Azatriquinanes: Synthesis, Structure, and Reactivity

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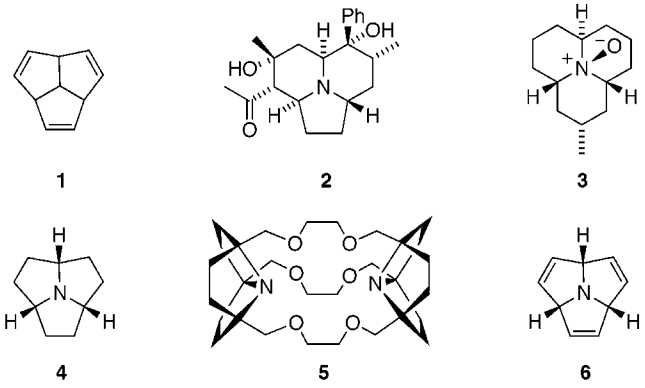
Azatriquinane, a tricyclic amine with rigid, hemispherical topology, is synthesized in six steps from pyrrole. This first example of a [2.2.2]cyclazine can be oxidatively dimerized to a novel, highly strained heptacycle or oxidized with chlorine to give an azatriquinacene, a theoretical precursor to diazadodecahedrane via Woodward dimerization.

Introduction

Triquinacene, the tricyclic hydrocarbon $C_{10}H_{10}$ (**1**), was first prepared by Woodward in an early attempt to synthesize dodecahedrane.[1] It was demonstrated that the photochemical [2 + 2 + 2 + 2 + 2 + 2]π-electrocyclic process which constitutes dimerization was theoretically allowed, although the reaction has never actually been experimentally observed.[2] The reason for this may be that the endo-endo superimposition which leads to the reactive configuration for dimerization of **1** would rarely be attained by random collisions of two hemispherical bodies.[3]

In the more than 30 years since the synthesis of triquinacene, it is interesting that no attempt has been made to prepare aza-analogues of this topologically interesting molecule, despite a long-standing interest in the higher [2.2.3]-, [2.3.3]-, and [3.3.3]cyclazines. For instance, a great deal of work has been published concerning the electronic properties of the unsaturated [2.2.3] and [3.3.3] heterocycles,[4] while the [2.3.3] and [3.3.3] ring systems turn up in no less than eight natural products,[5] of which crepidine (**2**) (ex. orchids),[6] and coccinelline (**3**) (ex. ladybird defense secretions)[7] are representative examples.

We recently developed an interest in the [2.2.2]cyclazine (i.e. 10-azatriquinane) molecule (**4**) from a number of perspectives. This rigid, convex tricycle whose amine function cannot invert could, for example, be desymmetrized by bis-α-substitution to give a novel type of chiral acid/base system.[8] It could also be incorporated into



cryptand macrobicycles (e.g. **5**), where the lone pairs of the apical nitrogens would be compelled to point into the cavity, leading to even more effective metal chelation. Finally, if azatriquinacene (**6**) could be prepared, the prospect of Woodward dimerization could be reexamined: The critical difference between **6** and **1** is that the former would be expected to possess some aqueous solubility (particularly as the hydrochloride). This would lead to states of aggregation in solution which could dramatically increase the probability of electrocyclic reaction. This phenomenon has already been described for [4 + 2] reactions, where very substantial acceleration of cycloaddition rates vs those in organic media are observed.[9] The achievement of 1,16-diazadodecahedrane by such means would be an important result not only from a fundamental standpoint but also in the provision of functional handles on a molecular Platonic solid. Although cage hydrocarbons and related polycycles have classically been of interest as major synthetic milestones,[3,10] they have gained more current relevance in the wider context of providing structurally well-defined, functionally interconnectable particles for nanotechnological purposes.[11]

We have reported in brief on the synthesis of azatriquinane **4**, its dimer **13**, and its oxidation to perchloroazatriquinacene **14**.[12] An updated and full account is

