–0.6 torr. Under these conditions, a minor side product was obtained that also analysed in the mass spectrum for *m*/*z* 351. At higher temperatures and/or lower pressures (*i.e.*, lower N_2 flow rates, which lead to longer residence times in the hot zone), the yield of **6** dropped, and more of the side product was obtained. Isolation of the side product by preparative HPLC and spectroscopic analysis revealed that the compound was an aryl nitrile (strong ν_{max} 2363 cm^{-1}). Most likely, this side product is formed from the desired azabowl (**6**) by thermal opening of the pyridine ring through the reverse of the process shown in eqn (1) (*cf.* also Scheme 3).

The mechanism of the cyclization in eqn (1) is not known in detail. It is conceivable that an isomerization of the nitrile to an isonitrile precedes the ring closure, but the symmetry of the systems in eqn (1) and Scheme 3 hide this step, if it occurs. Taking into account both possible pathways, we focused on aryl nitriles **16**, **17**, **18**, and **19** as the most likely structures for this side product from the FVP synthesis of **6** (Scheme 6).

Fig. 4 shows the low field region of the ^{1}H NMR spectrum of the isolated aryl nitrile, where all of the signals appear. The



Scheme 6 Plausible pathways for thermal opening of the pyridine ring in 5-azadibenzo[*a*,*g*]corannulene (**6**).

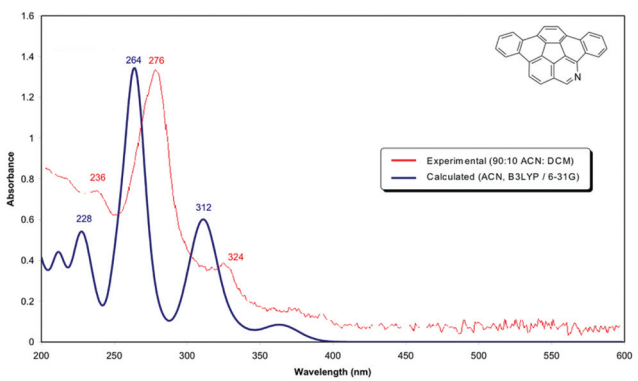


Fig. 3 Comparison between calculated (TD-DFT B3LYP/6-31G) and experimental UV-VIS spectra of 5-azadibenzo[*a*,*g*]corannulene (**6**).

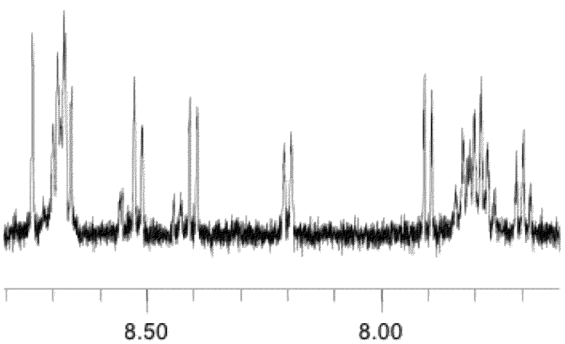


Fig. 4 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the aryl nitrile formed by thermal opening of the pyridine ring in 5-azadibenzo[*a*,*g*]corannulene (**6**).

Table 2 Comparison between experimental and calculated (GIAO/B3LYP/6-311++G**) ^{1}H NMR chemical shifts (ppm) of plausible structures for the thermal rearrangement product from 5-azadibenzo[*a*,*g*]corannulene (**6**, see Scheme 6)

	Experimental	Calcd for **16**	Δ	Calcd for **18**	Δ	Calcd for **19**	Δ
a	8.74	8.87	0.13	8.92	0.18	9.12	0.38
b	8.70–8.66	8.75–8.68	~0.04	8.87	~0.19	8.98–8.84	~0.22
c	8.51	8.57	0.06	8.77	0.26	8.84	0.33
d	8.40	8.39	0.01	8.23	0.17	8.62	0.22
e	8.20	8.16	0.04	7.98	0.22	8.31	0.11
f	7.89	7.83	0.06	7.75	0.14	7.90	0.01
g	7.82–7.77	7.69–7.63	~0.13	7.60	~0.19	7.79–7.72	~0.05
h	7.71–7.68	7.61–7.54	~0.10	7.28	~0.41	6.97	~0.71
|Δ Ave|			0.07		0.22		0.25

presence of a low field singlet (8.74 ppm) eliminates structure **17** from further consideration, but the remaining three isomers would all be expected to give rise to a low field singlet (from the H shown on each structure).

To decide among these three structures, we calculated ^{1}H NMR spectra for each (GIAO/B3LYP/6-311++G**)[25] and compared them to the experimental spectrum (Table 2). The calculated spectrum of **16** fits best and actually matches the experimental spectrum very well (average absolute deviation of only 0.07 ppm). The calculated spectra of **18** and **19** fit the experimental spectrum rather poorly (average absolute deviation of 0.22 and 0.25 ppm, respectively). Thus, we feel reasonably confident in assigning structure **16** to the aryl nitrile formed by thermal opening of the pyridine ring in **6**. The failure of **16** to isomerize further to **18** is consistent with the fact that this FVP was run at 1000 °C; the 5/6-ring switching process is commonly seen only at temperatures of 1100 °C or above.[14] If this assignment is correct, it means that the isomerization involves cleavage of the C–N bond, rather than the C–C bond, and the mechanism does not pass through an isonitrile intermediate.

Facile hydrolytic opening of the 5-azadibenzo[*a*,*g*]corannulene pyridine ring

Initial attempts to isolate and purify compound **6** by silica gel chromatography proved futile, as a single major product was obtained that was not the desired azabowl. Analysis of this compound by mass spectrometry revealed a molecular ion at *m*/*z* 369, corresponding to a molecular formula $C_{27}H_{15}NO$, which was confirmed by HRMS. The observed compound differs in its molecular formula from that of **6** ($C_{27}H_{13}N$) by one water molecule. Upon examination of the ^{1}H NMR spectrum of this side product (Fig. 5), the structure was determined to be amino aldehyde **20**, formed by hydrolysis of the C=N bond. A diagnostic singlet for the aldehyde hydrogen is observed at 10.0 ppm in the ^{1}H NMR spectrum, and a low-field signal for the carbonyl carbon atom is observed at 197.4 ppm in the ^{13}C NMR spectrum, which lends credence to the assigned structure.

As confirmation for the sensitivity of **6** to silica gel, a sample of the pure heterobuckybowl was stirred with silica gel in dry dichloromethane for 24 h. Analysis of the resulting material by ^{1}H NMR spectroscopy showed that amino aldehyde **20** was formed in greater than 50% conversion by cleavage of the bowl.

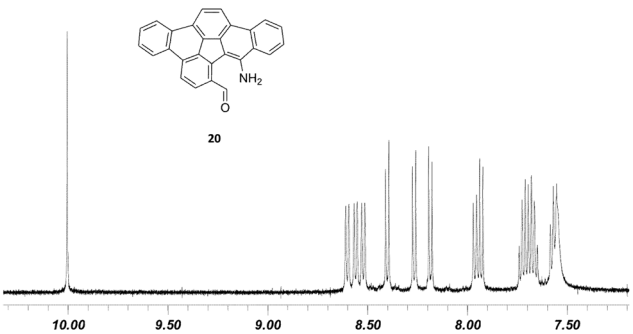


Fig. 5 ^{1}H NMR spectrum (500 MHz, $C_2D_2Cl_4$) of amino aldehyde (**20**) formed by hydrolytic opening of the pyridine ring in 5-azadibenzo[*a*,*g*]corannulene (**6**).

The driving force for this decomposition is proposed to be the relief of strain in the curved polyarene. Unlike ordinary polycyclic aromatic compounds, this "spring-loaded" heterocycle has an Achilles' heel at the heteroatom, which renders it vulnerable to acid-catalysed hydrolysis, as well as to high temperatures.

In an attempt to reverse the decomposition and regenerate the azabowl, amino aldehyde **20** was stirred in *o*-dichlorobenzene at 130 °C with phosphorus pentoxide to try to drive the equilibrium back towards the imine/pyridine. Unfortunately, 5-azadibenzo[*a*,*g*]corannulene was not formed. This failure can most likely be attributed to the insufficient exothermicity of such imine-forming reactions to overcome the introduction of strain in the system, even when generating an aromatic pyridine ring.

Calculated curvature of 5-azadibenzo[*a*,*g*]corannulene (6)

All attempts to grow crystals of the title compound, by two of us over a period of several years, were invariably thwarted by competing decomposition of the azabowl to amino aldehyde **20**. Crystal growth should be possible under absolutely anhydrous conditions, but we were never successful. The structural information reported here, therefore, is derived from the optimized geometry calculated at the B3LYP/6-31G** level of theory.[9] This level of theory has been shown to give geometric

parameters for geodesic polyarenes that match those obtained by X-ray crystallography, within the experimental error of the crystallography.[27]

The curved structures of geodesic polyarenes arise from pyramidalization of the carbon atoms comprising the embedded five-membered rings. The degree to which these carbon atoms deviate from planarity can be quantified using the p-orbital axis vector (POAV) analysis developed by Haddon.[28] As reference points, an sp^2 hybridized planar carbon atom, as in benzene, has a POAV angle of 0°, whereas the central carbon atoms of pentaindenocorannulene[29] have an average POAV angle of 12.6°, which represents the most curved fullerene fragment synthesized to date.

To understand how the curvature of a corannulene bowl is affected by the replacement of carbon atoms with nitrogen atoms on the periphery, the POAV angles of several azacorannulenes were calculated. Specifically, a comparison study was conducted on dibenzo[*a*,*g*]corannulene (**7**), 5-azadibenzo[*a*,*g*]corannulene (**6**), and 5,6-diazadibenzo[*a*,*g*]corannulene (**4**). Geometry optimizations were performed at the B3LYP/6-31G** level of theory;[9] POAV angles for each carbon atom of the central five-membered rings were then calculated and averaged.