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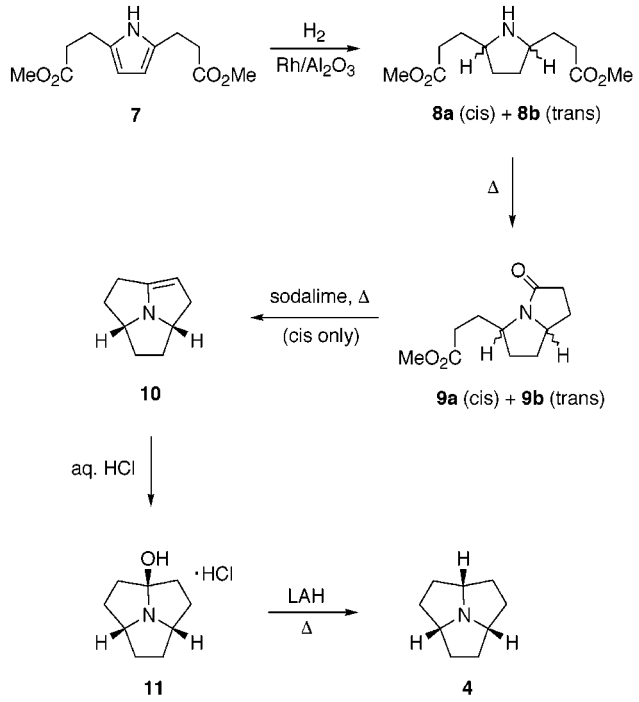
Scheme 1



now given of this work, in addition to structural studies of each of these three molecules. A study of the electronic properties of **4** has appeared elsewhere.[13]

Results and Discussion

The synthetic route taken to azatriquinane is presented in Scheme 1. The starting material, 2,5-pyrroledipropanoic acid dimethyl ester **7**, could be prepared on a large scale by bis-addition of pyrrole to methyl acrylate.[14] Hydrogenation over rhodium on alumina gave a mixture of pyrrolidines **8a** and **8b** in 88% yield. Although the desired cis isomer predominated, no separation could be effected at this point. Cyclization to the pyrrolizines was accomplished by prolonged heating at reflux in toluene, which gave a separable mixture of **9a** (84%) and **9b** (11%). Compound **9a** was carried on to the next stage, consisting of dry distillation from an intimate mixture with sodalime.[15] Careful workup allowed the isolation of the enamine **10** in 55% yield; however, better conversion to tricyclic product was achieved if the condensate was treated directly with aqueous acid to give the stable hemiaminal **11**. The parent triquinane **4** could then be derived from **11** in good yield by reduction with lithium aluminum hydride.

Compound **4** is a volatile white solid with a melting point just above room temperature. A crystalline tetrafluoroborate salt could be prepared, and single crystals suitable for X-ray diffraction were grown from CH_2Cl_2/ether. The structure of **4**·HBF_4 is shown in Figure 1. Although the molecule has averaged C_3 symmetry in solution (by NMR), no 3-fold crystallographic symmetry is imposed. An interesting feature of this structure is

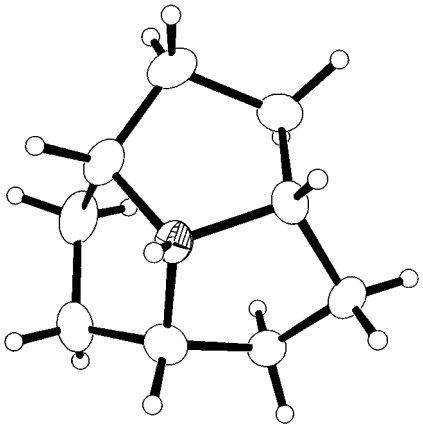


Figure 1. X-ray crystal structure of **4**·HBF_4. The counterion is omitted for clarity.

the involvement of the BF_4^- counterion in a short hydrogen bond to the protonated nitrogen, with an N···F distance of 2.817 Å and N−H−F angle of 176°.