According to the calculations, 5-azadibenzo[*a*,*g*]corannulene (**6**), resulting from the introduction of a single nitrogen atom on the rim of dibenzo[*a*,*g*]corannulene (**7**) gives the hub carbon atoms an average POAV angle of 8.30°, which makes them approximately 1° more pyramidalized than those in the parent hydrocarbon (7.33°). An even more acute angle of 9.07° is predicted for the analogue containing a 1,2-diaza-unit on its perimeter (**4**). This increase in pyramidalization can be explained by the shorter lengths of CN and NN bonds,[12] relative to CC bonds, which cause a contraction of the distance around the rim of the systems and, therefore, more severe "puckering". These results agree qualitatively with the predictions published many years ago by Sastry and co-workers.[30]

Basicity of 5-azadibenzo[*a*,*g*]corannulene (6)

In an effort to assess the influence of π-system curvature on the basicity of the nitrogen atom on the rim of our azabowl, we performed calculations[9] to compare **6** with a planar isomer with the nitrogen atom also located in a bay region (**21**). For such calculations, it is important to compare compounds of the same size, because charge stabilization in the gas phase scales directly with molecular size. Fig. 6 shows the isodesmic equation for proton transfer between **6** and **21**. At the B3LYP/6-31G** level of theory, we find that the bowl (**6**) is calculated to be *slightly less basic* than its planar isomer (**21**), but the difference in basicity is almost negligible (less than one pK unit).

On the experimental side, a solution of **6** in dry CH_2Cl_2 was spiked with an excess of trifluoroacetic acid (TFA); UV-VIS spectra were recorded both before and after acid addition. A clear red-shift of the spectrum is observed with the addition of TFA to the solution (ESI Fig. 1†); the maxima shift from 280 and 326 nm to 284 and 338 prior to and following the acid spike, respectively. In addition, a new shoulder grows in at

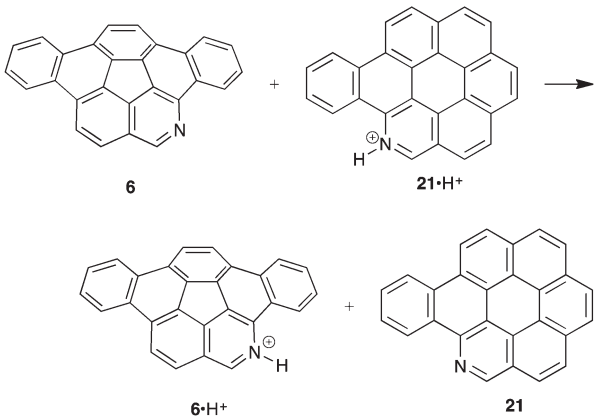


Fig. 6 Isodesmic equation for proton transfer between azabowl **6** and planar isomer **21**: E_{rxn} = +0.25 kcal mol^{-1} (B3LYP/6-31G** level of theory).

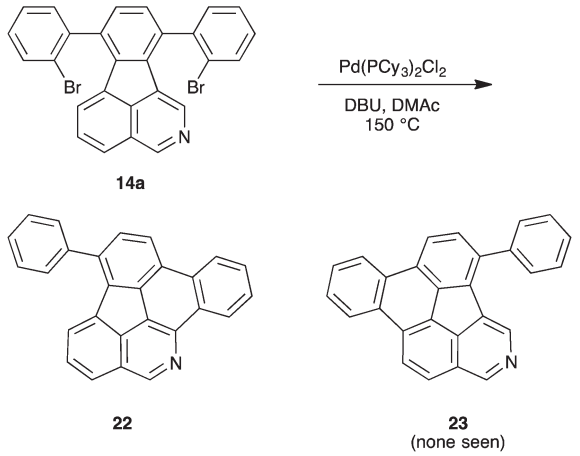
304 nm in the spectrum of the protonated species (**6**·H$^+$). Visually, no colour change of the solution was observed upon addition of TFA. More acid was repeatedly added to the same cuvette, and the spectra were recorded again to make certain that no further shifts occurred, thereby ensuring that all of the starting material had been protonated.

To test the reversibility of the protonation by TFA, an excess of triethylamine (TEA) was added to the cuvette, and the UV-VIS spectrum was recorded again. After neutralization of the acid, the trace is no longer red-shifted but has reverted back and directly overlays the original UV trace of **6** (ESI Fig. 2†). The short wavelength absorption of TEA accounts for the strong absorption from 230–270 nm[31] and is enhanced by the presence of copious base in the solution. These results demonstrate that the nitrogen atom on the rim of our azabowl can be protonated reversibly by TFA and that the UV-VIS spectrum of the protonated form shifts to longer wavelength.

Unsuccessful attempts at a solution-phase synthesis of 5-azadibenzo[*a*,*g*]corannulene (6)

The hydrocarbon analogue of **6**, dibenzo[*a*,*g*]corannulene (**7**), was first synthesized using FVP for the final strain-inducing cyclisations (eqn (2));[7] however, we later found that the same ring closures could be achieved at much lower temperatures in solution by Pd-catalysed intramolecular arylation reactions.[23] Consequently, we attempted an analogous solution-phase synthesis of **6**. Unfortunately, exposure of the dibromo precursor (**14a**) to the same palladium catalyst in the presence of base[32] gives a single isolable product, which was determined to be the result of monocyclization onto the nitrogen-containing ring and reductive dehalogenation of the other aryl substituent (**22**, Scheme 7). In the palladium-catalysed synthesis of the corresponding hydrocarbon (**7**), an analogous monocyclization/reductive dehalogenation is also observed, although only as a minor side reaction.[23]

Distinguishing between isomers **22** and **23** is straightforward by ^{1}H NMR spectroscopy. In compound **23**, the hetero-



Scheme 7 Unsuccessful attempt at a solution-phase synthesis of 5-azadibenzo[*a*,*g*]corannulene (**6**).

atom is sandwiched between two CH units, neither of which has any neighbouring hydrogen atoms. These protons *ortho* to the nitrogen should give rise to two unique downfield singlets in the ^{1}H NMR spectrum. The other isomer (**22**) has only one proton *ortho* to the heteroatom, because cyclization has occurred onto the other site. The ^{1}H NMR spectrum obtained from the isolated product shows only one downfield singlet (see ESI†), thus confirming the assigned structure as **22**. Interestingly, none of the second isomer was observed.

In our experience, aryl chlorides perform better than aryl bromides in Pd-catalysed intramolecular arylation reactions,[23] so the solution-phase synthesis of **6** from dichloro precursor **14b** was also attempted. Again, monocyclized product **22** was obtained, and none of isomer **23** was observed. In this case, however, some of the amino aldehyde **20** was also isolated. Apparently, at least a portion of the dichloro precursor **14b** was converted to the title compound (**6**), but the strained pyridine ring opened hydrolytically (as discussed above), either during the reaction or during the workup and isolation. Our attempts to suppress this unwanted hydrolysis were not successful; however, the results strongly suggest that the synthesis of **6** by two-fold Pd-catalysed intramolecular arylation reactions does work.

Conclusions

5-Azadibenzo[*a*,*g*]corannulene (**6**) has been synthesized in seven steps from 4-bromoisoquinoline (Scheme 5). In the bowl-forming step, flash vacuum pyrolysis (FVP) of intermediate **14a** at 1000 °C/0.5–0.6 torr gives the highest yield of **6** (28%). At lower pressures or higher temperatures, the azabowl suffers thermal opening of the strained pyridine ring to form the polycyclic aromatic nitrile **16** (Scheme 6). In retrospect, Rabideau's unsuccessful synthesis of the parent azacorannulene (**2**, Scheme 3), which was plagued by the same thermal sensitivity of the desired product, might be salvageable by fine-tuning the FVP conditions.

The strained pyridine ring in **6** also opens hydrolytically on silica gel chromatography to give amino aldehyde **20**. Fortunately, the azabowl survives reverse phase preparative HPLC, but this extreme sensitivity prevented us from ever growing X-ray quality crystals. Attempts to regenerate **6** from amino aldehyde **20** by an intramolecular condensation reaction were not successful.

Geometry calculations on **6** indicate that the short CN bonds, relative to CC bonds, enforce greater pyramidalization of the carbon atoms at the hub positions than of those in the corresponding hydrocarbon (**7**). Protonation of **6** with trifluoroacetic acid in dry CH_2Cl_2 causes a moderate red shift of the UV-VIS spectrum, and neutralization with triethylamine restores the original spectrum. Isodesmic calculations of proton affinities indicate that curvature of the π-system makes the nitrogen atom on the rim of azabowl **6** *less* basic than the nitrogen atom in a bay region on the rim of a planar isomer (**21**), although only slightly so (less than one pK unit).

This polyarene heterocycle **6** is the first azacorannulene in which the nitrogen atom is located on the rim.

Experimental

General

All chemicals were purchased from commercial sources and used without further purification. Dichloromethane, *o*-dichlorobenzene (ODCB), and *N*,*N*-dimethylacetamide (DMAc) were obtained dry from a Glass Contour solvent purification system. NMR analyses were performed on 500 MHz and 600 MHz Varian spectrometers. NMR shifts are reported in ppm downfield of TMS with chloroform-d_1 (δH = 7.26 and δC = 77.23) as the standard reference unless otherwise noted. Chromatography was performed with Sorbent Technologies silica gel (porosity = 60 Å, particle size = 32–63 μm) or standard grade neutral alumina (150 mesh). Preparative layer chromatography was performed on 20 cm × 20 cm Analtech reverse phase C18 silica gel plates. Mass spectrometry was carried out at the Boston College mass spectrometry facility with MALDI-TOF, DART-TOF, APPI and ESI spectrometers. Infrared spectra (IR) were recorded on a Nicolet Avatar 360 FT-IR spectrophotometer. UV-VIS spectra were recorded on a Hewlett Packard diode array spectrophotometer with a 1 cm cell.