The ionization potential of the nitrogen lone pair of **4** is 7.8 eV.[13] This low value[16] is reflected in the molecule's high basicity, estimated to be about 0.5 pK_a units beyond that of quinuclidine[17] by acid−base equilibrium measurements.[18] We therefore proposed making use of these electrons in their rigid framework by incorporation into a macrobicycle (i.e. **5**) and for chiral electrophile delivery (H^+, X^+), as mentioned earlier. In either case this would involve substitution at the positions α to the nitrogen atom. A classical method for effecting this transformation is *N*-oxide formation followed by deprotonation and quenching with an electrophile. Previous work had shown that the reaction was successful for quinuclidine,[19] and accordingly the oxide **12** was prepared from **4** using hydrogen peroxide in methanol. Treatment of **12** with *tert*-butyllithium at −78 °C followed by addition of iodopentane did result in the formation of a new compound, but without incorporation of the electrophile. Indeed, the same outcome was observed after deprotonation and simple quenching with methanol. Spectroscopic data indicated that the product was formally an oxidative dimer of **4**, and the evidence pointed to the rather remarkable structure **13**. Fortunately, single crystals of this material were available and the assignment could be secured by X-ray diffraction (Figure 2). In stark contrast to **4**, compound **13** is essentially nonbasic, and models confirm that protonation at nitrogen seriously violates the van der Waals radii of the adjacent hydrogens on the ethylene bridge. This hitherto unknown ring system shows the evidence of extraordinary ring strain in the length of the C−C bonds which connect the two tricycles together (C6−C9A, 1.584 Å) and in the 25° range in bond angles (from 100.0° for N1−C6−C9A to 125.3° for C5−C6−C9A). The observation of **13** is presumably the result of the elimination of LiO^- from the molecule and deprotonation of the resulting iminium salt to give the corresponding azomethine ylide, followed by 3 + 3

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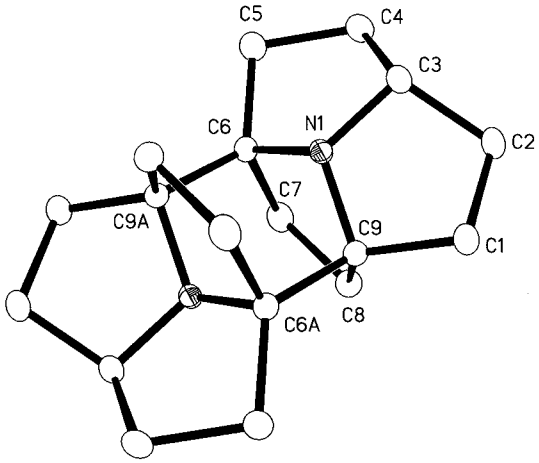
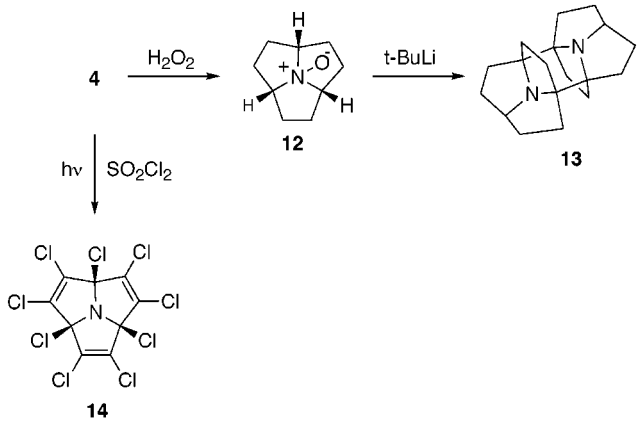


Figure 2. X-ray crystal structure of **13**. The molecule lies on a crystallographic inversion center. Hydrogen atoms have been omitted and the ellipsoids are represented at the 20% probability level for clarity.

Scheme 2



dimerization.[20] The molecule is not particularly stable in solution and decomposes in the course of a few days into an as yet unidentified rearrangement product.

A major objective of this research program was the attainment of azatriquinacene **6**, and efforts turned toward the dehydrogenation of **4** (Scheme 2). The Cl_2 oxidation−partial reduction protocol by which Jacobson was able to convert triquinane into triquinacene[21] appeared promising, and we therefore irradiated a solution of **4** in sulfuryl chloride and in this way obtained the first example of an azatriquinacene (**14**) in excellent yield. This nonachlorotricycle could be crystallized from pentane and the X-ray crystal structure is shown in Figure 3. Unfortunately, dechlorination with lithium and *tert*-butyl alcohol as described[21] led only to decomposition, and further attempts across a wide range of reductive conditions have failed to produce any characterizable product.

In conclusion, the first synthesis of the [2.2.2]cyclazine ring system has been accomplished by sequential annelations onto pyrrole.[22] The rigid tricyclic framework enforces pyramidalization at the apical nitrogen with consequent enhancement of its basicity. An unexpected reaction of the *N*-oxide **12** links two molecules of **4** through a common six-membered ring to produce a novel heptacycle **13**. Azatriquinane **4** can be oxidized with chlorine to give perchloroazatriquinacene **14**, from which, however, the parent azatriquinacene **6** could not be derived. Work continues along varied lines on the goal of substituting azatriquinane α to the nitrogen in order to exploit its unique structural properties, and on the eventual achievement of the triene **6**.