Synthetic procedures and characterization data

4-(Trimethylsilylethynyl)isoquinoline (9).[19] A mixture of 4-bromoisoquinoline (10.0 g, 48.1 mmol), trimethylsilylacetylene (5.67 g, 57.7 mmol), bis(triphenylphosphine) palladium dichloride (1.01 g, 1.44 mmol), copper(I) iodide (500 mg), and triethylamine (17 mL) was stirred in a pressure vessel at 70 °C for 5 h. The reaction mixture was cooled to room temperature, diluted with water and extracted with diethyl ether. The organic extracts were dried over magnesium sulphate and concentrated to dryness under vacuum. Flash chromatography on silica gel using ether as the eluent gave 10.3 g (95%) of the desired product (**9**) as a brown oil. **^{1}H NMR**

(500 MHz, $CDCl_3$) δ (ppm): 9.19 (s, 1H), 8.70 (s, 1H), 8.23 (dd, J = 8.5 Hz, 0.5 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.79 (ddd, J = 8.5 Hz, 7.0 Hz, 1.5 Hz, 1H), 7.65 (ddd, J = 8.0 Hz, 7.0 Hz, 1.0 Hz, 1H), 0.35 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.2, 146.9, 135.7, 131.1, 127.9, 127.8, 127.7, 125.1, 115.8, 102.6, 99.9, −0.02; **IR** (KBr, cm^{-1}): 2152 (C≡C); **HRMS** (ESI^+) calcd for $C_{14}H_{16}NSi$ $(M + 1)^+$ 226.1057, found 226.1061.

4-Ethynylisoquinoline (10).[19] A solution of 4-(trimethylsilylethynyl)isoquinoline (**9**, 10.3 g, 45.8 mmol) in 25 mL of methanol was added drop wise to 50 mL of 1 N KOH (aq), and the mixture stirred at room temperature for 1 h. The resulting suspension was acidified with 3 N HCl (~20 mL), and the methanol was removed by rotary evaporation. Water was added to dissolve the residue, which was subsequently made alkaline with solid K_2CO_3, extracted with diethyl ether, and concentrated to dryness under reduced pressure. Alumina chromatography of the crude product using ether as the eluent afforded 5.10 g (73%) of pure **10** as a tan solid: mp 66–67 °C (lit[19] 64.5–66 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 9.20 (s, 1H), 8.73 (s, 1H), 8.24 (dd, J = 8.5 Hz, 0.5 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.77 (ddd, J = 8.5 Hz, 7.0 Hz, 1.5 Hz, 1H), 7.64 (ddd, J = 8.0 Hz, 7.0 Hz, 1.0 Hz, 1H), 3.55 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.5, 147.3, 135.8, 131.2, 127.89, 127.86, 127.6, 124.9, 114.7, 84.4, 78.8; **IR** (KBr, cm^{-1}): 3162 (C≡C–H), 2085 (C≡C); **HRMS** (ESI^+) calcd for $C_{11}H_7N$ $(M + 1)^+$ 154.0662, found 154.0666.

Cyclopenta[*de*]isoquinoline (11).[18] A sample of 4-ethynylisoquinoline (**10**, 5.50 g) was pyrolysed in three batches at oven temperatures ranging from 900–1000 °C using the FVP apparatus described elsewhere.[14d] The starting material sublimed from a suspension on quartz sand with a steady stream of nitrogen carrier gas as previously described.[14d] The system pressure was maintained at 0.4–0.6 torr throughout the experiments. At the conclusion of the reactions, the crude pyrolysates were extracted from the tube and traps using dichloromethane. Chromatography on silica gel using 10 : 1 dichloromethane : ethyl acetate as the eluent gave 2.76 g (50%) of **11** as a brown oily solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 9.25 (s, 1H), 8.77 (s, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 7.0 Hz, 1H), 7.61 (dd, J = 8.5 Hz, 7.0 Hz, 1H), 7.15 (d, J = 5.5 Hz, 1H), 7.09 (d, J = 5.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.0, 139.8, 139.1, 133.7, 132.2, 130.1, 129.1, 128.9, 127.6, 126.2, 124.1; **HRMS** (ESI^+) calcd for $C_{11}H_8N$ $(M + 1)^+$ 154.0656, found 154.0653.

Cyclopenta[*de*]isoquinoline-4,5-dione (12)[18] and isoquinoline-4,5-dicarboxylic anhydride (15). A mixture of cyclopenta[*de*]isoquinoline (**11**, 1.00 g, 6.54 mmol) and benzeneselenic anhydride (4.71 g, 13.1 mmol) in 100 mL of chlorobenzene was stirred at 120 °C for 24 hours. The reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. Analysis of the crude residue showed two products: the desired quinone (**12**) and trace amounts of an anhydride side product (**15**). Separation of the two products on silica gel was possible using a solvent system ranging from pure dichloromethane to a 4 : 1 ratio of dichloromethane : ethyl acetate. The desired quinone (**12**) was isolated (0.746 g, 62%) as an orange solid. Several milligrams of the anhydride side product (**15**) were isolated as a yellow solid from multiple reactions and characterized spectroscopically. **Cyclopenta[*de*]isoquinoline-4,5-dione (12): mp** >222–224 °C (lit[18] 225–226 °C); **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 9.70 (s, 1H), 9.18 (s, 1H), 8.45 (dd, J = 8.0 Hz, 0.5 Hz, 1H), 8.33 (dd, J = 7.0 Hz, 0.5 Hz, 1H), 8.00 (dd, J = 8.0 Hz, 7.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 186.9, 186.6, 155.3, 147.4, 138.6, 132.1, 129.8, 128.0, 126.4, 126.1, 121.7; **IR** (KBr, cm^{-1}): 1726 (C=O); **HRMS** (ESI^+) calcd for $C_{11}H_6NO_2$ $(M + 1)^+$ 184.0404, found 184.0407. **Isoquinoline-4,5-dicarboxylic anhydride (15): mp** >200 °C (dec); **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 9.68 (s, 1H), 9.55 (s, 1H), 8.81 (dd, J = 7.5 Hz, 0.5 Hz, 1H), 8.50 (dd, J = 8.5 Hz, 0.5 Hz, 1H), 8.00 (dd, J = 8.5 Hz, 7.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.5, 159.3, 157.8, 149.4, 137.0, 134.7, 132.9, 129.1, 126.3, 118.4, 113.3; **IR** (KBr, cm^{-1}): 1783, 1742 (C=O, anhydride); **HRMS** (ESI^+) calcd for $C_{11}H_6NO_3$ $(M + 1)^+$ 200.0353, found 200.0359.

7,9-Bis(2-bromophenyl)-8*H*-pentaleno[1,2,3-*de*]isoquinolin-8-one (13a). Cyclopenta[*de*]isoquinoline-4,5-dione (**12**, 0.550 g, 3.01 mmol) and 1,3-bis(*o*-bromophenyl)acetone (1.11 g, 3.01 mmol) were combined in a 50 mL Erlenmeyer flask. A solution of KOH (0.150 g, 3.91 mmol) in 25 mL of methanol was added, and the mixture was stirred at room temperature overnight. A colour change from yellow to deep purple was observed immediately upon addition of the KOH solution. The precipitate was filtered and washed extensively with methanol to give 1.39 g (90%) of **13a** as a purple solid: **mp** 228–230 °C; **^{1}H NMR** (500 MHz, $CDCl_3$, for a mixture of diastereomers) δ (ppm): 9.29 (s, 1H), 8.674 (s, 1H of major diastereomer), 8.667 (s, 1H of minor diastereomer), 8.00 (d, J = 7.0 Hz, 1H), 7.78–7.69 (m, 4H), 7.52–7.45 (m, 4H), 7.35–7.30 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$, for a mixture of diastereomers) δ 198.9, 198.6, 154.6, 154.5, 154.1, 153.9, 150.4, 147.3, 140.3, 140.0, 133.5, 133.4, 133.3, 132.3, 132.22, 132.19, 132.14, 132.00, 131.95, 131.51, 131.46, 130.62, 130.60, 130.2, 130.0, 129.8, 127.3, 127.2, 127.0, 126.9, 125.6, 123.9, 123.8, 123.7, 123.6, 123.2, 123.0, 122.7, 122.5; **IR** (KBr, cm^{-1}): 1712 (C=O); **HRMS** (ESI^+) calcd for $C_{26}H_{14}NOBr_2$ $(M + 1)^+$ 513.9447, found 513.9444.

7,9-Bis(2-chlorophenyl)-8*H*-pentaleno[1,2,3-*de*]isoquinolin-8-one (13b). Cyclopenta[*de*]isoquinoline-4,5-dione (**12**, 0.150 g, 0.820 mmol) and 1,3-bis(*o*-chlorophenyl)acetone (0.229 g, 0.820 mmol) were combined in a 25 mL Erlenmeyer flask. A solution of KOH (0.042 g, 1.07 mmol) in 10 mL of methanol was added, and the mixture was stirred at room temperature overnight. A colour change from yellow to deep purple was observed immediately upon addition of the KOH solution. The precipitate was filtered and washed extensively with methanol to give 0.315 g (90%) of **13b** as a purple solid: **mp** 230–232 °C; **^{1}H NMR** (500 MHz, $CDCl_3$, for a mixture of diastereomers) δ (ppm): 9.28 (s, 1H), 8.67 (s, 1H), 8.01 (d, J = 7.5 Hz, 1H of major diastereomer), 8.00 (d, J = 7.5 Hz, 1H of minor diastereomer), 7.75–7.71 (m, 2H), 7.60–7.52 (m, 4H), 7.42–7.39 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$, for a mixture of diastereomers) δ 199.3, 155.1, 154.5, 150.3, 147.4, 140.3, 134.1, 132.0, 131.6,

130.7, 130.2, 130.1, 130.0, 129.9, 129.81, 129.75, 127.3, 126.9, 126.8, 126.6, 126.6, 125.7, 121.1, 120.5; **IR** (KBr, cm^{-1}): 1711 (C═O); **HRMS** (ESI^+) calcd for $C_{27}H_{14}NOCl_2$ $(M + 1)^+$ 426.0452, found 426.0458.