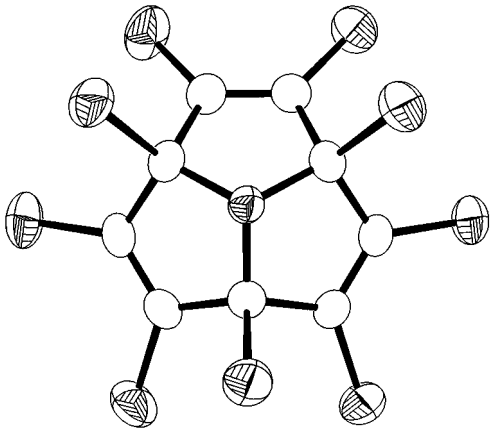


Figure 3. X-ray crystal structure of **14**.

Experimental Section

Dimethyl *cis*-2,5-Pyrrolidinedipropanoate (8a) and Dimethyl *trans*-2,5-Pyrrolidinedipropanoate (8b). Rhodium on alumina (5%, 663 mg) and a solution of pyrrole **7**[14] (29.9 g, 125 mmol) in acetic acid (125 mL) were placed in an 1-L Parr apparatus. After multiple cycles of evacuation and flushing with hydrogen, the mixture was shaken under 40 psi of hydrogen for 24 h. The solvent was evaporated and the residue partitioned between dichloromethane (200 mL) and saturated aqueous K_2CO_3 (200 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 200 mL). The combined organic extracts were washed with saturated aqueous K_2CO_3 (200 mL) and dried over $MgSO_4$. Chromotography (4:1 ether/MeOH) gave a mixture of the pyrrolidines **8a** and **8b** (26.9 g, 88%) as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) (major isomer **8a** only) δ 3.67 (6 H, s), 3.05 (2 H, m), 2.38 (4 H, dt, *J* 1.5 and 7.6), 1.99 (1 H, br s), 1.86 (2 H, m), 1.76 (4 H, q, *J* 7.1), 1.35 (2 H, m); ^{13}C NMR (100.6 MHz; $CDCl_3$) (major isomer **8a** only) δ 174.1 (C), 58.1 (CH), 51.5 (CH_3), 31.7 (CH_2), 30.8 (CH_2); HRMS (FAB) found, *m*/*z* 244.15309 (M + H), $C_{12}H_{22}NO_4$ requires 244.15488.

***cis*-Hexahydro-5-[2-(methoxycarbonyl)ethyl]-3H-pyrrolizin-3-one (9a) and *trans*-Hexahydro-5-[2-(methoxycarbonyl)ethyl]-3H-pyrrolizin-3-one (9b).** A mixture of pyrrolidines **8a** and **8b** (33.2 g, 136 mmol) was heated at reflux in toluene (250 mL) for 10 d under nitrogen. The solvent was evaporated and the residue chromatographed (30:1 → 10:1 ether/MeOH) to give **9a** (24.3 g, 84%) and **9b** (3.27 g, 11%) as colorless oils.

9a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (1 H, septet, *J* 5.2), 3.67 (3 H, s), 3.60 (1 H, br m), 2.74−2.64 (1 H, m), 2.63−2.54 (1 H, m), 2.48 (1 H, dd, *J* 8.6 and 16.4), 2.44−2.29 (2 H, m), 2.28−2.15 (2 H, m), 1.96−1.88 (2 H, m), 1.86−1.76 (1 H, m) 1.73−1.62 (1 H, m), 1.47−1.38 (1 H, m); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 173.4 (C), 171.9, (C), 64.2 (CH), 52.7 (CH), 51.5 (CH_3), 37.6 (CH_2), 33.5 (CH_2), 31.0 (CH_2), 29.3 (CH_2), 28.2 (CH_2), 26.4 (CH_2); HRMS (EI) found, *m*/*z* 211.1204 (M^+), $C_{11}H_{17}NO_3$ requires 211.1208.

9b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89−3.82 (1 H, m), 3.79 (1 H, quintet, *J* 7.1), 3.59 (3 H, s), 2.60 (1 H, dt, *J* 10.0 and 16.7), 2.37 (2 H, t, *J* 7.7), 2.32 (1 H, ddd, *J* 2.7, 9.8, and 16.8),

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2.26−2.18 (2 H, m), 2.01−1.94 (1 H, m), 1.74 (2 H, q, *J* 7.5), 1.70−1.55 (2 H, m), 1.24 (1 H, quintet, *J* 10.2); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 175.6, 173.6, 61.0, 53.5, 51.3, 34.3, 33.4, 32.6, 31.1, 30.7, 26.1; HRMS (EI) found, *m/z* 211.1206 (M^+), $C_{11}H_{17}NO_3$ requires 211.1208.

***cis*-10-Azatricyclo[5.2.1.0^{1,10}]dec-1-ene (10).** An intimate mixture of pyrrolizine ester **9a** (2.11 g, 10.0 mmol) and powdered sodalime (7.0 g) was flame pyrolyzed under an argon atmosphere in a microdistillation apparatus. Heating was continued until no more liquid could be seen condensing out of the reaction and the residue had become gray. The distillate was transferred into a mixture of water (5 mL) and CH_2Cl_2 (5 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL), and the combined organic phases were dried over $MgSO_4$. Evaporation of the solvent under vacuum at room temperature gave the crude product as a brown oil (1.16 g). Short path distillation (Kugelrohr) at 1 Torr gave the enamine **10** (0.74 g, 55%) as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (1 H, s), 3.52 (1 H, q, *J* 7.3), 3.47−3.41 (1 H, m), 2.94−2.87 (1 H, m), 2.45 (1 H, dd, *J* = 3.1 and 14.9), 2.39−2.32 (1 H, m), 2.24−2.19 (2 H, m), 1.80−1.71 (1 H, m), 1.67−1.53 (3 H, m), 1.40−1.33 (1 H, m); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 156.3, 93.2, 64.0, 59.8, 39.4, 34.4, 32.2, 29.5, 23.8; HRMS (EI) found, *m/z* 135.1054 (M^+), $C_9H_{13}N$ requires 135.1048.

***cis,cis,cis*-10-Azatricyclo[5,2,1,0^{1,10}]decan-1-ol Hydrochloride (11).** Compound **9a** (1.00 g, 4.73 mmol) was treated as described above in the synthesis of **10**, but the distillate was transferred with the aid of a little CH_2Cl_2 into 1.0 M HCl (30 mL). All volatiles were removed under reduced pressure to give a brown solid which was chromatographed (CH_2Cl_2 → 4:1 CH_2Cl_2/MeOH) to give **11** (0.628 g, 70%) as a beige solid: mp 160 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.44 (2 H, quintet, *J* = 5.8), 2.54−2.40 (4 H, m), 2.22−2.13 (2 H, m), 2.12−2.03 (2 H, m), 1.83−1.73 (4 H, m); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 109.4, 65.2, 35.8, 29.7, 29.6; HRMS (FAB) found, *m/z* 154.1257 (M + H), $C_9H_{16}NO$ requires 154.1232. Anal. Calcd for $C_9H_{16}ClNO$: C, 56.99; H, 8.50; N, 7.38; Cl, 18.69. Found: C, 56.77; H, 8.63; N, 7.37; Cl, 18.76.