7,10-Bis(2-bromophenyl)indeno[1,2,3-*de*]isoquinoline (14a). A sample of 7,9-bis(2-bromophenyl)-8*H*-pentaleno[1,2,3-*de*]isoquinolin-8-one (**13a**, 1.30 g, 2.52 mmol) was heated in refluxing norbornadiene (50 mL) for 3 days. The resulting mixture was cooled to room temperature and concentrated to dryness under reduced pressure. Chromatography on silica gel using a 9 : 1 ratio of dichloromethane : ethyl acetate gave 1.06 g (82%) of **14a** as a yellow solid: **mp** >200 °C (dec); **^{1}H NMR** (500 MHz, $CDCl_3$, for a mixture of diastereomers) δ (ppm): 9.18 (s, 1H), 7.93 (two overlapping singlets, 1H), 7.86–7.83 (m, 3H), 7.591 (t, J = 7.5 Hz, 1H of major diastereomer), 7.588 (t, J = 7.5 Hz, 1H of minor diastereomer), 7.54–7.50 (m, 3H), 7.46–7.40 (m, 3H), 7.35–7.31 (m, 2H), 6.97 (d, J = 7.0 Hz, 1H of major diastereomer), 6.96 (d, J = 7.0 Hz, 1H of minor diastereomer) **^{13}C NMR** (125 MHz, $CDCl_3$, for a mixture of diastereomers) δ 150.2, 141.00, 140.98, 140.94, 140.92, 138.9, 137.5, 137.2, 136.7, 136.6, 136.0, 135.8, 133.33, 133.26, 133.19, 133.11, 131.08, 131.96, 130.8, 130.69, 130.65, 130.47, 130.46, 129.88, 129.85, 129.73, 129.70, 129.42, 129.39, 129.31, 129.09, 129.08, 127.93, 127.88, 127.83, 127.78, 126.1, 125.8, 125.3, 123.6, 123.5, 123.4, 123.3; **HRMS** (ESI^+) calcd for $C_{27}H_{16}NBr_2$ $(M + 1)^+$ 511.9654, found 511.9658.

7,10-Bis(2-chlorophenyl)indeno[1,2,3-*de*]isoquinoline (14b). A sample of 7,9-bis(*o*-chlorophenyl)-8*H*-pentaleno[1,2,3-*de*]isoquinolin-8-one (**13b**, 0.250 g, 0.587 mmol) was heated in refluxing norbornadiene (15 mL) for 3 days. The resulting mixture was cooled to room temperature and concentrated to dryness under reduced pressure. Chromatography on silica gel using a 9 : 1 ratio of dichloromethane : ethyl acetate gave 0.162 g (65%) of **14b** as a yellow solid: **mp** >200 °C (dec); **^{1}H NMR** (500 MHz, $CDCl_3$, for a mixture of diastereomers) δ (ppm): 9.18 (s, 1H), 7.97 (broad s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.66–7.63 (m, 2H), 7.60 (t, J = 7.5 Hz, 1H of minor diastereomer), 7.59 (t, J = 7.5 Hz, 1H of major diastereomer), 7.55–7.44 (m, 7H), 7.364 (d, J = 8.0 Hz, 1H of major diastereomer), 7.361 (d, J = 8.0 Hz, 1H of minor diastereomer), 7.344 (d, J = 8.0 Hz, 1H of major diastereomer), 7.341 (d, J = 8.0 Hz, 1H of minor diastereomer), 7.014 (d, J = 7.0 Hz, 1H of minor diastereomer); 7.013 (d, J = 7.0 Hz, 1H of major diastereomer) **^{13}C NMR** (125 MHz, $CDCl_3$, for a mixture of diastereomers) δ 150.2, 138.9, 136.84, 136.83, 136.0, 135.8, 135.74, 135.73, 135.43, 135.41, 133.6, 133.5, 133.3, 131.2, 131.1, 131.0, 130.9, 130.5, 130.14, 130.07, 129.99, 129.90, 129.7, 129.6, 129.3, 127.33, 127.26, 127.23, 127.16, 126.0, 125.8, 125.3; **HRMS** (ESI^+) calcd for $C_{27}H_{16}NCl_2$ $(M + 1)^+$ 424.0659, found 424.0665.

5-Azadibenzo[*a*,*g*]corannulene (6). A 54.7 mg (0.107 mmol) sample of 7,10-bis(2-bromophenyl)indeno[1,2,3-*de*]isoquinoline (**14a**) was suspended on quartz sand and placed in two oven-dried quartz boats. The boats were placed in a quartz tube with a steady stream of nitrogen carrier gas. The tube was placed in a pyrolysis set up as previously described.[14d] The material was sublimed and pyrolysed at 1000 °C with a sublimation temperature ranging from 75–175 °C. The system pressure was maintained at 0.572–0.531 torr for the duration of the experiment. At the conclusion of the experiment, the system was cooled to room temperature, and the crude pyrolysates were extracted immediately from the tube and trap with distilled dichloromethane. The solvent was removed under reduced pressure to provide a crude brown solid. The crude material was purified on reverse phase C18 preparative layer chromatography using a 2 : 1 mixture of acetonitrile : dichloromethane as the eluent, affording 10.7 mg (28%) of **6** as a yellow solid: **mp** >200 °C (dec); **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 9.46 (s, 1H), 9.06–9.04 (m, 1H), 8.64 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 8.62–8.59 (m, 2H), 8.243 (s, 1H), 8.241 (s, 1H), 8.22 (d, J = 8.5 Hz, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.80–7.74 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.0, 143.27, 143.26, 139.5, 135.9, 135.4, 135.2, 134.7 133.8, 133.1, 132.5, 131.7, 130.7, 129.6, 129.0, 128.4, 128.3, 127.7, 127.5, 126.9, 125.5, 125.4, 125.3, 125.2, 124.7; **UV-VIS** (CH_2Cl_2) λ_{max} (ε, cm^{-1} M^{-1}) 240 (9800), 280 (20 000), 326 (5200), 392 (1100); **HRMS** (ESI^+) calcd for $C_{27}H_{14}N$ $(M + 1)^+$ 352.1126, found 352.1140. **Indeno[4,3,2,1-*fghi*]picene-1-carbonitrile**: the side product formed by thermal opening of the azabowl (**18**) was collected over the course of multiple reactions. Decomposition over time of the side product prevented ^{13}C NMR analysis. **mp**: >300 °C (dec). **HRMS** (DART-TOF): Calcd for $C_{27}H_{14}N$ $(M + 1)^+$ 352.1126, found 352.1111. **^{1}H NMR** (500 MHz, $CDCl_3$): 8.74 (s, 1H), 8.70–8.66 (m, 4H), 8.51 (d, J = 8.0 Hz, 1H), 8.40 (d, J = 8.5 Hz, 1H), 8.20 (d, J = 8.0 Hz), 7.89 (d, J = 8.0 Hz, 1H), 7.82–7.77 (m, 3H), 7.71–7.68 (m, 1H). **IR** (NaCl, cm^{-1}): 2363 (C≡N).

14-Aminoindeno[1,2,3,4-*ghij*]picene-1-carboxaldehyde (20). Exposure of 5-azadibenzo[*a*,*g*]corannulene (**6**) to silica gel or to air for prolonged periods of time resulted in quantitative decomposition to the corresponding amino aldehyde **20**. Stirring a solution of azabowl **6** in dichloromethane with silica gel at room temperature for 24 h resulted in greater than 50% conversion to the amino aldehyde, as determined by integration of the ^{1}H NMR spectrum. The amino aldehyde (**20**) was isolated by silica gel chromatography using dichloromethane as the eluent: **mp** >190 °C (dec); **^{1}H NMR** (500 MHz, $C_2D_2Cl_4$) δ (ppm): 10.00 (s, 1H), 8.60 (d, J = 8.0 Hz, 1H), 8.56 (d, J = 8.0 Hz, 1H), 8.52 (d, J = 7.5 Hz, 1H), 8.40 (d, J = 8.5 Hz, 1H), 8.26 (d, J = 8.5 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.72 (t, J = 8.0 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.57 (t, 8.0 Hz, 1H), 7.55–7.54 (m, 2H); **^{13}C NMR** (125 MHz, $C_2D_2Cl_4$) δ 197.4, 147.7, 137.1, 134.0, 133.7, 132.9, 132.8, 132.7, 132.5, 130.9, 129.4, 128.9, 128.8, 127.7, 127.34, 127.28, 127.0, 126.0, 125.8, 124.9, 124.1, 124.0, 121.9, 120.5, 118.5, 116.7, 110.7; **IR** (KBr, cm^{-1}): 1644 (C═O), 2853 (CHO); **UV-VIS** (CH_2Cl_2) λ_{max} (ε, cm^{-1} M^{-1}) 266 (sh), 280 (14 000), 292 (13 000), 334 (sh) 366 (3100), 476 (2000); **HRMS** (ESI^+) calcd for $C_{27}H_{16}NO$ $(M + 1)^+$ 370.1232, found 370.1239.

3-Phenylfluoreno-[1,9,8-*cdef*]-1-phenanthridine (22). Under a nitrogen atmosphere, 7,10-bis(2-bromophenyl)indeno[1,2,3-*de*] isoquinoline (**14a**, 0.100 g, 0.194 mmol) and $Pd(PCy_3)_2Cl_2$

(0.029 g, 0.039 mmol) were added to a 15 mL flame-dried pressure vessel equipped with a stir bar. The tube was evacuated and filled with nitrogen three times. Anhydrous *N*,*N*-dimethylacetamide (3.0 mL) and DBU (1.18 g, 7.76 mmol) were added, and the vessel was sealed. The reaction mixture was stirred in a preheated oil bath at 150 °C for 3 d. After being cooled to room temperature, the resulting mixture was flashed through a short pad of alumina using dichloromethane as the eluent. The filtrate was washed with two 25 mL portions of aqueous hydrochloric acid and two 25 mL portions of water. The organic layer was dried over magnesium sulphate and concentrated to dryness under reduced pressure. Purification of the crude product by column chromatography on silica gel using 9 : 1 dichloromethane : ethyl acetate afforded 0.010 g (15%) of the singly closed product **22** as a yellow solid: **mp** 200–202 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 9.65 (s, 1H), 9.20–9.18 (m, 1H), 8.81–8.79 (m, 1H), 8.51 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 7.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.96 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.88–7.84 (m, 3H), 7.67 (dd, J = 8.0 Hz, 7.0 Hz, 1H), 7.65 (t, J = 7.0 Hz, 2H), 7.55 (tt, J = 7.5 Hz, 1.7 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.0, 140.0, 139.9, 139.1, 138.0, 136.0, 134.0, 133.6, 133.3, 131.7, 130.5, 129.7, 129.0, 128.9, 128.4, 128.2, 127.7, 127.3, 126.6, 126.2, 125.0, 124.8, 124.4, 124.3, 123.5; **HRMS** (ESI^+) calcd for $C_{27}H_{16}N$ $(M + 1)^+$ 354.1283, found 354.1266.

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