***cis,cis,cis*-10-Azatricyclo[5,2,1,0^{1,10}]decane (4).** Lithium aluminum hydride (0.67 g, 18 mmol) was added to a stirred suspension of **11** (0.843 g, 4.44 mmol) in THF (100 mL). When gas evolution had ceased, a further portion of lithium aluminum hydride (0.90 g, 24 mmol) was added and the suspension was heated at reflux for 62 h. The mixture was cooled to 0 °C and water (0.5 mL) was cautiously added, followed by 2 M aqueous NaOH (10 mL). The slurry was stirred at room temperature for 30 min and K_2CO_3 (20 g) added. The mixture was stirred for a further 1 h at room temperature, before being filtered through layers of Celite and K_2CO_3. The solid residues were washed with CH_2Cl_2-MeOH (20:1, 20 × 10 mL). To the combined filtrates was added 0.5 M aqueous HCl (30 mL), and all volatiles were removed under reduced pressure to give a pale yellow oil. Chromatography (CH_2Cl_2 → 4:1 CH_2Cl_2/MeOH) gave the hydrochloride salt (**4**·HCl) as a hygroscopic beige solid (0.746 g, 97%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.75 (1 H, br s), 4.25 (3 H, br s), 2.19 (6 H, br m), 1.62 (6 H, br m); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 66.5, 29.7. The compound was analyzed as its crystalline tetrafluoroborate salt (**4**·HBF_4), which is produced in essentially quantitative yield by dissolving **4**·HCl in a 20-fold molar excess of saturated aqueous $NaBF_4$ followed by extraction with CH_2Cl_2: mp 200 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (1 H, br s), 4.33 (3 H, br s), 2.29−2.21 (6 H, m), 1.88−1.80 (6 H, m); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 68.3, 29.5; HRMS (FAB) found, *m/z* 138.1284 (M + H), $C_9H_{16}N$ requires 138.1283. Anal. Calcd for $C_9H_{16}BF_4N$: C, 48.04; H, 7.17; N, 6.22. Found: C, 47.87; H, 7.18; N, 6.15. To obtain the free base **4**, the hydrochloride salt **4**·HCl (121 mg, 0.700 mmol) was introduced into a mixture of ether (5 mL) and 2 M aqueous KOH (0.7 mL). After vigorous agitation for 2 min the layers were separated, and the aqueous layer was extracted with ether. The combined organic phase was dried over $MgSO_4$ and the solvent cautiously evaporated to give **4** (89 mg, 93%) as a white solid: mp ca. 30 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 3.50 (3 H, m), 1.67−1.57 (6 H, m), 1.25−1.15 (6 H, m); ^{13}C NMR (100.6 MHz; C_6D_6) δ 65.8, 30.9; HRMS (EI) found, *m/z* 137.1255 (M^+), $C_9H_{15}N$ requires 137.1205.

***cis,cis,cis*-10-Azatricyclo[5,2,1,0^{1,10}]decane *N*-Oxide (12).** Hydrogen peroxide (30%, 0.50 mL) was added to a solution of amine **4** (0.254 g, 1.85 mmol) in methanol (10 mL) at room temperature. After standing for 45 min, another portion of hydrogen peroxide (30%, 0.50 mL) was added. After 38 h a final aliquot of hydrogen peroxide (30%, 0.50 mL) was added. Stirring was then initiated and a small amount of platinum black introduced. When gas evolution had ceased, additional platinum black was added until no further gas evolution was observed. The suspension was filtered through Celite, and the solid residues were washed with methanol. The solvent was evaporated to give a colorless oil which solidified on drying (40 °C, 0.1 Torr, 72 h). Oxide **12** is extremely hygroscopic and therefore no reliable yield determination was possible. It decomposes gradually on standing and was used directly in the next step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (3 H, m), 2.48−2.39 (6 H, m), 1.85−1.76 (6 H, m); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 84.9, 29.3; HRMS (FAB) found, *m/z* 154.1290 (M + H), $C_9H_{16}NO$ requires 154.1232.

19,20-Diazaheptacyclo[7.5.2.2^{2,8}.1^{1,9}.1^{2,8}.0^{5,20}.0^{12,19}]eicosane (13). *Tert*-butyllithium (1.6 M in hexanes, 1.0 mL, 1.6 mmol) was added dropwise to a stirred suspension of **12** (0.125 g, 0.82 mmol) in THF (20 mL) at −78 °C. The resulting pale yellow, homogeneous solution was stirred for 20 min before being allowed to slowly warm to 0 °C. Methanol (1 mL) was then added, and the solvents were evaporated. Chromatography (CH_2Cl_2 → 4:1 CH_2Cl_2/ether) gave **13** (0.053 g, 48%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.43−3.36 (2 H, m), 1.95−1.81 (16 H, m), 1.61−1.50 (4 H, m), 1.11−1.08 (4 H, m); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 79.6 (C), 58.9 (CH), 39.7 (CH_2), 35.2 (CH_2), 33.3 (CH_2); HRMS (FAB) found, *m/z* 271.2188 (M + H), $C_{18}H_{27}N_2$ requires 271.2174.

***cis,cis,cis*-1,2,3,4,5,6,7,8,9-Nonachloro-10-azatricyclo-[5.2.1.0^{1,10}]deca-2,5,8-triene (14).** A solution of **4**·HBF_4 (0.225 g, 1.00 mmol) in freshly distilled sulfuryl chloride (40 mL) was irradiated with a 240 W tungsten lamp for 16 h. The heat from the lamp maintained the system at gentle reflux during the irradiation period. The solution was cooled to room temperature and the excess sulfuryl chloride was evaporated. Chromatography (petroleum ether) gave **14** (0.415 g, 94%) as a white solid: ^{13}C NMR (100.6 MHz; CD_2Cl_2, −60 °C) δ 131.0, 94.0; MS (EI) isotopic cluster for $(C_9Cl_8N)^+$, *m/z* 412 (6.4), 410 (25.1), 409 (6.3), 408 (63.3), 407 (10.0), 406 (100), 405 (9.0), 404 (91.4), 403 (3.5), 402 (35.5).

Crystallographic Studies. Crystal data for **4**·HBF_4: $C_9H_{16}N^+BF_4^-$, *M* = 225.04, orthorhombic, space group $P2_12_12_1$, *a* = 6.7150(6), *b* = 9.3320(9), *c* = 16.814(5) Å, *U* = 1053.6(3) Å^3 (by least squares refinement of the setting angles for 250 reflections with θ = 2.4−25.0°), *T* = 120(2) K, *Z* = 4, D_x = 1.419 g cm^{-3}, μ(Mo Kα) = 0.132 mm^{-1}. Data were collected using a FAST TV area detector diffractometer following previously described methods.[23] From the ranges scanned, 3666 data were recorded ($2\theta_{max}$ = 50°) and merged to give 1647 unique reflections (R_{int} = 0.044) with intensity > 0. The structure was solved using automatic direct methods.[24] Refinement was by full-matrix least squares[25] on F^2 with all non-hydrogen atoms anisotropic. The hydrogen atoms were located from the difference map and refined isotropically. The weighting scheme, $w = 1/[\sigma^2(F_o)^2 + (0.0444P)^2]$, where $P = {}^1/_3[(F_o)^2 + 2F_c^2]$, gave satisfactory agreement analyses. Final R_1 [$F \geq 4\sigma(I)$] = 0.0362 and wR_2[all F^2 data] = 0.0838, $S[F^2]$ = 0.99 for all 1647 reflections and 200 parameters. The final ΔF synthesis showed no peaks above 0.24 e Å^{-3}.

Crystal data for **14**: C_9Cl_9N, *M* = 441.14, orthorhombic, space group *Pbca*, *a* = 14.814(6), *b* = 12.722(2), *c* = 15.847(3) Å, *U* = 2986(14) Å^3 [from 2θ values of 32 reflections measured at $\pm\omega$ (14 ≤ θ ≤ 16°, λ = 0.71073 Å, *T* = 298 K)], *Z* = 8, D_x =

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(24) Sheldrick, G. M. *Acta Crystallogr., Sect. A*, **1990**, *46*, 467.
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1.962 g cm^{-3}, μ(Mo $K\alpha$) = 1.667 mm^{-1}. Data were collected using a Stoe Stadi-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ X-radiation, ω/θ scans, 2687 reflections measured ($2\theta_{max} = 50°$), 2630 being unique [R_{int}= 0.005 after application of absorption corrections (T range 0.0464−0.0525) based on ψ scans], giving 2068 with $F \geq 4\sigma(F)$ and 2623 which were retained in all calculations. No crystal decay was observed. The structure was solved using automatic direct methods.[24] Refinement was by full-matrix least squares[25] with all atoms anisotropic. The weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.027P)^2 + 3.11P]$, where $P = {}^1/_3[\mathrm{MAX}(F_o^2,0) + 2F_c^2]$, gave satisfactory agreement analyses. Final R_1 [$F \geq 4\sigma(F)$] = 0.0333, wR_2 [all F^2 data] = 0.0768, $S[F^2] = 1.04$ for 173 refined parameters. An extinction correction[25] refined to 0.00026(10) and the final ΔF synthesis showed no peaks above 0.35 e $Å^{-3}$.

For the crystal data for compound **13** consult ref 12.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra for compounds **8a**/**b**, **9a**, **9b**, **10**, **4**·HCl, **4**, **12**, and **13**, the ^{13}C NMR spectrum for compound **14**, and tables of crystallographic data for compounds **4**·HBF_4 and **14** (29 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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